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HIGH-PRECISION COULOMETRIC TITRATIONS OF ACIDS

Iowa State University PH.D. 1980

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High-precision coulometric titrations of acids

by

Michael Charles Hadka

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

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Iowa State University
Ames, Iowa

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I. INTRODUCTION

A. Background of Coulometric Titrations

Coulometry is the analytical technique by which the amount of a material is determined by measuring the quantity of electricity required to generate at an electrode an amount of a second chemical just necessary to react completely and stoichemically with the material being determined. Faraday's Laws of electrolysis relate a quantity of electricity passed to the amount of a chemical changed at an electrode. The relationship is given by the equation

$$G = \frac{1}{F} It \frac{\text{Mol. Wt.}}{n} \qquad (1)$$

in which G is the weight of the chemical undergoing a change at the electrode, in grams; F is a proportionality constant called the faraday, the current value (19,46) of which is 96,486.57 1972 NBS coulombs per gram-equivalent-weight; I is the current, in amperes; t is the time, in seconds; Mol. Wt./n is the equivalent weight of the chemical undergoing the change at the electrode, that is, the molecular weight divided by the number of electrons involved in the reaction. All of the factors in equation (1) can be measured with a high degree of accuracy and precision.

1. The electron as the ultimate chemical standard

The electron has been chosen as the ultimate standard in chemistry. There is only one kind of electron and it is the only really pure chemical known. The electron can be delivered to or removed from a liquid in any convenient quantity and this quantity can be measured with great accuracy and precision. The electron can be delivered or removed from a liquid at any desired potential over a range of some five volts and thus a variety of electrochemistry can be performed. One faraday of electricity contains one Avogadro's number of electrons, that is, one mole of electrons. Thus, one faraday is equivalent in chemical action to one liter of a one normal solution of an oxidizing agent, or of a reducing agent. The faraday is a surprisingly large amount of electricity; put into other units 96,486.57 coulombs is 26.80183 ampere-hours (per gram-equivalent-weight).

2. History of coulometric titrations

The history of coulometric titrations begins with the work of Szebelledy and Somogyi (80) prior to the second World War. Since then, coulometry has been applied to the determination of a variety of materials and improvements in the accuracy and precision have accompanied the development. Really high-precision coulometric titrations were first made in 1959 by Taylor and Smith (84). Later, Marinenko and

Taylor (62,63,64,65) used coulometry to assay primary standard materials. In 1958, Tutzundzic (86) suggested that the electron be regarded as the ultimate primary standard. Starting in 1969, Diehl and co-workers carried the technique to the highest degree of perfection (18,19, 39,42,43,45,46,47,48,51). A majority of this work was directed toward the determination of a value for the faraday of high accuracy; the route chosen was the titration of an organic base, 4-aminopyridine.

B. Current Status of the Faraday

Since 1960, the accepted value of the faraday was that determined by Craig, Hoffman, Law and Hamer (15) by the anodic dissolution of silver. The Craig value of the faraday has been recalculated since the work was performed to reflect (a) the change in the definition of the NBS ampere and volt, (b) the drift in the standard cells with time (up to 1972), (c) the change of the atomic weight table to the carbon-12 basis, and (d) a redetermination of the abundance ratio of the silver isotopes in the silver used by Craig. The recalculations of the Craig data were made by Hamer (35), Taylor, Parker and Langenberg (83) and Cohen and Taylor (12). The current value of the faraday as recalculated from the Craig silver dissolution work is given in Table 1 along with the uncertainty in the work. The work of Craig was viewed with suspicion by Hoyle (38) because of the problem of recovering all of the silver which flaked from the electrode because of the undercutting of the electrode during electrolysis.

In 1968, Marinenko and Taylor (62) determined the faraday by the coulometric titrations of benzoic acid and of oxalic acid dihydrate. The benzoic acid used was prepared by Bates and Wichers (2) by zone refining. The oxalic acid was prepared by Torgesen and Strassburger (85). Marinenko and Taylor used only the optically clear fragments of oxalic acid and stored the crystals in an atmosphere of adjusted humidity. The results of the titration of benzoic acid and oxalic acid dihydrate along with the weighted average in the two results are given in Table 1.

In the course of an exhaustive, least squares treatment of the fundamental physical constants, Taylor, Parker and Langenberg (83) calculated the value of the faraday from the various physical constants. Cohen and Taylor (12) in 1973, using various physical constants calculated a value for the faraday, Table 1. This indirect calculation was based on measurements of the atomic mass of the proton, the gyromagnetic moment of the proton in high and low magnetic fields, the ratio of the ampere as maintained to the absolute ampere, and the ratio of the magnetic moment of the proton to the nuclear magneton. The difference between the Craig value for the faraday, as recalculated, and the calculated value of Cohen and Taylor is some 20 parts per million (p.p.m.). This discrepancy was highly disturbing to the physicists. Taylor, Parker and Langenberg (83) in 1969 had already called for a redetermination of the electrochemical value of the faraday and Cohen and Taylor (12) in 1973, rejected the Craig value outright.

Since then, two more electrochemical determinations of the value of the faraday have been made, by Diehl and coworkers (19,46,47) and by Bower and Davis (6). Diehl used an organic base, 4-aminopyridine, to determine the value of the faraday by the direct high precision titration of the base at a newly devised "hydrazine-platinum" anode. The organic base was analyzed also indirectly by adding an excess of perchloric acid and titrating the excess acid at the cathode. The perchloric acid was standardized in a separate titration by generating hydroxide at the cathode. A weight buret was used to measure the amount of perchloric acid used in the titrations. The work of Bower and Davis was based on the anodic dissolution of silver. The values of the faraday obtained by Diehl and by Bower and Davis are given in Table 1.

In 1975, Cohen and Taylor (12) reviewed the work of Marinenko and Taylor (62), Koch _et al_. (46,47) and Bower and David (6); they obtained as a mean the value given

Table 1. Recent values for the faraday[a]

Author, (Literature reference), Location, Year, Method	Value for the faraday[b,c] (Uncertainty p.p.m.)[d] A_{BI69}.sec.(g.-eq.-wt.)$^{-1}$
1. Craig, Hoffman, Law and Hamer (15), NBS, 1960. Anodic dissolution of silver. As recalculated.[e]	96,486.72(6.8)
2. Marinenko and Taylor (62), NBS, 1968. Reduction of benzoic acid.[f] As recalculated.[g]	96,487.30(12)

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[a] As taken from my M.S. thesis (34).

[b] In accord with the practice of Taylor, Parker and Langenberg (83) and Cohen and Taylor (12), one figure beyond the uncertainty is reported to avoid rounding off errors.

[c] Current is reported in the 1969 ampere of the Bureau International des Poids et Measures, designated A_{BI69}. This ampere and the 1972 NBS ampere are now identical (reference 12, p. 678).

[d] The uncertainty includes random and systematic errors and is reported as one standard deviation of the mean (70 per cent confidence level), expressed in p.p.m.

[e] After repeated recalculations to reflect the shift in the basis of the atomic weight table to carbon-12, a redetermination of the ratio of the isotopes of silver, and changes in the definition of the volt and ampere as maintained at NBS, the latest recalculations being those of Taylor, Parker and Langenberg (83) and Cohen and Taylor (12).

[f] Reduction in the sense of titration with hydroxide ion generated at the cathode.

[g] Recalculation by Cohen and Taylor (12).

Table 1. (Continued)

Author, (Literature reference), Location, Year, Method	Value for the faraday[b,c] (Uncertainty p.p.m.)[d] A_{BI69}.sec.(g.-eq.-wt.)$^{-1}$
3. Marinenko and Taylor (62), NSB, 1968. Reduction of oxalic acid dihydrate.[f] As recalculated.[g]	96,486.25(16)
4. Weighted average of 2 and 3. As recalculated.[g]	96,486.95(9.6)
5. Koch, Hoyle and Diehl (47), 1975. Iowa State University. Reduction[f] and oxidation[h] of 4-aminopyridine. Weighted average of two procedures. As recalculated.[i]	96,486.62(8.4)
6. Koch and Diehl (46), 1976. Repetition of 5 at NBS. Weighted average of two procedures.	96,486.55(5.9)
7. Koch and Diehl (46), 1976. Weighted average of 5 and 6.	96,486.57(4.9)
8. Koch, Hoyle and Diehl (47). 5 as recalculated by Taylor and Cohen.[j]	96,486.41(8.5)
9. Bower and Davis (6), 1975. NBS. Anodic dissolution of silver.	96,486.41(3.1)

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[h] Oxidation in the sense of titration with hydrogen ion generated at the hydrazine-platinum anode (39).

[i] The recalculation, to reflect a better value for the density of 4-aminopyridine, changed the results from 96,486.69 to 96,486.62 coulombs per gram-equivalent-weight reported above.

[j] Recalculated by Taylor and Cohen (82) using for the molecular weight of 4-aminopyridine 94,116.84 rather than the 94,117.02 used by Koch, Hoyle and Diehl (47), and Koch and Diehl (46) and Kroeger <u>et</u> <u>al</u>. (51).

Table 1. (Continued)

Author, (Literature reference), Location, Year, Method	Value for the faraday[b,c] (Uncertainty p.p.m.)[d] A_{BI69}.sec.(g.-eq.-wt.)$^{-1}$
10. Average of 4, 8 and 9. As calculated by Taylor and Cohen (82), 1975. Taylor (81), 1976. NBS.	96,486.46(2.8)
11. Indirect, calculated. Cohen and Taylor (12), 1973.[k] NBS.	96,484.56(2.8)

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[k] For later discussions of the problems of the interrelations of the faraday and other fundamental constants, see Taylor and Cohen (82) and Taylor (81).

in Table 1, line 10. The values for the faraday obtained from the electrochemical work agreed surprisingly closely with each other. The value of the faraday calculated by the indirect method of Cohen and Taylor (12) was again some 20 p.p.m. lower than the electrochemical value.

At the present, there are two values of the faraday, the electrochemical value, 96,486.57 1972 NBS coulombs per gram-equivalent-weight and the physicist's value, 96,484.56 1972 NBS coulombs per gram-equivalent-weight. On reexamination of the problem, Taylor (81) in 1976 stated that the electrochemical value of the faraday was probably correct and recommended a reexamination of the work on which the calculated value rested. Diehl (19) in 1979 stated that he felt the electrochemical value of the faraday might be the value in error. The status of the problem is summed up neatly in a quote by Koch and Diehl (46):

> "The conclusion must be drawn that the work leading to the lower value of the faraday as calculated by Cohen and B. N. Taylor from other physical measurements should be re-examined. Alternatively, if the electrochemical value is incorrect, the electrode process in water must be more closely examined for some basic flaw common to such different processes as the anodic generation of hydrogen ions, and the cathodic generation of hydroxyl ions. Establishing a value for the faraday by electrochemistry in a non-aqueous solvent might contribute to the solution of the problem."

The present work is directed to the redetermination of the value of the faraday using a different chemical than 4-aminopyridine, specially using the acids potassium hydrogen phthalate, benzoic acid, furoic acid and adipic acid as primary chemicals and to use as solvents mixtures of water and nonaqueous solvents.

C. Reexamination of the Value for the Faraday

1. <u>Errors in the evaluation of the faraday</u>

In high-precision coulometric titrimetry, time and the current can be measured with a high degree of accuracy and by standards traceable to the standards maintained at the National Bureau of Standards. The molecular weight of the substance being titrated can be calculated from the table of atomic weights, Atomic Weights of the Elements, issued by the Commission on Atomic Weights of the International Union of Pure and Applied Chemistry (see Appendix for references to the various reports). The isotope ratios of the elements used in the calculation of the atomic weights are known to a high degree of accuracy. The weight of a sample can be measured on a microbalance to within one microgram, that is to better than one p.p.m., although currently there is a question about the determination of the density of air needed to correct weighings for the buoyancy of air, and even some question as to whether the subdivision of the standard of mass, the platinum-iridium International Kilogram, has been made with part per million accuracy (19). In evaluating the faraday, it should also be noted, mass must be measured in absolute terms.

The largest error in coulometric titrations is probably in the location of the equivalence-point. Koch, Hoyle and Diehl (47) felt that the location of the equivalence-point was the largest error in the high-precision titrations they used in their evaluation of the faraday. Koch and Diehl (46) estimated this uncertainty to be from three to seven p.p.m. I now believe this to be underestimated.

The primary standard chemical used in the determination of the faraday must be 100.0000 per cent pure as determined by an independent method. Kroeger and co-workers (51) used the freezing-point-depression method to determine the purity of their 4-aminopyridine. The limit of the method is 10 p.p.m. Presently, no independent method of determining the purity of a substance to better than 10 p.p.m. is available.

The electrode process itself is another source of error. A current efficiency of 100.0000 per cent is required. Current efficiency is determined by the titration of a "pure" chemical and calculating the purity of the chemical. Once the current efficiency is established at 100.0000 per cent the value of the faraday can be determined from another coulometric titration. In establishing the current efficiency, the value of the faraday is used and in turn, the current efficiency is used in the calculation of the faraday; this is a cyclic process. Hoyle and co-workers (39) determined the current efficiency of the generation of hydrogen ions at the hydrazine-platinum anode by comparing the results from the analysis of tris(hydroxymethyl)-aminomethane titrated directly at the hydrazine-platinum anode with the results from the titration at the cathode of the excess perchloric acid added to the sample. The perchloric acid was standardized by titration at the cathode. The results from the titration of the base involving two different electrode processes were identical.

In examining the relationship of charge transfer kinetics at the electrode to the current efficiency, Bishop (3) found that the "ideal" conditions for 100.0000 per cent current efficiency were during the coulometric titration of either strong acids or strong bases in water.

As stated in the previous sections, the current electrochemical value of the faraday is some 20 p.p.m. greater than the physical value. The higher value of the electrochemical faraday could result from some of the current passing through the titration cell without effecting any electrochemical work at the electrode. This current would be measured by the current sensing resistor and the faraday calculated would be high. The hydrated electron has been suggested (Diehl, private speculation and communication, Iowa State University) as a method of transporting electrons through the solution in the titration cell. Hydrated electrons have a high mobility in solution but the half-life of the existence of the hydrated electron is very short (36,50,55). In water, hydrogen ions are scavengers of the hydrated electron and react with the hydrated electron to produce hydrogen; the net result is 100.0000 per cent current efficiency (36,50).

Electromigration of ions between the compartments of the coulometric titration cell is another possible source of error. Cations are attracted toward the cathode and anions are attracted toward the anode. The supporting electrolyte added to the solution in the compartments of the titration cell helps to minimize errors caused by migration. However, hydrogen ions and hydroxide ions have a higher mobility than the ions from the supporting electrolyte and can migrate under certain conditions. A positive flow of the solution in the intermediate compartment of the titration cell from the intermediate compartment into the compartments housing the anode and cathode, a) helps to prevent the physical mixing of the solution in the counter-electrode compartment with the solution in the working-electrode compartment; b) helps to prevent the migration of hydrogen and hydroxide ions between the compartments. The disadvantage of the high flow rate is that impurities in the solution in the intermediate compartment are transferred into the working-electrode compartment. Thus, the design of the titration cell is important.

In my examination of the possible errors that could occur during a coulometric titration, I found that the determination of the equivalence-point and the electromigration of certain ions were the source of considerable errors. The problem of migration is discussed in Chapter IV. The location of equivalence-points and the theoretical aspects of the problem for strong acid-strong base titrations are given in Chapter III.

D. Selection of Primary Chemicals and Solvents

1. Selection of Primary Chemical

Carboxylic acids were chosen as the primary standard chemicals in this work because a material requiring different chemistry from the titration of 4-aminopyridine by Koch, Hoyle and Diehl (47) was desired. Crystals of a chemical grown from solution always contain occluded mother liquor in cavities in the crystal and are impossible to remove completely (45,91,93). Melting the crystals removes the liquid but some materials decompose on heating at the temperature required for fusion. Sublimation of the material also removes occluded mother liquor but the number of organic materials which can be sublimed is limited.

Three organic acids were used in the present work: benzoic acid, furoic acid and adipic acid; can be sublimed. Benzoic acid was considered by Bates and Wichers (2) as the ultimate primary standard. The benzoic acid prepared by them was purified by zone refining; the benzoic acid used in the present work was purified by sublimation. Furoic acid was first proposed as a primary standard by Kellog and Kellog (41) because the acid was easily sublimed. Furoic acid was suspected to undergo decarboxylation during sublimation (34) and the material used in the present work was sublimed at a low temperature. Adipic acid had been suggested as a primary standard much earlier, Van Voorst (88), and had been titrated coulometrically with high-precision by Taylor and Smith (84). In the present work it was found that adipic acid can be sublimed, although curiously I found no mention of this in the literature.

Potassium hydrogen phthalate was also studied in the present work although it cannot be purified by sublimation and it was necessary to titrate crystals prepared from water solution. A well-analyzed sample of this material was available from the National Bureau of Standards, SRM 84d, Potassium Hydrogen Phthalate. This particular sample had been titrated four times in the past by high-precision techniques (2,24,42,84).

2. Selection of the solvent

Nonaqueous solvents have been used in the past in coulometric titrations but not in high-precision work leading to a value for the faraday. Among the solvents which have been used are: methanol (13,14), ethanol (14), 2-propanol (8,14,40), t-butanol (26), acetone (26,79), tetrahydrofuran (9), m-cresol (4), dimethylsulfoxide (5) and benzene-alcohol mixtures (14). In all of these titrations, small amounts of the sample were used and the relative standard deviations ranged from 0.2 to 2 per cent. In most cases, traces of water were required in the nonaqueous solvent for 100 per cent current efficiency. In one study of alcohols, the current efficiency was found to drop as the number of carbon atoms of the alcohol increased (13).

Mixtures of water and water miscible solvents have also been used in coulometric titrations. Water was added to 2-propanol in large amounts to obtain 100 per cent current efficiency (13). Carson and Ko (8) obtained satisfactory results using 30:70 water:2-propanol mixtures in the coulometric titration of micro samples of organic acids. Yoshimori (92) titrated benzoic acid in a 70:30 water:ethanol mixture; the relative standard deviation being 89 p.p.m.

Nonaqueous solvents, because of the poor precision obtained, would appear to be pretty much ruled out as a solvent for the determination of the faraday. Also, the high resistance of the nonaqueous solvents requires a higher maximum voltage from the constant current source than available in the apparatus used in the present work. Mixtures of water with water miscible nonaqueous solvents have a much lower resistance than completely nonaqueous solvents. Most of the common salts used as electrolytes will dissolve in the mixed solvents at the high concentrations essential in coulometry. Mixtures of water with methanol, 2-propanol, acetone and acetonitrile were studied in the present work. These mixed solvents were used in the titration of benzoic acid and of furoic acid, Chapters VI and VII, respectively.

II. APPARATUS AND PROCEDURE FOR HIGH-PRECISION COULOMETRIC TITRATION

A. Introduction

The effort to reduce the uncertainty in the value of the faraday to less than one part per million (1 p.p.m.) by the electrochemical method began with a review of the sources of uncertainties in the various measurements involved in the latest work, passed to the assembly and calibration of the necessary devices for the high-precision physical measurements, and finally went on to chemical problems.

Estimates of the so-called *systematic uncertainties* at the one standard deviation (70 per cent confidence level) in their work were made by Koch and Diehl (ref. 46, p. 511, Table 3) and combined with the *random uncertainty* expressed as the standard deviation of the mean of the results of the titrations. Examination of the systematic uncertainties, indicated that although the apparatus of Koch and Diehl was acceptable for the 10 p.p.m. level, the various units, with the possible exception of the device for the measurement of time, and possibly the measurements of resistance and potential, were marginal at the 1 p.p.m. level. It seemed best, therefore, to make a clean sweep and to secure new devices and better calibration of each of the measurements. Fortunately, and what made the work possible at all, a grant of $11,900 was obtained from the Iowa State University Research Foundation for the purchase of apparatus and several successive, voluntary grants were received from Mr. and Mrs. Clifford C. Hach of Loveland, Colorado, for the purchase of apparatus, for operating expenses, and for stipends.

As reported in detail in the various sections below, each of the various units of the coulometric titration apparatus was subjected to scrutiny and new equipment was obtained and carefully calibrated.

The constant current source used by Koch and Diehl was failing toward the end of their work; this unit, a Leeds & Northrup Company, "Coulometric Analyzer", Model 7960 was retired to the teaching laboratory and a new unit was obtained. This constant current source was based on the Kroeger-Rhinehart circuit (52), was stable to a few parts in 10^7, and was built in the electronic shop of the Ames Laboratory of the Department of Energy.

Two, new 10-ohm resistors were purchased from the Leeds & Northrup Company. These resistors were calibrated at the Electricity Division of the National Bureau of Standards.

A modification of the current measuring circuit, which eliminated the Leeds & Northrup Company Type K-5 Potentiometer, was adopted. In this modification, an invention of Dr. George Marinenko of the National Bureau of Standards, the potential drop over the standard resistor is opposed directly to the potential of a standard cell and the difference in potential measured with a micropotentiometer. The resistance of the standard resistor and the value of the current from the constant current source were so chosen that the difference between the two potentials was a matter of only a few microvolts. In the event, because the chemistry employed later in the investigation proved no where near good to 1 p.p.m., much of the chemical work reported was followed with the K-5 Potentiometer.

A new bank of four saturated Weston cells, with built-in temperature regulation, was purchased. These cells were calibrated at the Electricity Division of the National Bureau of Standards against the Josephson junction and transported by air freight to Ames.

A new timing device, with a stability of 0.5 p.p.m., was obtained. This device was calibrated against the time signals from the Fort Collins broadcasting station, WWV, of the National Bureau of Standards. To obtain the signals clearly, a new antenna was mounted on the roof of Chemistry Hall. It is probable that my calibration of the Fluke timer, which involved personal manipulation of a switch on receipt of the signal, was poorer than the calibration by the manufacturer.

A microbalance manufactured by Mettler Instrument Corporation, Hightstown, New Jersey, Model M5SA, was purchased. This balance was mounted in a walk-in constant temperature box inside the constant temperature room. The temperature within the balance case was measured with a platinum resistance thermometer.

Additional 1-piece, Class M weights were purchased from the Ainsworth Division, Denver Industries, to build the earlier 1- and 10-gram Class M weights to a complete set from one through fifty grams. This set was calibrated at the Electricity Division of the National Bureau of Standards by Dr. W. F. Koch and Mr. J. S. Gibson during 1976 against a set of platinum weights newly back from the International Bureau of Weights and Measures. The earlier work of Knoeck and Diehl (42) and of Koch, Hoyle and Diehl (47) was done with the 1- and 10-gram Class M weights just mentioned and a rhodium-plated brass set which had been calibrated at the National Bureau of Standards in 1944 and 1967 (at the Mass and Volume Section) and again in 1974 (in the Electricity Division).

Of the physical measurements involved in evaluating the faraday, the measurement of mass is that subject to the greatest uncertainty. The problems connected with improving the measurement of mass were under investigation concurrently with the present work and in the same laboratory, by

Mr. J. S. Gibson. Specifically, he has been concerned with: (a) the measurement of the density of air with sufficient accuracy so that the correction for buoyancy could be made with an uncertainty less than 1 p.p.m.; and (b) the subdivision (dissemination) of mass from the standard kilogram to the working 1- and 2-gram weights with accuracy of 1 p.p.m. By January 1980, the first of these problems was about solved but work on the second problem was still under way. Solving the problem of measuring the density of air accurately, involved Mr. Gibson in the construction of a walk-in constant temperature box inside the constant temperature room (the same room used for the coulometric titration apparatus) and in the construction and installation of equipment for the high-precision measurement of barometric pressure, temperature, and water and carbon dioxide contents of the atmosphere. Use was made of certain of Mr. Gibson's apparatus in the present work.

The coulometric titration cell used was basically the same three-compartment cell of Eckfeld and Shaffer, Knoeck and Diehl, and Koch, Hoyle and Diehl, but was more carefully constructed with respect to the electrical connections, shielding and grounding, was designed to minimize loss of material by migration through the membrances, permit ease of washing, and reduce loss of material by entrapment by escaping gases. The J-shaped titration compartment of Koch, Hoyle and Diehl was rejected in favor of a cylindrical cell which was easier to wash. A bubble trap was perfected by which gases evolved at the working electrode were freed of electrolyte before venting.

Especial care was taken in the preparation of chemicals employed. In particular, the supporting electrolytes were freed of suspended silica by filtration through micropore filters.

As a result of the new apparatus and improvements just outlined, the titration apparatus finally assembled was inherently of such quality that a coulometric titration could be made on it with an uncertainty less than 1 p.p.m., with the possible exception of the measurement of mass. Unfortunately, the chemistry studied, the titration of pure acids with alkali generated at the platinum cathode, was found to be considerably less trustworthy. Each of the various features of the apparatus is now described in more detail.

B. Apparatus and Measurement of the Various Physical Quantities

1. Basic electrical circuit

The basic electrical circuit used is shown in schematic form in Figure 1. The constant current source A was essentially two constant current sources, delivering

Figure 1. Circuit of coulometric titration apparatus

A. Constant-current source

B. Standard resistor, 10-ohm

BB. Standard resistor, 20-ohm

C. Microvolt potentiometer, Honeywell, Model 2779

CC. Potentiometer, Leeds & Northrup Company, Type K-5

D. Standard cell, unsaturated

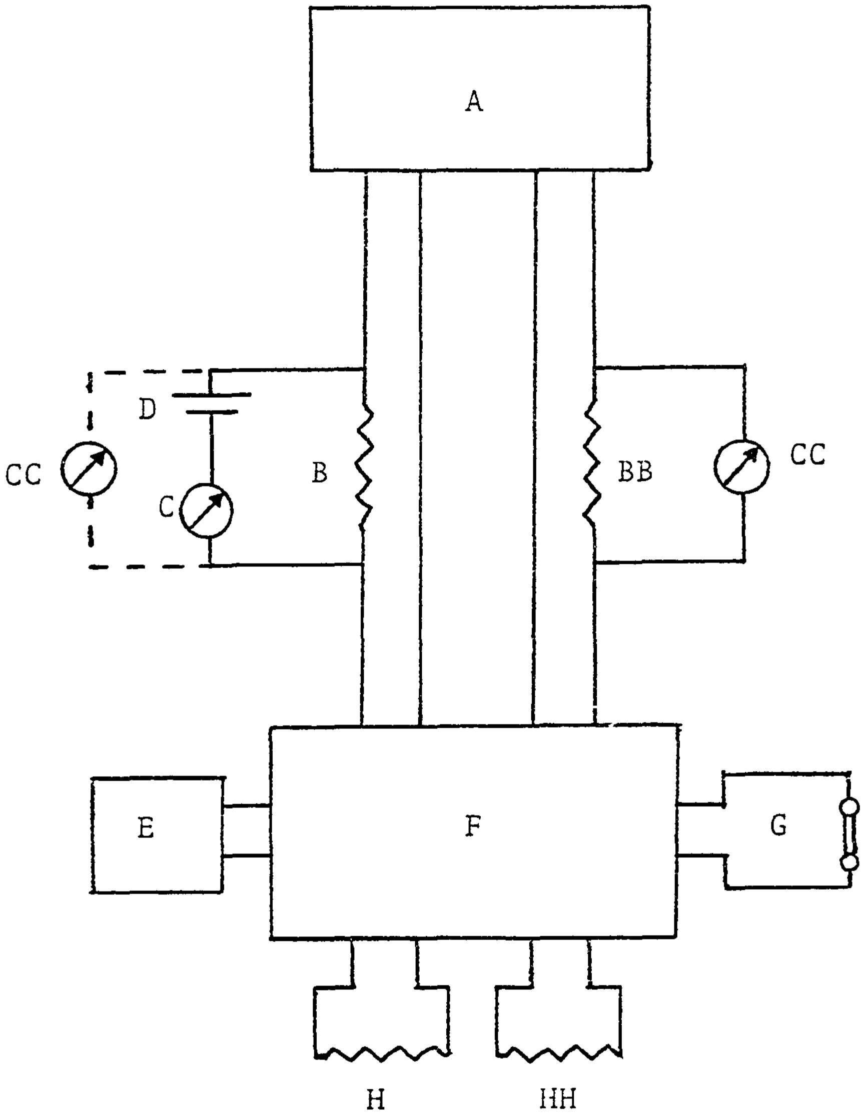
E. Electronic timer, Fluke, Model 1952A

F. Relays and switches

G. Titration cell

H. Dummy load, 100-mA circuit

HH. Dummy load, 5-mA circuit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H
HH

respectively 100-mA and 5-mA. These currents passed through the multiple, gang switch F so that each current when not being used in a titration was passed through a dummy load, H for the 100-mA current, HH for the 5-mA current. During a titration, one or the other current was passed through the titration cell G, the timer E being turned on and off simultaneously with the current. Switch F was also designed so that the polarity of the current supplied the electrodes of titration cell G could be reversed. The currents were measured by measuring the potential drop over the standard resistors B and BB. The potential drop over the 10-ohm standard resistor B was measured by one or the other of two methods: (a) opposing the potential drop over B to a standard, unsaturated Weston cell D with a micropotentiometer C, or (b) directly with a Type K-5 potentiometer CC. The potential drop over the 20-ohm standard resistor was measured directly with the Type K-5 potentiometer.

All external wiring was made with insulated, number 12 copper wire, two such wires being twisted together and inserted into braided metallic shield which was connected to a good earth ground. No solder was used at any electrical connection. Considerable attention was devoted to eliminating pick-up of electromagnetic radiation (noise): ground loops were eliminated; isolation transformers were installed; specific parts of each unit of the apparatus were grounded or deliberately not grounded; the grounding circuit of the alternating current, house main was disconnected. The approach was essentially empirical but in the end the noise was reduced to essentially zero at the 1 μV level.

The titration cell was housed in a plastic box. The titration cell, all of the electrical apparatus, and the necessary constant temperature oil baths and boxes housing the resistors and standard cells were assembled in a constant temperature room, Room 137A Chemistry Hall. This room was held to within ±1°; the temperature in the neighborhood of the electrical and titration equipment varied less than ±0.5°.

2. Constant current source

The constant current source consisted of a solid state device based on the Kroeger-Rhinehart circuit (52). The device was powered by a well-regulated supply powered in turn by an electrically shielded power transformer which eliminated ground loops. The amplifier used in the circuit was the Analog 232J chopped, stabilized, operational amplifier. An emitter-following transistor was used to boost the power from the operational amplifier to the 100-mA output, the latter being delivered at a voltage up to a maximum of 25 V. This constant current source provided two currents, 100-mA and 5-mA. A switching circuit was incorporated into the instrument so that a constant current could be passed through the standard resistors at all times and the current switched from a dummy load to the titration cell, activating simultaneously the timing device. The circuit was devised so that switching transients were eliminated.

3. Standard resistors

Two, new Standard resistors were purchased from the Leeds & Northrup Company. These resistors were of the wire-wound, four terminal, NBS-type, made from a manganese-nickel alloy, Catalog Number 4025-B. These resistors were calibrated during October to December 1974 by the Electricity Division of the National Bureau of Standards, Test Number 21101:

10-Ohm Resistor, Serial Number 1838973 9.999,966 ohms
(25.00°; uncertainty 0.016 p.p.m.)

10-Ohm Resistor, Serial Number 1838965 9.999,978
(25.00°; uncertainty 0.016 p.p.m.)

The 20-ohm resistor used was the one used earlier by Koch, Hoyle and Diehl manufactured on special order by the Leeds & Northrup Company, Catalog Number 4025-B-S, and calibrated by the company, by Professor C. A. Swenson using other resistors calibrated at the National Physical Laboratory, and by the Electricity Division of the National Bureau of Standards (see Ref. 47, p. 719, Table 2):

20-Ohm Resistor, Serial Number 1711765 19.999,703 ohms
(25.00°; uncertainty 0.2 p.p.m.)

The two resistors in use during the course of the work described later in this dissertation, Number 183873 for measuring the 100-mA current, Number 1711765 for measuring the 5-mA current, were totally immersed in an oil bath maintained at 24.80 ± 0.05°; the terminals were covered by the oil in conformity with the manner in which the resistors were calibrated. The operating currents were passed through the resistors at all times, the currents passing through dummy loads when a titration was not in progress. The internal heating thus provided brought Number 183873 to 25.00° and Number 1711765 to 24.80°. The effect of the difference in temperature between calibration (25.00°) and use (24.80°) on the resistance of Number 1711765 was less than the uncertainty in the calibration (see Ref. 47, p. 719 for the temperature coefficients of the Leeds & Northrup Company resistors).

4. Measurement of potential drop across resistors

The potential drop across the 10-ohm resistor was measured in two ways: (a) directly with a Type K-5 Potentiometer, and (b) by opposing the potential drop to that of standard cell and measuring the difference in potential with a Microvolt Potentiometer.

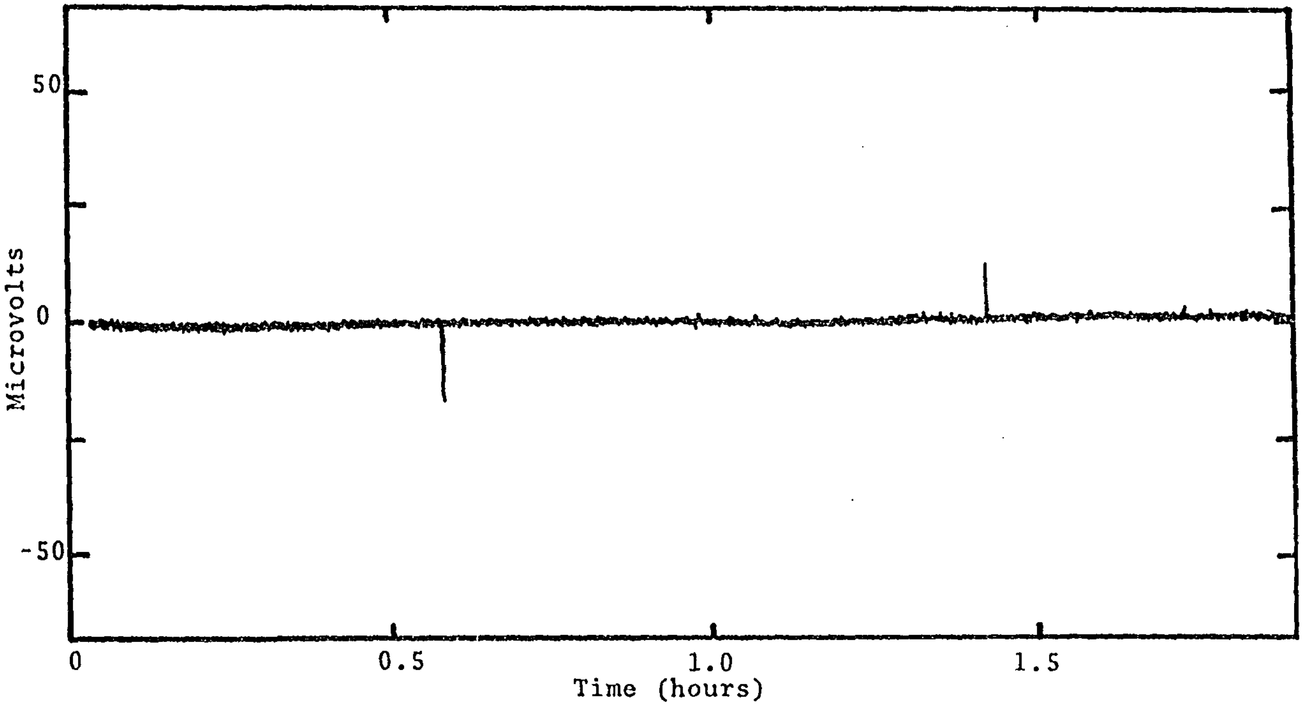
The direct measurement was made with a Leeds & Northrup Company Type K-5 Potentiometer, Model 7555-1B, Serial Number 1713729, equipped with a D. C. Null Detector, Leeds &

Northrup Company Catalog Number 9834-1. With the potentiometer on the 1.6 V range, the potentiometer can be read to 1 μV. The K-5 Potentiometer was calibrated following the directions of the manufacturer, a procedure which involved determining the uncertainty in each dial. The calibration correction to the potential drop across the 10-ohm resistor was +1 μV. The potentiometer was calibrated with an unsaturated Weston cell, potential 1.019,192,1 V; the uncertainty in the potential drop across the 10-ohm resistor resulting from the uncertainty in the calibration was 2 μV. The D. C. Null Detector is provided with output terminals through which the off-balance would be put on a recorder; thus, the changes in the potential drop across the resistor during a titration was recorded on a Hewlett Packard Strip Chart Recorder (Model Number 17133A).

The noise in the measurement of the potential drop across the 10-ohm resistor by the K-5 Potentiometer was less than 2 μV; a typical example, taken during the course of a titration, is shown in Figure 2. The drift in potential during the titration was 2 μV or less although the potential sometimes drifted up to 5 μV during the first few minutes of a titration.

In the opposition-off balance method of measuring the potential drop over the 10-ohm resistor, the difference in potential was measured with a Honeywell Low Range Microvolt

Figure 2. Strip chart recording of the potential drop across the 10-ohm standard resistor during a titration



50
0
-50
Microvolts
0
0.5
1.0
1.5
Time (hours)

Potentiometer, Model 2779, Serial Number P2264, calibrated by Professor C. A. Swenson and on loan from him. A Keithley Model 155 Nulldetector Microvoltmeter was used as a null-point detector. As in the direct method, the output of the Nulldetector Microvoltmeter was recorded continuously on a strip chart recorder during a titration. The uncertainty in the Honeywell Microvolt Potentiometer was estimated to be 0.02 per cent of the reading plus 0.1 μV; the uncertainty when the off-balance was 500 μV was thus less than 0.2 μV.

The 5-mA current was measured by measuring the potential drop across the 20-ohm standard resistor with the K-5 potentiometer on the 0.16-V range. On the 0.16-V range, the instrument can be read to 0.1 μV and the calibration correction is +0.3 μV; the maximum uncertainty in the measurement of the drop over the 20-ohm resistor is estimated to be 0.7 μV.

5. Standard cells

The electrical potential standards used in the present work were: (1) a bank of our standard, Weston saturated cells in a constant temperature box, calibrated at NBS, and (2) three standard, Weston unsaturated cells, calibrated against the bank of saturated cells and used as working standards.

A new bank of standard saturated cells, manufactured by The Eppley Laboratory, Inc., Newport, RI, Model 125, Serial

Number 5081, was delivered directly to NBS, calibrated by NBS (Test Number 211.10-13-76), and shipped air freight to Des Moines. The values for the potentials of the four standard cells are given in Table 2.

Table 2. Potentials of saturated standard cells in 1972 NBS volts

Eppley Model 125, Serial Number 5081

Cell Position	Cell Number	Eppley Laboratory[a] Volt	NBS Laboratory[b] Volt	Uncertainty[c] Microvolt
1	F1351	1.018,224	1.018,228,0	0.48
2	F1363	1.018,224	1.018,226,0	0.48
3	F1353	1.018,225	1.018,225,9	0.48
4	F1354	1.018,223	1.018,224,1	0.48

[a] Calibrated by Eppley reference standards traceable through the National Bureau of Standards, Test Number 212275, May 1975. Temperature of the cells were 28.04° during calibration. Calibration completed January 6, 1976.

[b] Calibrated during February to March 1976 at the National Bureau of Standards, Test Number 211.01-13-76. Mean operating temperature during calibration was 28.0370°.

[c] Uncertainty in the NBS value including random fluctuations in the cell under test and in NBS equipment and standards. The random error component was computed from the standard deviation of the mean at the three sigma level.

With respect to the calibration of this bank of cells, it should be noted that when received in Des Moines, and promptly taken to Ames, that the temperature of the box (built-in thermometer) was considerably below the temperature at which calibrated by the Eppley Laboratory and the NBS. The temperature control in the box housing the cells is powered by the 110 V A.C. main or alternatively (for shipment or failure of the power line) by a bank of nickel-cadmium batteries. The difficulty was traced to the improper installation of two fuses and the burn-out of the most critical one. The calibration sheet from NBS states that: "This standard cell enclosure was received 19 Jan. 1976 not under power with an internal temperature far below its normal operating level." Apparently, the defect was not traced and corrected at NBS and the calibration there was apparently made with sole reliance on the control of the temperature of the laboratory. After the defect was corrected, the bank was stored in Room A20, Physics Hall, a room of fairly uniform temperature, and as an alternative in the event of a power failure, the bank was powered with two 12-V storage batteries in parallel.

Because the chemistry of the coulometric titrations reported later in this dissertation proved poorer, by one order of magnitude or more, than the precision of the measurements, the very exact values of the potentials of the cells of the bank proved immaterial. For any work of high accuracy, however, this bank should be recalibrated; this should be done (early 1980) in any event because of the normal, slight drop in potential of standard cells on aging.

The three standard, unsaturated cells used in this work as working standards were manufactured by The Eppley Laboratory, Inc., Catalog Number 100, Serial Numbers 791896, 906020, and 860823. The history of cells 791896 and 806020 was reported by Koch, Hoyle and Diehl (47). Cell 860823 was purchased in July 1978 and the certificate of calibration by Eppley Laboratory gives for the value 1.01920 V at 22° (calibration June 1978). The unsaturated standard cells were housed in a polystyrene box in constant temperature room 137A Chemistry Hall and held at 25.0 ± 0.3°. The three standard, unsaturated cells were calibrated against cells number 1 and 4 of the bank of saturated cells by connecting the cells in opposition and measuring the potential difference with the Honeywell Low Range Microvolt Potentiometer. This potential difference could be determined to within 0.1 μV. The temperature of the unsaturated cells during the calibration was 25.0°, the temperature of the saturated cells was 28.045°. The potentials of the unsaturated cells are given in Table 3.

Table 3. Potentials of unsaturated standard cells in 1972 NBS volts

Serial Number	Temperature C°	Potential Volts
	Calibration made during June 1979	
791896	25.0	1.019,026,0
806020	25.0	1.019,149,0
860823	25.0	1.019,192,1

6. Measurement of time

A new timing device was obtained from the John Fluke Mfg. Co., Toronto, Ontario: Digital Counter Timer, Model 1952A, Serial Number 0679-C, modified for control by the switching system of our constant current source. The last digit of the Fluke timer records thousandths of a second. The timer was found to be less than 0.5 p.p.m. slow as detailed in my M.S. thesis (34). The major error in my calibration of the timer was the human error in turning the switch on and off in response to the signal from NBS Station WWV. The calibration of the manufacturer is probably better than my calibration.

A more accurate method of calibrating timers, although not used in this work because of the lack of time, is now available to almost any laboratory; this method makes use of the 5-MHz Rubidium time standard maintained by the television networks. The 5-MHz Rubidium standard is used to generate a very accurate 3.58 MHz subcarrier frequency which is broadcast by the networks through local television stations. Color television sets phase-lock the 3.58-MHz signal for use as a standard frequency. The very accurate, phase-locked, 3.58-MHz signal from a television set can be used as a standard frequency for comparison to local oscillator timers by appropriate and relatively simple electronics (16,17,37). The 10-MHz time base oscillator of the Fluke timer could be adjusted by this method to a relative error of only 1 in 10^9. The difference in the network standard frequency (5 MHz) and the NBS time and frequency standard is published monthly in *NBS Time and Frequency Services Bulletin*.

C. Measurement of Mass.

Weighing Samples for Titration

The "true mass" or "mass in vacuum" of an object is calculated from its mass in air by

$$W_{o,v} = W_{o,a} \frac{(1 - d_a/d_w)}{(1 - d_a/d_o)} \qquad (2)$$

$W_{o,v}$ being the "true mass" of the sample;

$W_{o,a}$ being the sum of the "true mass" of the weights used in weighing the sample in air;

d_a being the density of air;

d_w being the density of the weights;

d_o being the density of the object being weighed.

The density of air (29) was calculated from the prevailing temperature, barometric pressure, and relative humidity by

$$d_a = \frac{0.001{,}292{,}3(P_{bp}) - 0.037{,}80(P_{H_2O,t})(\text{Rel. Hum.}/100)}{(1 + 0.003{,}600{,}99(t))(760)} \qquad (3)$$

P_{bp} being the barometric pressure in mm. of mercury;

$P_{H_2O,t}$ being the partial pressure of water vapor at the temperature of the air;

t being the temperature of the air (C°).

All samples were weighed on the Mettler microbalance, Model M5SA. The balance was capable of weighing a maximum of twenty grams; direct reading to 1 μg. The temperature inside of the balance was measured by the platinum resistance thermometer (see Section D) placed inside the top of the balance. The barometric pressure was measured by a mercurial barometer, fixed canister type manufactured by the Julien P. Friez & Sons, Baltimore, Maryland, Catalog Number 715B. The relative humidity was measured by an Airguide, Model 113B, hygrometer.

The stainless steel weights in the balance were calibrated by the manufacturer at an arbitrarily chosen density of air and density of the weights (see Appendix II of the

M.S. thesis of J. S. Gibson (29)). The stainless steel weights in the balance were calibrated with a set of two piece rhodium-plated brass weights manufactured by the Wm. Ainsworth & Sons, Inc., Serial Number 9156. These weights were calibrated by the National Bureau of Standards in 1944 and 1967 (Test Number G37168) by the Volume Section and in 1974 by the Electricity Division. The "true mass" of each of the stainless steel weights in the balance was determined.

The sample to be titrated was weighed in a glass sample boat with a handle made of platinum wire. The glass boat was first weighed after which the sample was placed in the glass sample boat and both weighed. The "true mass" of the weights in the balance (nominal plus correction) actually used in weighing the sample was determined. The "true mass" of the sample was calculated by equation (2) to correct for the buoyancy of air on the weights and the sample.

D. Measurement of Temperature

The temperature inside the case of the microbalance was measured by the change in the resistance of a platinum resistance thermometer. Five platinum resistance thermometers, element type W63-01, with a resistance of 100 ohms were obtained from the Degussa, Inc., Teterboro, New Jersey. The resistance of the thermometers at different temperatures were determined by M. S. Anderson of the Physics Department using a Leeds & Northrup Company standard platinum thermometer calibrated by the National Bureau of Standards. Seven temperatures between 273 K° and 306 K° were used. In this temperature range, the change in the resistance of the thermometers with temperature was linear.

One of the platinum resistance thermometers was placed in the top of the balance case. A constant current source based on the Kroeger-Rhinehart (52) circuit was built to provide a constant current to the platinum resistor. The current output of the constant current source was adjusted to provide the same current under which the thermometers were calibrated; 85 mA. A 100-ohm, oil filled standard resistor, Model Number CH46-T4, manufactured by the Julie Research Laboratory, was placed in series with the platinum resistance thermometer. This resistor was used to measure the current passing through the platinum resistance thermometers and was calibrated by M. S. Anderson. The standard resistor was placed in a polystyrine insulated box to moderate the temperature changes of the resistor.

The potential difference across the platinum resistance thermometer and the 100-ohm standard resistor were measured by a White Double Potentiometer, Model Number 7623, Serial Number 766847, manufactured by Leeds & Northrup Company and on loan from Professor B. C. Gerstein of the Ames Laboratory of the Department of Energy. A Keithley Model 155 Null-detector Microvoltmeter was used as the nulldetector. Two constant current sources based on the Kroeger-Rhinehart circuit were built to power the potentiometer. The temperature of the platinum resistance thermometer was calculated from a first order equation relating the resistance of the platinum thermometer to the temperature.

E. Measurement of pH

All measurements of pH, except when stated otherwise, were made with a meter manufactured by the Hach Chemical Company, Loveland, Colorado, Model 8596, Serial Number 100. The output of this pH meter, 100 mV per pH unit, was measured with a digital voltmeter manufactured by Data Precision Corporation, Wakefield, Massachusetts. In the 1-V range, this voltmeter, which incorporates a four and a half digit display, can be read from +1.9999 V to -1.9999 V with an uncertainty of 0.0001 V. Thus, digital reading multiplied by 10 gave pH.

The electrical circuit of the Hach pH meter was also modified to increase the sensitivity of the fine offset dial. It was also modified to eliminate some of the switches, a modification which improved the correlation between scales on shifting ranges. The latter change also reduced the frequency of calibration needed and made calibration easier in that only two variable resistors were then needed, the fine offset and the slope.

A Beckman "High Alkalinity" glass electrode, Beckman Instrument Company, Catalog Number 39301, was used in conjunction with a saturated calomel reference electrode. When the solution under study contained perchlorate, a modified reference electrode was used in which the saturated potassium chloride solution was replaced by a saturated solution of sodium chloride; this prevented the precipitation of potassium perchlorate at the junction of the reference electrode and the solution under study.

The pH meter was calibrated using two NBS standard buffers, pH values 4.008 and 7.413 at 25.0°. With the electrodes immersed in the 4.008-buffer, the fine offset of the pH meter was adjusted to 0.0000 V on the digital voltmeter. The electrodes were immersed in the 7.413-buffer and the slope of the pH meter was adjusted to read 0.3405 V, corresponding to the 3.405 difference in pH between the two buffers. The fine offset was adjusted to produce a reading of 0.7413 V corresponding to a pH of 7.413. The 4.008-buffer was then rechecked; if the reading was off by more than 0.002 pH units, the above procedure was repeated. As an additional check, the pH of another NBS standard buffer, pH 6.865 was measured. In this procedure, the interaction between the gain of the amplifier of the pH meter (slope) and the input to the amplifier is avoided because the input voltage to the amplifier is set to zero.

The pH meter was calibrated before every coulometric titration, but experiments indicated that the drift over a 24-hour period was less than 0.002 pH units.

It was found that the pH meter must not be grounded, otherwise ground loops between the meter and the constant current source were set up. In the pH meter, the reference electrode was connected directly to ground and the ground loop created when the current was flowing through the titration cell caused interference both in the measurement of the current with the K-5 potentiometer and the pH. When the ground to the pH meter was disconnected, the noise in the K-5 potentiometer was less than 1 μV in the measurement of the 100-mA current.

F. Titration Cell

1. General design of a three-compartment cell

The titration cell used in this work was a hybridization of the cells of Koch, Hoyle and Diehl (47), Knoeck and Diehl (42), and Eckfeldt and Shaffer (24). The J-shaped titration compartment of Koch, Hoyle and Diehl was found to be hard to wash and was rejected in favor of a simple, 300-ml., tall-form beaker without lip. This beaker was covered with a tightly fitting lid of Plexiglass pierced to carry the glass electrode, the reference electrode, the platinum working electrode, the intermediate compartment (shield tube), a nitrogen inlet tube, and an opening through which the boat carrying the sample could be introduced. The opening for the boat was closed by a Teflon plug through which passed a platinum rod used to manipulate the boat. The assembly is shown in Figure 3. The working electrode was a coil of platinum wire surrounded by a bubble shield (described in detail below).

The intermediate compartment, Figure 4, consisted of a glass tube, 30 mm. in diameter, to the bottom of which was fastened a porous membrane of either unfused Vycor or ultra fine glass frit. Provision was made for passing nitrogen into the compartment.

The compartment containing the counter electrode consisted of a glass tube, 14 mm. in diameter, with a disc of unfired Vycor sealed to the bottom. The counter electrode compartment was inserted through a rubber stopper and placed inside the intermediate compartment. The counter electrode was a platinum foil, 2.0 by 1.2 cm. in size, supported and connected electrically by a platinum wire. Provision was made to remove electrolyte from the counter electrode compartment by suction.

Figure 3. Coulometric titration cell

A. Plexiglass cover

B. Counter electrode compartment

C. Platinum counter electrode

D. Unfired Vycor membrane sealed to bottom of the counter electrode compartment

E. Intermediate compartment

F. Unfired Vycor sealed to the bottom of the intermediate compartment

G. Bubble shield containing the platinum working electrode

H. Magnetic stirring bar

I. Glass and reference electrodes

J. Opening for boat and platinum rod

K. Nitrogen inlet

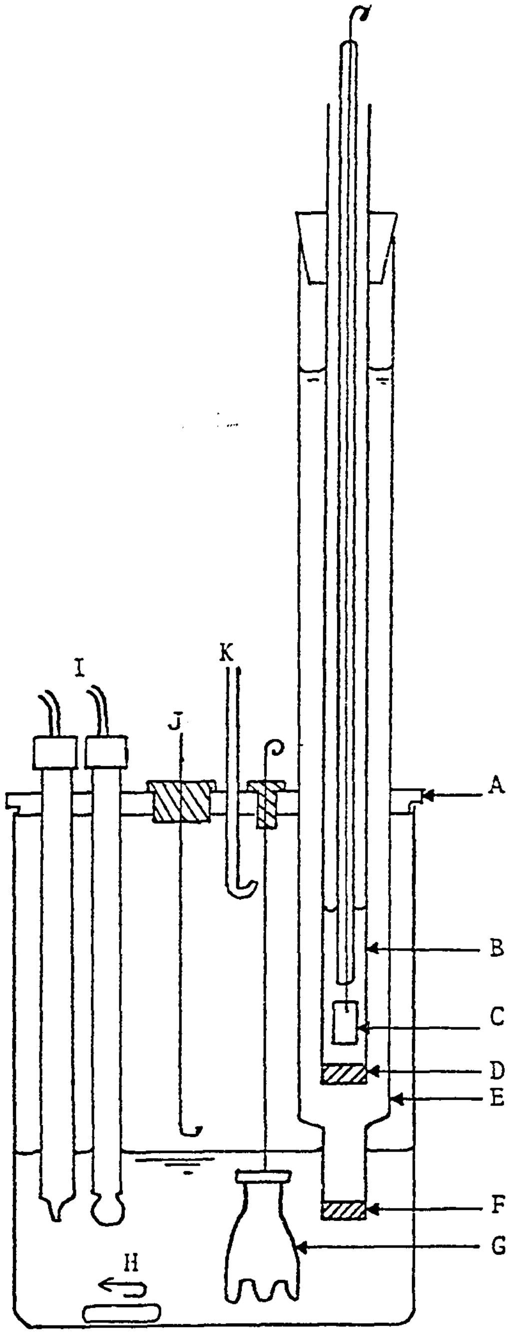

I
K
J
A
B
C
D
E
F
G
H

Figure 4. Intermediate compartments and counter-electrode compartment

I. Intermediate compartment with glass frit membrane

II. Intermediate compartment with unfired Vycor membrane

A. Platinum counter electrode

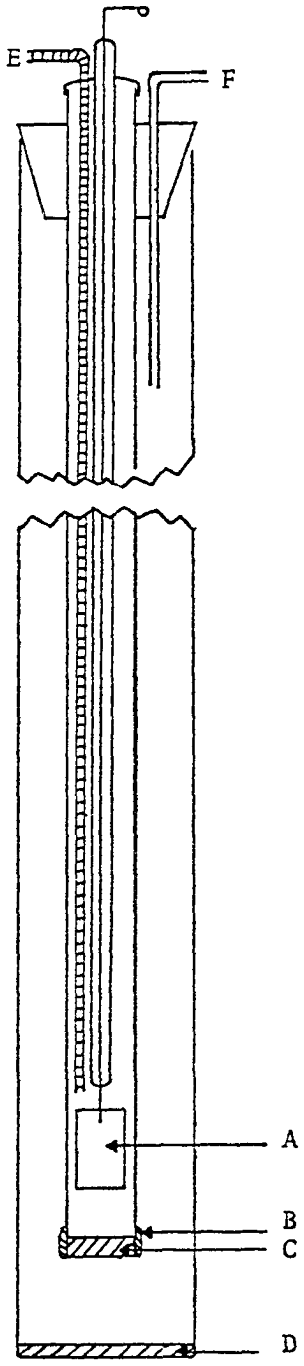
B. Silicone rubber seal

C. Unfired Vycor membrane

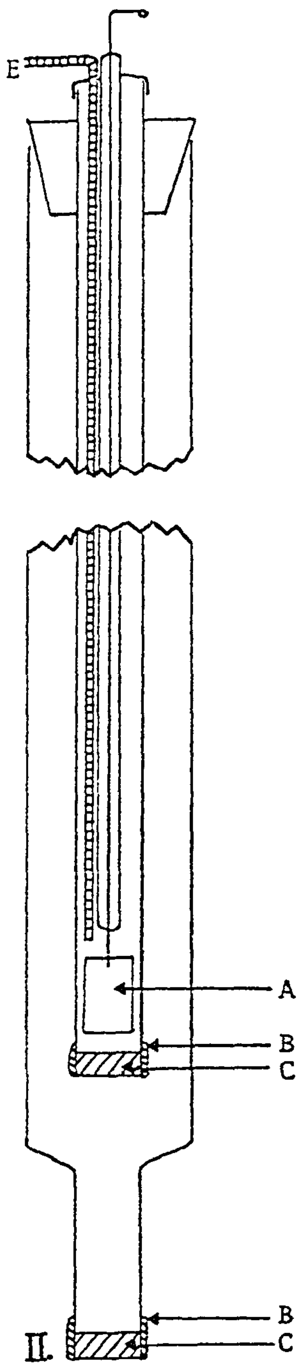
D. Glass frit membrane

E. Siphon tube

F. Nitrogen inlet



I.



II.

2. Porous membrances of glass frit and unfired Vycor

Discs of glass frit were sealed to the bottom of the tubes to be used as intermediate compartments by shrinking the tube about the frit and fusing the two together; care was exercised not to melt the frit during this operation. The glass frit membranes were cleaned by pulling water through them by suction.

The short rods of unfired Vycor were sealed to the tubes to be used as intermediate compartments by two methods, both suggested by Koch, Hoyle and Diehl (47). In the first method, unsatisfactory in my hands, the rod of unfired Vycor, 3 to 5 mm. long and 14 mm. in diameter, was butted against the bottom of the glass tube, which had been drawn down to the same diameter, and rod and tube covered with a length of heat-shrinkable Teflon tubing. The assembly then was given the necessary heat treatment. The seals prepared in this way all leaked as was clearly observed by the slow but definite passage of water colored with dye stuff between the Teflon tubing and the unfired Vycor.

The second method of sealing the rods of unfired Vycor to the glass tubes made use of Silicone Rubber Seal manufactured by the General Electric Company. The seal was allowed to cure for two weeks before use.

Unfired Vycor apparently swells when wetted. Koch, Hoyle and Diehl sealed their unfired Vycor rods inside the glass tube (with Silicon Rubber Seal) and reported that the Vycor rod frequently shattered. No shattering was experienced in the present work, probably because the Vycor was free to expand when butted against the end of the glass tube.

The unfired Vycor membranes were conditioned by soaking them for two to seven days in the supporting electrolyte to be used, then assembling in the titration apparatus and electrolyzing for six hours. This treatment was apparently effective in removing any acid left in the pores of the Vycor from the acid leach used in the manufacture. Between titrations, the unfired Vycor membranes were soaked in the same supporting electrolyte and care was taken not to use a membrane which had been immersed in a sodium perchlorate solution later in a potassium chloride solution, and vice versa; if these solutions were mixed, crystallization of potassium perchlorate occurred causing the membranes to crack.

3. Problem with spray. A bubble trap

Evolution of a gas at the working electrode always accompanies the coulometric titration of an acid or a base, hydrogen gas if an acid is being titrated

$$2H^+ + 2e^- = H_{2(g)}$$

or alternatively

$$2H_2O + 2e^- = 2OH^- + H_{2(g)},$$

oxygen or nitrogen if a base is being titrated

$$2H_2O = 4e^- + 4H^+ + O_{2(g)}$$

$$N_2H_5{}^+ = 4e^- + 5H^+ + N_{2(g)}$$

The gas appears as bubbles on the electrode, bubbles which grow with time and ultimately rise to the surface of the electrolyte, burst and spray the electrolyte about. The problem is especially severe with hydrogen, the low density of the gas causing the bubbles to travel faster and farther before bursting. Eckfeldt and Shaffer (24) stated that they felt as much as 0.1 per cent of an acid being titrated could be lost by spray. They relied principally on washing down the walls of the titration compartment toward the end of the titration but also placed a trap in the nitrogen vent which could be washed down periodically and this proved essential to their high-precision work.

The seriousness of the spray problem became quickly evident from observations with the coulometric titration apparatus described in preceding sections of this dissertation. During the titration of acids using the platinum cathode and the tall-form, 300-ml. beaker as cathode compartment, spray covered the walls of the vessel as far up as 5 cm. above the electrolyte and some spray reached the lid and some was even carried into the vent. It appeared immaterial whether the electrolyte was stirred or not. The amount of spray was very greatly increased if the stream of nitrogen gas, passed through the space above the electrolyte to insure the removal of carbon dioxide, was directed toward the surface of the electrolyte; this source of difficulty was about eliminated by turning the end of the nitrogen inlet tube in the form of the letter J.

The spray problem, coupled with the difficulty of washing the spray from all of the various items passing through the lid and down into the electrolyte (glass electrode, reference electrode, intermediate compartment, platinum electrode wire, nitrogen inlet tube) and the very inadvisability of even opening the titration compartment at all, prompted search for a spray trap. Of various devices tried, the best was a plastic shield, with a loosely fitting cover, which surrounded the platinum working electrode, Figure 5. The shield was made from the detachable polyethylene shield protecting the tip of the glass electrodes manufactured by the Fisher Scientific Company. The bottom of the shield was cut off so that the shield was small enough to be totally immersed by 100 ml. of electrolyte. A Teflon cap was made to loosely cover the open top of the shield. The platinum wire was coiled to form a helix which fitted into the interior of the shield without extending below the open bottom. The platinum wire passed through the center of

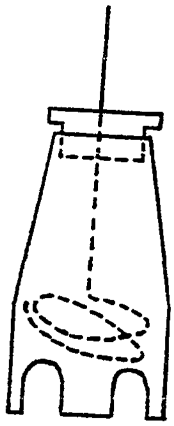


Figure 5. Spray trap

the Teflon cap and up through the lid of the titration compartment. It thus served to introduce the electricity and to support the shield and Teflon cap. The Teflon cap provided an excellent baffle which completely eliminated the spray.

During the passage of the 100-mA current during a titration, the shield was positioned in the electrolyte with the top 1.5 cm. above the surface of the electrolyte. With the stirring rate at less than two revolutions of the stirring bar per second, very few bubbles escaped from the bottom of the shield into the electrolyte. No spray was found on the various surfaces inside the titration compartment. Toward the end of the titration, the shield was simply lowered beneath the electrolyte and any spray collected on it and the Teflon cap were returned to the solution. Usually at this stage of the titration, the current was reduced to 5-mA and the final stage of the titration begun. This was effected with the shield completely immersed, the Teflon cap raised above the surface, and the rate of stirring increased; mixing of the electrolyte then took place more quickly. Before the final data for calculating the end-point were taken, the lid was raised briefly and walls of the beaker and the various items passing through the lid were washed down to insure that any spray which might have reached the walls was returned.

G. Reagents

1. Standard buffers

Three NBS Standard Buffers, 0.05 M potassium hydrogen phthalate, 0.025 M potassium dihydrogen phosphate-0.025 M disodium hydrogen phosphate and 0.008695 M potassium dihydrogen phosphate-0.03043 M disodium hydrogen phosphate were made according to Bates (1). At 25°, the pH of these buffers is 4.008, 6.865, and 7.413, respectively. The exact pH of the buffers at a given temperature was calculated by the equation of Bates (1, p. 75).

2. Sodium perchlorate

Sodium perchlorate solutions were prepared from vacuum distilled-perchloric acid. The acid was first boiled, and after cooling, was freed of chlorine by bubbling nitrogen through it. The acid was diluted to 4 0 M with water and the solution was cooled in an ice bath. A solution of 4.0 M sodium hydroxide was added slowly to the cooled solution of perchlorate acid until the pH, as measured by a pH meter, reached about 7.0. The 4.0 M sodium hydroxide solution was prepared from 50 per cent sodium hydroxide which in turn was prepared from "electrolytic pellets" purchased from the Fisher Scientific Company. The 50 per cent sodium hydroxide was filtered before use. The sodium perchlorate solution was diluted to the concentrations called for in the chapters which follow. The sodium perchlorate solutions were filtered before use through a Gelman Magnetic Filter Funnel, Model Number 4200, using a 0.45 µm. membrane filter.

The sodium perchlorate solution used in the intermediate chamber was made from sodium perchlorate monohydrate crystals. The crystals were dissolved in water to make a 7.0 M solution of sodium perchlorate. This solution was filtered through the 0.45 µm. membrane filter.

3. Sodium chloride

The sodium chloride solutions used in both the working-electrode compartment and the intermediate compartment was made fresh daily by dissolving potassium chloride purchased from the Fisher Scientific Company in water. The potassium chloride was diluted to the appropriate concentration and filtered through the 0.45 µm. membrane filter.

The solution in the counter-electrode compartment when sodium perchlorate was used as the electrolyte, consisted of 0.1 M sodium hydrogen phosphate and 1.0 M sodium perchlorate. When potassium chloride was used as the electrolyte, the solution in the counter-electrode compartment consisted of 0.1 M potassium dihydrogen phosphate saturated with potassium sulfate. The pH of these solutions were 10.0 except in Chapter IV, the pH was 7.0.

4. Distilled water

All solutions were made from distilled water redistilled from alkaline permanganate. Before the water was used to make the solutions, the purified water was filtered through the 0.45 μm. membrane filter. All wash water was bubbled with nitrogen to remove carbon dioxide.

5. Nitrogen

Commercial, prepurified cylinder nitrogen was treated by passage through a tube containing Ascarite and then a tube containing anhydrous magnesium perchlorate. The nitrogen was then passed through three scrubbers:
(a) vanadium(II) sulfate in 1.0 M sulfuric acid over amalgamated zinc; (b) alkaline potassium permanganate; and (c) water. Before the nitrogen entered the titration cell, the nitrogen was passed through an empty scrubber to eliminate any spray carried by the nitrogen.

H. Calculation of Results

The per cent purity of the sample of acid titrated with the coulometric titration apparatus was calculated by

$$\text{Per cent purity} = \frac{(C_{\text{total}})(\text{Equivalent Wt. of Acid})(100)}{(F)\ (W_{o,v})} \qquad (4)$$

in which F is the faraday, 96,486.56 1972 NBS coulombs per gram-equivalent-weight, $W_{o,v}$ is weight of the sample corrected for the buoyancy of air as calculated from equation (2), and C_{total} is the total coulombs of electricity required to titrate the sample as calculated by

$$C_{total} = A + B + C \tag{5}$$

A being the number of coulombs delivered during the 5-mA titration of the electrolyte from the point of inflection of the pretitration to the beginning of the passage of the 100-mA current

$$A = E_1 t_1 / R_{(20\text{-ohm})} \tag{6}$$

B being the number of coulombs delivered during the 100-mA titration given by

$$B = \frac{(E_{\text{unsaturated standard cell}} - E_{\mu\text{V potentiometer}})(t_2)}{R_{(10\text{-ohm})}} \tag{7}$$

or alternatively

$$B = E_2 t_2 / R_{(10\text{-ohm})} \tag{8}$$

C being the number of coulombs delivered during the 5-mA titration of the acid from the end of the 100-mA titration to the equivalence-point given by

$$C = E_3 t_3 / R_{(20\text{-ohm})} \tag{9}$$

E_1, E_2, and E_3 are the potential drops over the standard resistors measured by the K-5 potentiometer. Equation (6) or (8) was used depending on whether the potential of the 10-ohm resistor was measured by the difference between the 10-ohm resistor and an unsaturated Weston standard cell or measured directly by the K-5 potentiometer. The equivalence-points were determined by calculating the inflection point in the pH vs. time curve by the Yan method (90) using four points at the inflection point.

III. LOCATION OF EQUIVALENCE-POINT

A. Introduction

Of all the variables in high-precision coulometric titrations, the location of the equivalence-point, I believe, may be that least accurately determined. In the most recent high-precision titration, that of 4-aminopyridine, employed by Koch and Diehl (46) in a determination of the value of the faraday, an estimate of the uncertainty in locating the equivalence-point placed the figure at three parts per million (3 p.p.m.), and curiously this estimate was made the same in both the direct, anodic titration of the 4-aminopyridine and in the cathodic standardization-titration of the perchloric acid used in an indirect, "back" titration of the 4-aminopyridine. That the uncertainty in titrating a strong acid should be no better than that in the titration of a weak base (or acid) is curious, but really points up that Koch and Diehl were skirting a much older problem, namely: are the point of inflection of a titration curve and the stoichiometric equivalence-point identical? Diehl (19) later acknowledged that that was exactly what they were doing, hoping that by obtaining two titration curves in each titration, a pretitration curve on the supporting electrolyte alone before adding the sample, and a final titration curve, that the error in each would be in the same direction and would cancel. As he quite correctly observed, this was not the best sort of science.

The difference between inflection-point and equivalence-point is not a new problem; it has a history that goes back fifty-five years, but it deserves renewed attention because of the higher level of accuracy which the coulometric technique now makes it possible to attain in titrations. Nor has the problem been ignored in recent years. Marinenko and Champion (61) made a study of the very problem, using the coulometric titration of the weak acid boric acid plus mannitol to test the so-called Roller equation (72,73,74), and in my own thesis (34) for the degree Master of Science, I reported a study of the variables affecting the equivalence point in the titration of the weak acid, furoic acid. In the present work, I am concerned about answering the question just raised as it pertains to the strong acids, hydrochloric acid and perchloric acid, and with an examination of the various mechanical, graphical, and mathematical mechanisms which have been used to extract the point of inflection from titration data.

B. Location of the Point of Inflection on a Titration Curve

Over the past sixty years, a variety of methods have been devised for locating the point of inflection in the region of the equivalence-point of a titration curve, visual, graphical, mathematical, mechanical, and even electrical.

The simplest method, visual inspection of a plot of the titration data is entirely satisfactory for most purposes, the titration of weak acids or bases as well as of strong acids or bases. The steeper the curve through the equivalence-point region the better, of course, and for the large majority of analyses in industrial control or investigative work, conditions can be arranged to provide the steepness deemed necessary. In the limit, it is a matter of the degree of accuracy required, the concentrations of the reactants (in turn dependent on the amount of sample available), and the strength of the acid or base being determined; in the extreme, cases in which the slope is small, aid must be brought to bear, and such aid may simply be sought to eliminate the tedium of arithmetic and of curve plotting.

A plot of the first derivative of a titration curve through the equivalence-point region exhibits a maximum at the point of inflection of the titration curve and because the regions on either side of the maximum may be almost linear, the identification of the maximum appears easier, and is certainly more reassuring than picking out a point of inflection. The arithmetic is relatively easy and the experimental work can be arranged to make it even easier, that is, the titrant can be added in equal increments so that $\Delta pH/\Delta cm.^3$ (or the equivalent $\Delta E/\Delta cm.^3$) is immediately at hand for plotting against volume delivered. Even further simplification is possible and an earlier generation had no end of fun devising schemes for mechanically isolating a small portion of the solution momentarily and with two identical indicating electrodes getting the increment of response for each increment of titrant. The most sophisticated of these mechanical differential titration gadgets was that of MacInnes and Jones (58) which underwent successive improvements (57,59) and was employed much later by Bates and Wichers (2) in titration of primary standard benzoic acid, probably the most accurate of all purely chemical (noncoulometric) analyses ever made. More recently, electronics has been brought to bear and the data taken, the differentiation made and the differential plotted without the mind of man being involved (Busch and Freyer, 7).

Other graphical methods are based on manipulating the original data obtained in the titration to obtain straight lines on either side of the inflection-point, extrapolation of which yields an intersection corresponding to the inflection-point. Gran (33) plots the reciprocal, $\Delta V/\Delta pH$, against the volume of titrant; in principle this yields two straight lines intersecting at the point of inflection but in practice the lines are curved, although better if correction is made for the increase in the volume of the solution resulting from adding the titrant.

Three mathematical methods of locating the point of inflection have been described, each based on applying a cubic equation to the data. The cubic equation was selected because it is a relatively simple function with a convenient number of constants to be determined by the curve fitting and a point of inflection; there is no theoretical basis for the choice. The Fortuin (25) and the Yan (90) methods are based on a finite difference treatment, the Fortuin method requiring that the titrant be added in equal increments, the Yan method being more general and applicable to data obtained adding unequal increments of titrant. In the method of Koch, Poe and Diehl (48), a third order polynomial is fitted to the data by computer, the second derivative calculated, set equal to zero and solved for the point of inflection of the original curve. The method is very satisfactory for the titration of weak bases but failed when applied to the titration of perchloric acid.

C. Theoretical Treatment of the Equivalence-Point Region in the Titration of a Strong Acid with a Strong Base

A theoretical treatment of the titration of acids with bases was developed by Eastman (23); see also later papers for corrections and extensions (21,22)). This very general treatment covered both weak and strong acids titrated with weak or strong bases and resulted in a fourth order equation in the concentrations of the hydrogen ion as a function of the concentration of the substance titrated, of the titrant added, and of the dissociation constants of the acid and base involved and of water. The equation involved no less than ten terms, and of course, has since been simplified by considering special cases separately, for example the titration of a weak acid with a strong base. More particularly, the equation has been simplified to quadratic equations by considering separately the different portions of the titration curve; and it has been simplified even further to first order (linear) equations by making certain simplifying assumptions regarding the relative concentrations of various species. For example, for the titration of a strong acid with a strong base, the fourth order equation simplifies to a quadratic equation and at the stoichiometric equivalence-point becomes

$$[H^+] = (K_w)^{\frac{1}{2}} \tag{10}$$

The text books of the last fifty years are full of this material, particularly good treatments being in Glasstone (32) and Diehl (20, Chapter 10).

The fourth order equation developed by Eastman (23) is reduced to a quadratic equation for the special case of the titration of a strong acid with a strong base; this comes about simply by setting the dissociation constants of the acid and the base to infinity. The equation is usually given in a somewhat more complicated form taking into account the changes in concentration resulting from the increase in volume, see for example Lingane (53, p. 75) and McCallum and Midgley (56). Using this form of the equation, Meites and Goldman (66) showed, by obtaining and manipulating the second derivative, that even in the titration of a strong acid with a strong base the inflection-point and the equivalence-point can never coincide and in fact the inflection-point always precedes the equivalence-point.

A singular feature of the coulometric titration is that no change in the volume of the solution occurs during the titration. Below, I have repeated the derivation of the quadratic equation describing the titration curve of a strong acid titrated with a strong base, obtained the second derivative, and showed that for a coulometric titration, the inflection- and equivalence-points do coincide. The derivation follows basically the early, more complicated derivation of Eastman, setting up at the start mathematical equations describing the material and electrical balances in the solutions. The experimental work which follows the derivation was designed as a check on the theory: The work was done with perchloric acid in solutions of sodium perchlorate of varying concentration and again with hydrochloric acid in solutions of potassium chloride of varying concentrations. Various ways of handling the data are then given.

1. Derivation of the basic equations

A strong acid and a strong base are by definition one hundred per cent dissociated in water. The general equation representing the neutralization of a strong acid, HA, by a strong base, BOH, is

$$HA + BOH = H_2O + BA$$

where all species except for water are one hundred per cent dissociated. The dissociation constant for water is defined by

$$K_w = [H^+][OH^-] \qquad (11)$$

The condition for eléctroneutrality is

$$[H^+] - [OH^-] = [A^-] - [B^+] \qquad (12)$$

During the coulometric titration of a strong acid, HA, using the salt, BA, as the supporting electrolyte, the reactions at the cathode are

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

$$2H_2O + 2e^- = 2OH^- + H_2$$

Since the supporting electrolyte is one hundred per cent dissociated, the number of B^+ ions and A^- ions contributed from the supporting electrolyte are equal. The contribution of the B^+ ions and the A^- ions from the supporting electrolyte need not be included in equation (12) because their contribution to the terms, $[B^+]$ and $[A^-]$ are equal. The $[A^-]$ term in equation (12) includes only the A^- ions derived from the original amount of strong acid, HA, present

$$[A^-] = C_a^o \qquad (13)$$

in which C_a^o is the original concentration of the strong acid.

The term $[B^+]$ represents the amount of base generated at the cathode. For each electron that reacts at the cathode, either a B^+ ion migrates into the cathode compartment or an A^- ion migrates from the cathode compartment and into the intermediate compartment of the titration cell. There is a net increase of B^+ ions over A^- ions in the cathode compartment and this increase is represented by

$$[B^+] = \frac{It}{FV} = \frac{b}{V} \qquad (14)$$

in which b represents the number of equivalents of electrons passed through the titration cell, V is the volume of the solution in the cathode compartment in liters, I is the current in amperes, t is the time in seconds and F is the faraday. Substituting equations (11), (13) and (14) into equation (12) yields

$$[H^+] - \frac{K_w}{[H^+]} = C_a^o - \frac{b}{V} \tag{15}$$

Equation (15) is the basic quadratic equation for the coulometric titration of a strong acid by the generation of a base at the cathode.

In actual titrations, the pH meter reads the activity of hydrogen ion concentration defined as

$$pH = -\log a_H = -\log [H^+]\, f_H \tag{16}$$

$$pOH = -\log a_{OH} = -\log [OH^-]\, f_{OH} \tag{17}$$

$$K_w' = [H^+][OH^-]\, f_H f_{OH} \tag{18}$$

where f_H and f_{OH} are the activity coefficient of hydrogen ions and hydroxide ions which correct for the nonideal behavior of ions in solution. Combining equations (15), (16), (17) and (18) yields an equation similar to that of McCallum and Midgley (56) except that the new equation applies to coulometric titrations

$$\frac{10^{-pH}}{f_H} - \frac{K_w'}{f_{OH} 10^{-pH}} = C_a^o - \frac{b}{V} \tag{19}$$

2. Inflection-point versus equivalence-point

The basic equation describing the coulometric titration of a strong acid by base generated at the cathode, equation

(15), was rearranged and solved for hydrogen ion concentration. The first and second derivatives were then calculated in the manner of Meites and Goldman (66). In equation (15) let

$$-\alpha = -\left(\frac{b}{V} - C_a^o\right) \tag{20}$$

Substituting equation (20) into equation (15) and solving for hydrogen ion concentration using the usual formula for solving a quadratic equation yields

$$[H^+] = \frac{\alpha \pm \sqrt{\alpha^2 + 4K_w}}{2} \tag{21}$$

Equation (21) is converted to read directly in pH units by the use of equation (16) to give

$$\mathrm{pH} = -\log\,[H^+]f_H = -\log(\alpha \pm \sqrt{\alpha^2 + 4K_w}) + \log 2 - \log f_H \tag{22}$$

The derivative of equation (22) with respect to α yields

$$\frac{d\mathrm{pH}}{d\alpha} = \frac{d(-\log(\alpha \pm \sqrt{\alpha^2 + 4K_w}))}{d\alpha} + \frac{d\log 2}{d\alpha} - \frac{d\log f_H}{d\alpha} \tag{23}$$

Because the ionic strength is constant during a coulometric titration, the activity coefficient, f_H, is also constant and the derivative of f_H in equation (23) is zero. Solving equation (23) yields

$$\frac{dpH}{d\alpha} = \frac{-0.434}{\sqrt{\alpha^2 + 4K_w}} \tag{24}$$

Multiplying the right side of equation (24) by db/db and rearranging yields

$$\frac{dpH}{db} = \frac{-0.434}{\sqrt{\alpha^2 + 4K_w}} \frac{d\alpha}{db} \tag{25}$$

Taking the second derivative of equation (25) and setting the resulting equation equal to zero to determine the inflection-point yields

$$\frac{d^2pH}{db^2} = \frac{d\left[\frac{-0.434}{\sqrt{\alpha^2 + 4K_w}}\right] \frac{d\alpha}{db}}{db} = 0 \tag{26}$$

$$\frac{d^2pH}{db^2} = \frac{0.434}{\sqrt{\alpha^2 + 4K_w}} \left(\left[\frac{\alpha}{\alpha^2 + 4K_w}\right]\left[\frac{d\alpha}{db}\right]^2 - \frac{d^2\alpha}{db^2}\right) = 0 \tag{27}$$

If the inflection-point coincides with the equivalence-point, equation (27) must be equal to zero when $b/V = C_a^o$ and $\alpha = 0$,

$$\frac{d\alpha}{db} = \frac{d(b/V - C_a^o)}{db} = \frac{1}{V} \tag{28}$$

$$\frac{d^2\alpha}{db^2} = \frac{d(1/V)}{db} = 0 \tag{29}$$

Thus, substituting $\alpha = 0$ and equation (29) into equation (27), both sides of equation (27) are equal to zero and the inflection-point coincides with the equivalence-point when the pH versus equivalents of base generated at the cathode is plotted. Because the equivalents of base generated are directly proportional to the time the current passes, the inflection-point of a pH versus time plot is also equal to the equivalence-point.

3. Experimental work

Small amounts of perchloric acid were titrated both coulometrically and volumetrically, the pH range covered being from 2 to 10 and the pH measured with the glass electrode. The titrations were made repeatedly, with changes in the concentration of sodium perchlorate in the solution, successively: 0.3, 0.6, 1.0, 1.2 and 1.5 M.

A similar sequence of titrations were also made of hydrochloric acid in solutions of potassium chloride, successively: 0.5, 1.0, 1.5 and 2.0 M.

The coulometric titrations were performed in the coulometric titration cell described in Chapter II, the intermediate compartment being one that carried a membrane of unfired Vycor. The titration cell was placed in a constant-temperature water bath and the temperature of the solution being titrated was measured with a 0.1° thermometer inserted through the cover of the cell and immersed in the solution.

Each of the various, accurately prepared solutions of sodium perchlorate was treated with a drop or two of perchloric acid, sufficient to bring the pH to 2. Nitrogen was then bubbled through the solutions to remove carbon dioxide. The solutions of potassium chloride were similarly treated with hydrochloric acid and made free of carbon dioxide. The salt solution to be titrated was transferred accurately by pipet into the dry titration cell, 250.0 ml. of the various, slightly acid, carbon dioxide-free solutions of sodium perchlorate and 100.0 ml. of the various solutions of sodium chloride. The solution was first "pretitrated" by passing the 5-mA current through it long enough to bring the pH to 10. One or two drops of the acid, perchloric or hydrochloric, were added to lower the pH to 3. The titration was then performed by the successive addition of very small and accurately measured increments of the 5-mA current. After each increment, time was allowed for the solution to reach equilibrium and the pH was measured. The titration was continued to just beyond pH 10.

The volumetric titrations were performed in a beaker covered with a Plexiglass lid through which were inserted the pH electrodes, the thermometer, nitrogen inlet and vent, and the tip of the buret. The buret used, 10-ml. capacity readable to 0.01 ml., was the automatic type with a reservoir in which the sodium hydroxide solution was placed and protected with an atmosphere of nitrogen. The sodium hydroxide titrant was prepared separately for each titration from the same sodium perchlorate solution to be used in the titration, thus the ionic strength was maintained constant throughout each titration; the salt solution was first made free of carbon dioxide by bubbling nitrogen through it, then sufficient 50 per cent sodium hydroxide (carbonate-free) was added to make the solution about 0.03 M in sodium hydroxide. Each such solution was standardized by titrating primary standard potassium hydrogen phthalate. Each of the various, accurately-prepared solutions of sodium perchlorate was treated with a drop or two of perchloric acid, sufficient to bring the pH to 2. Nitrogen was then bubbled through the solutions to remove carbon dioxide. The salt solution to be titrated was transferred accurately by pipet into the titration beaker, 100.00 ml. of the sodium perchlorate solutions were used. The sodium hydroxide titrant was added until a pH of 3.0 was reached, the volume of titrant used up to this time was noted. The buret was refilled with the titrant and the titrant was added in small volume increments (0.40 to 0.05 ml.) until a pH of 10 was reached; the titration required about 10 ml. of titrant.

The volumetric titration was repeated using a solution containing no sodium perchlorate but slightly acidic with perchloric acid. The concentration of perchloric acid in the solution was 0.0038 M. This solution was titrated with a solution consisting of 0.03 M sodium hydroxide without any sodium perchlorate in the same manner above.

4. Results and discussion

A plot of $10^{-pH} - K_w/10^{-pH}$ against b/V, ignoring the activity coefficients in equation (19), should yield a straight line having a slope of minus one and an intercept with the x-axis at C_a^o; at this point the value of $10^{-pH} - K_w/10^{-pH}$ is zero and if equation (19) is true, the intercept with the x-axis is also the equivalence-point. Such a plot of the data from the coulometric titration of perchloric acid in 1.0 M sodium perchlorate is given in Figure 6. The plot in Figure 6 is not a straight line and the slope is not minus one. In fact, there appears to be two straight lines of different slopes which curve toward each other near the intercept with the x-axis. Similar curves were obtained when the data from the titration of perchloric acid in 0.3, 0.6, 1.2 and 1.5 M sodium perchlorate were plotted. The slope of the two straight lines varied with the concentration of sodium perchlorate.

Perchloric acid was also titrated with sodium hydroxide added from a buret. The data were handled in the same manner except that $C_bV/(V_o + V)$ was plotted instead of b/V to take into account the dilution (McCallum and Midgley, 56); C_b is the concentration of the base; V is the volume of base added; V_o is the original volume of the solution containing the acid. A plot of the data from the volumetric titration of perchloric acid in 1.0 M sodium perchlorate is given in

Figure 6. Plot of the data from coulometric and volumetric titrations of perchloric acid

○ $10^{-pH} - K_w/10^{-pH}$ versus b/V, coulometric titration in 1.0 M $NaClO_4$

□ $10^{-pH} - K_w/10^{-pH}$ versus $V_bC_b/(V_o + V)$, volumetric titration in 1.0 M $NaClO_4$

△ $10^{-pH} - K_w/10^{-pH}$ versus $V_bC_b/(V_o + V)$, volumetric titration, no added $NaClO_4$

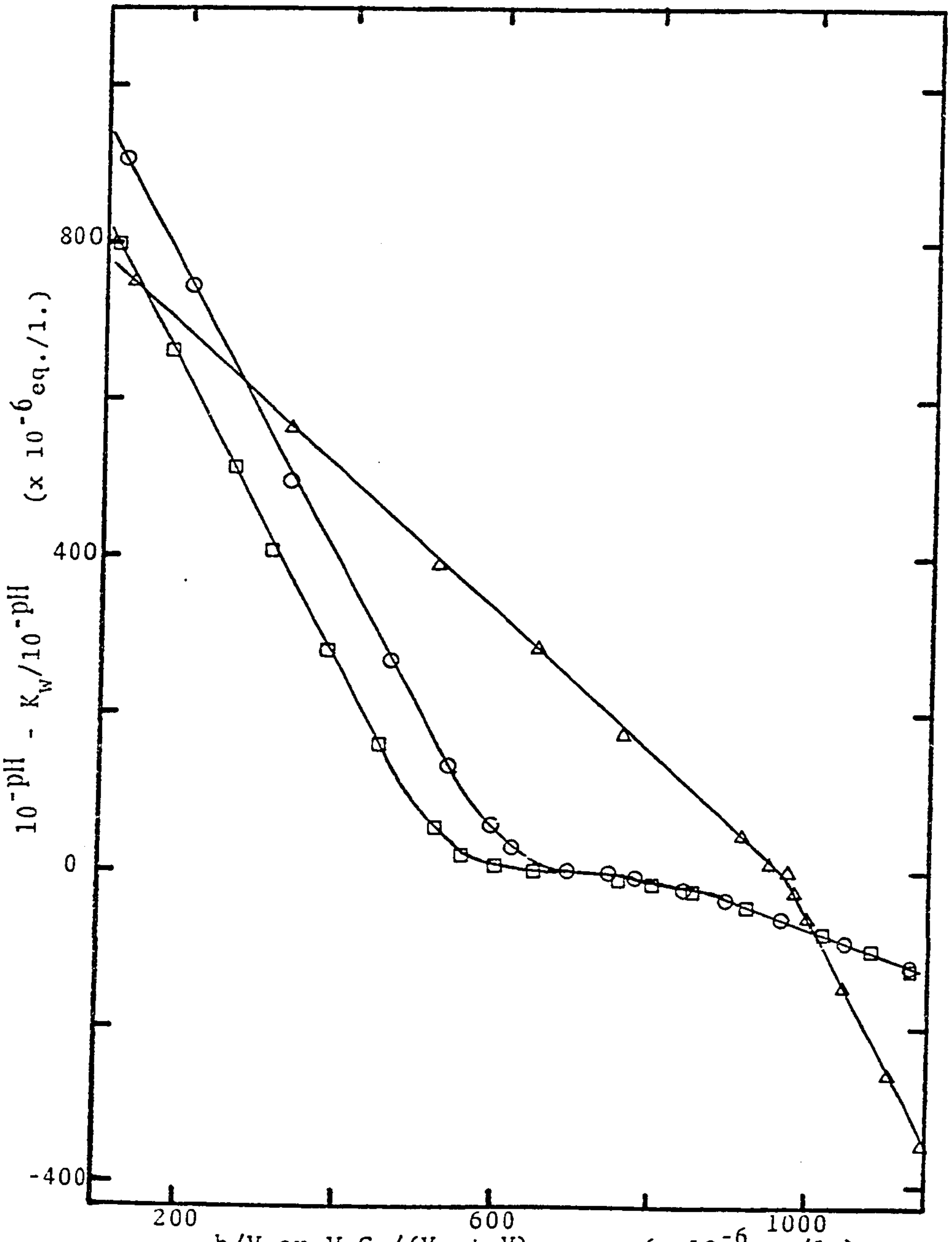

800
400
0
-400
$10^{-pH} - K_w/10^{-pH}$ (x 10^{-6}eq./1.)
200
600
1000
b/V or $V_bC_b/(V_o + V)$ (x 10^{-6}eq./1.)

Figure 6. This plot is identical to the plot of the data from the coulometric titration of perchloric acid in the same concentration of sodium perchlorate, also in Figure 6. For comparison, the volumetric titration of perchloric acid without any added sodium perchlorate is given in Figure 6.

The slope of the plot of $10^{-pH} - K_w/10^{-pH}$ against b/V or $C_bV/(V_o + V)$ before the equivalence-point (x-axis intercept, at which point $10^{-pH} - K_w/10^{-pH}$ becomes zero) and after the equivalence-point varied with the concentration of sodium perchlorate. The two slopes for the coulometric titration and the volumetric titration were identical when the titration was performed in the same concentrations of sodium perchlorate. Before the equivalence-point, the $10^{-pH}/f_H$ term in equation (19) is much greater than the $K_w'/f_{OH}10^{-pH}$ term and vice versa after the equivalence-point. The slopes before and after the equivalence-point must be related somehow to the activity coefficients; the activity coefficients are in turn related to the ionic strength of the solution. The relationship between the slope before the equivalence-point and after the equivalence-point with the concentration of sodium perchlorate are given in Figure 7. The slopes for the volumetric titrations are identical to the slopes for the coulometric titrations when the same concentration of sodium perchlorate was used. Also given in Figure 7 are the slopes

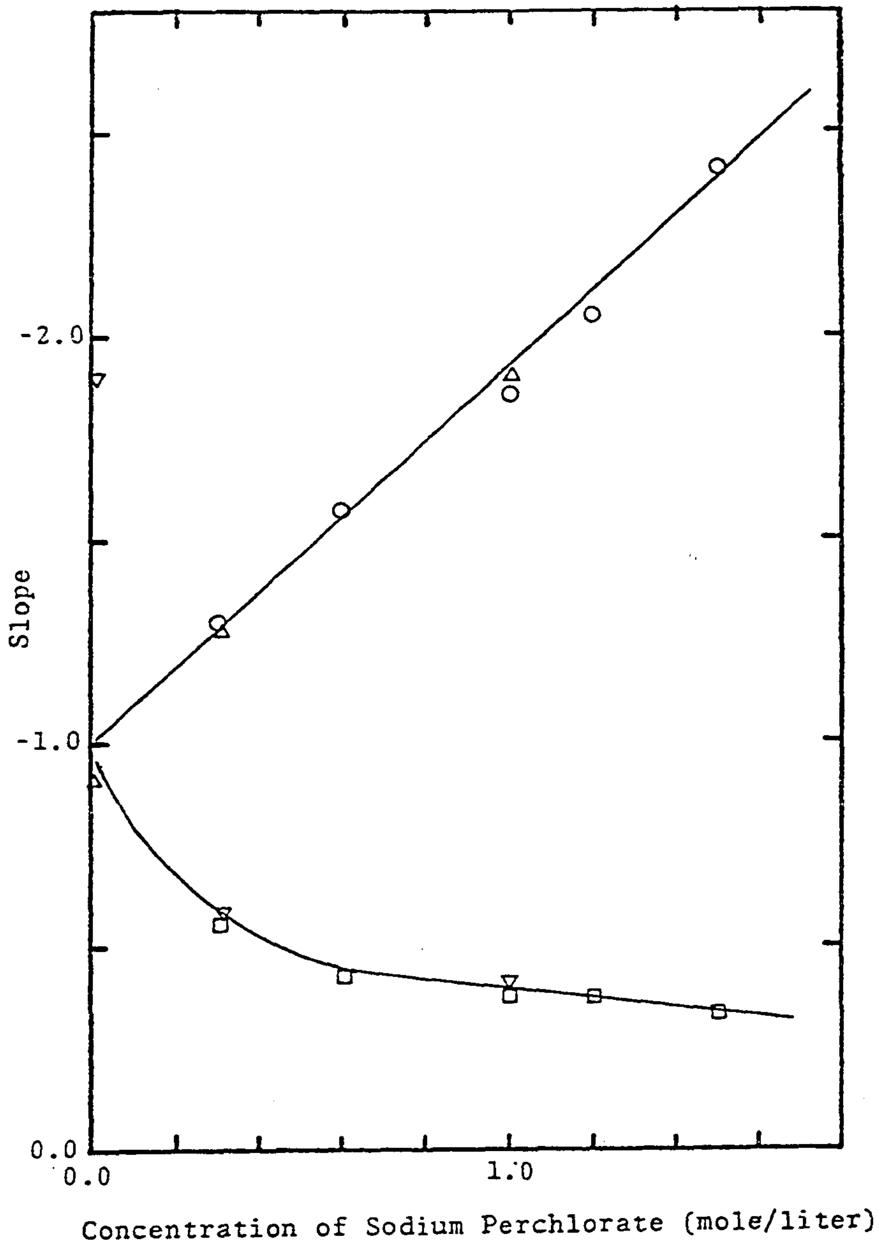
Figure 7. Effect of the concentration of sodium perchlorate on the slope before and after the equivalence-point in the titration of perchloric acid

○ Slope before the equivalence-point, coulometric titration

□ Slope after the equivalence-point, coulometric titration

△ Slope before the equivalence-point, volumetric titration

▽ Slope after the equivalence-point, volumetric titration


-2.0
-1.0
0.0
0.0
1.0
Slope
Concentration of Sodium Perchlorate (mole/liter)

from the volumetric titration of perchloric acid without any added sodium perchlorate; the values being -0.91 before and -1.90 after the equivalence-point.

The value of the slope before the equivalence-point, defined here as slope_1, were linear with respect to the concentration of sodium perchlorate and approached the theoretical value of minus one as the concentration of sodium perchlorate approached zero. The value of the slope after the equivalence-point, called slope_2, was not linear with respect to the concentration of sodium perchlorate but the value of slope_2 appeared to approach minus one as the concentration of sodium perchlorate approached zero. The plot of the square root of concentration of sodium perchlorate against slope_2 was not a straight line.

Using the values of slope_1 and slope_2, the titration data were corrected for the effect of the concentration of sodium perchlorate in the hope that the theoretical straight line with a slope of minus one would be obtained. In Figure 8, $10^{-pH}/\text{slope}_1 - K_w/(\text{slope}_2)10^{-pH}$ was plotted against b/V for the coulometric titration of perchloric acid in 1.0 M sodium perchlorate. The plot of the data in Figure 8 curved near the equivalence-point but the slopes before and after the equivalence-point were minus one. In the equivalence-point region, both the $10^{-pH}/f_H$ term and the $K_w/f_{OH}10^{-pH}$ term are important but apparently the correction factors

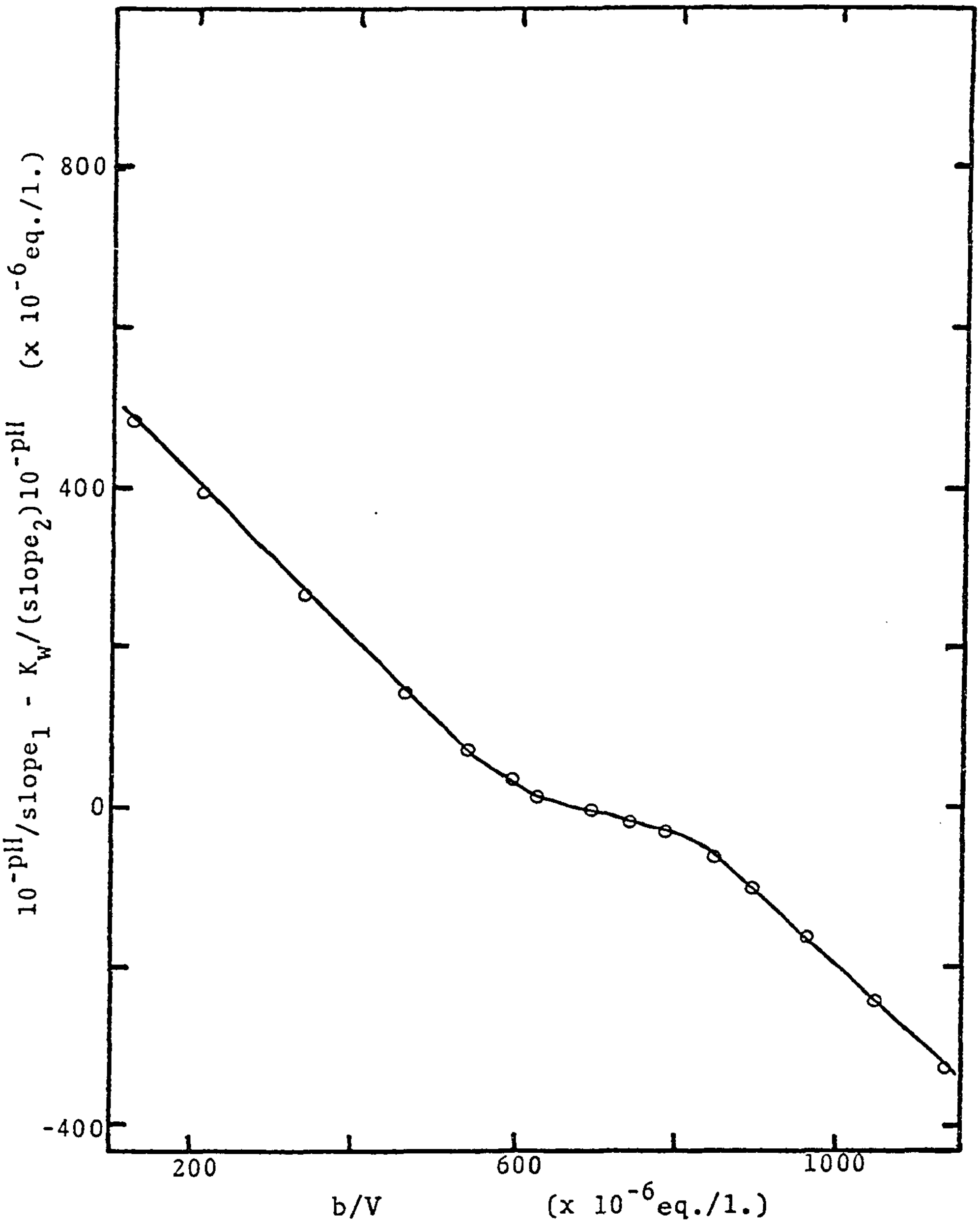


Figure 8. Plot of the data from the coulometric titration of perchloric acid in 1.0 M sodium perchlorate using the correction factors, slope_1 and slope_2

applied to the plot of the data in Figure 8 are not the only factors involved. It must be pointed out that in my experience and in the experience of others, the measurement of the pH of an unbuffered solution with a glass electrode becomes more difficult as the equivalence-point is approached. Between three and six minutes are required to make the measurement because of the slow response of the electrodes in this region.

The value of b/V at the equivalence-point has been calculated for the coulometric titrations of perchloric acid in sodium perchlorate by determining the x-axis intercept of the plot of $10^{-pH} - K_w/10^{-pH}$ with and without the correction factors. Since the plot of the data curves near the equivalence-point, only the four data points in the immediate vicinity of the x-axis intercept were used (more data points were available than shown in Figures 6 and 8). A plot of these four data points produced a straight line; a least squares analysis was performed on the four data points and the x-axis intercept was calculated mathematically. The results are given in Table 4 along with the value of b/V calculated by the Yan method. The results, Table 4, calculated by the three methods varied greatly in some instances. The value of b/V calculated by the graphical method without the correction factor, $slope_1$ and $slope_2$, was always greater than that obtained by the other methods.

Table 4. Equivalence-point in the coulometric titrations of perchloric acid in varying concentrations of sodium perchlorate and of hydrochloric acid in varying concentrations of potassium chloride determined by the Yan method and the graphical method

Acid/Electrolyte	Yan Method[a]	Graphical Methods[a]			
		Uncorrected[b]	Δ[c]	Corrected[d]	Δ[e]
$HClO_4$/1.5 M $NaClO_4$	590.52	593.24	+2.72	589.09	-1.43
$HClO_4$/1.0 M $NaClO_4$	689.13	689.56	+0.43	686.90	-2.23
$HClO_4$/0.6 M $NaClO_4$	655.02	656.16	+1.14	654.34	-0.68
HCl/2.0 M KCl	440.75	441.38	+0.63	440.55	-0.20
HCl/1.5 M KCl	520.37	521.11	+0.74	440.39	+0.02
HCl/1.0 M KCl	620.83	621.15	+0.32	620.28	-0.55
HCl/0.5 M KCl	735.47	736.18	+0.71	735.54	+0.07

[a] In units of eq./l. x 10^6.

[b] Intercept of a plot of $10^{-pH} - K_w/10^{-pH}$ versus b/V with the x-axis.

[c] Difference between the value of b/V calculated by the uncorrected method and the Yan method.

[d] Intercept of a plot of $10^{-pH}/slope_1 - K_w/(slope_2)10^{-pH}$ versus b/V with the x-axis.

[e] Difference between the value of b/V calculated by the corrected method and the Yan method.

The data from the coulometric titration of hydrochloric acid in varying concentrations of potassium chloride were handled in the same manner as the data from the titration of perchloric acid. The plot of $10^{-pH} - K_w/10^{-pH}$ against b/V for the titration of hydrochloric acid in 1.0 M potassium chloride is shown in Figure 9. The curve in Figure 9 was almost identical to that of perchloric acid, Figure 6. In Figure 10, the values of $slope_1$ and $slope_2$ are plotted against the concentration of potassium chloride. The plot of $slope_1$ and $slope_2$ for the titration of hydrochloric acid in Figure 10 is identical to the plot of $slope_1$ and $slope_2$ for the titration of perchloric acid in Figure 7.

The correction factors for the effect of the concentration of potassium chloride on the titration of hydrochloric acid were applied. In Figure 9, the plot of $10^{-pH}/slope_1 - K_w/(slope_2)10^{-pH}$ against b/V for the titration of hydrochloric acid in 1.0 M potassium chloride, is given. This plot had less curvature near the equivalence-point than the same plot for perchloric acid, Figure 8.

The values of b/V were calculated for the titrations of hydrochloric acid in potassium chloride when $10^{-pH} - K_w/10^{-pH}$ became zero (x-axis intercept). Only the four data points in the immediate vicinity of the intercept with the x-axis were used; a least squares method was used to determine the intercept. The value of b/V calculated in the manner along

Figure 9. Plot of data from the coulometric titration of hydrochloric acid in 1.0 M potassium chloride

○ Plot of $10^{-pH} - K_w/10^{-pH}$ versus b/V

□ Plot of $10^{-pH}/\text{slope}_1 - K_w/(\text{slope}_2)10^{-pH}$ versus b/V

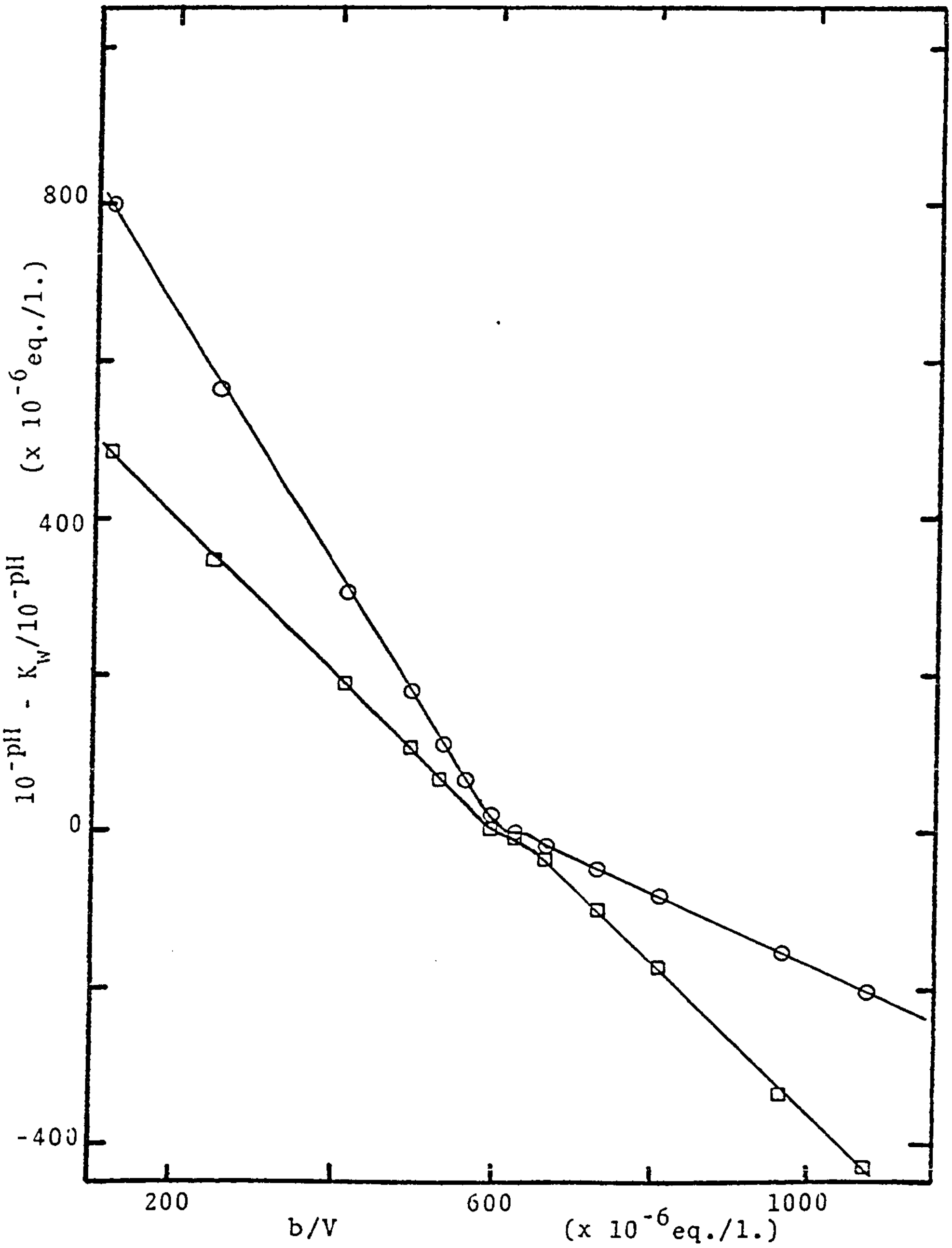
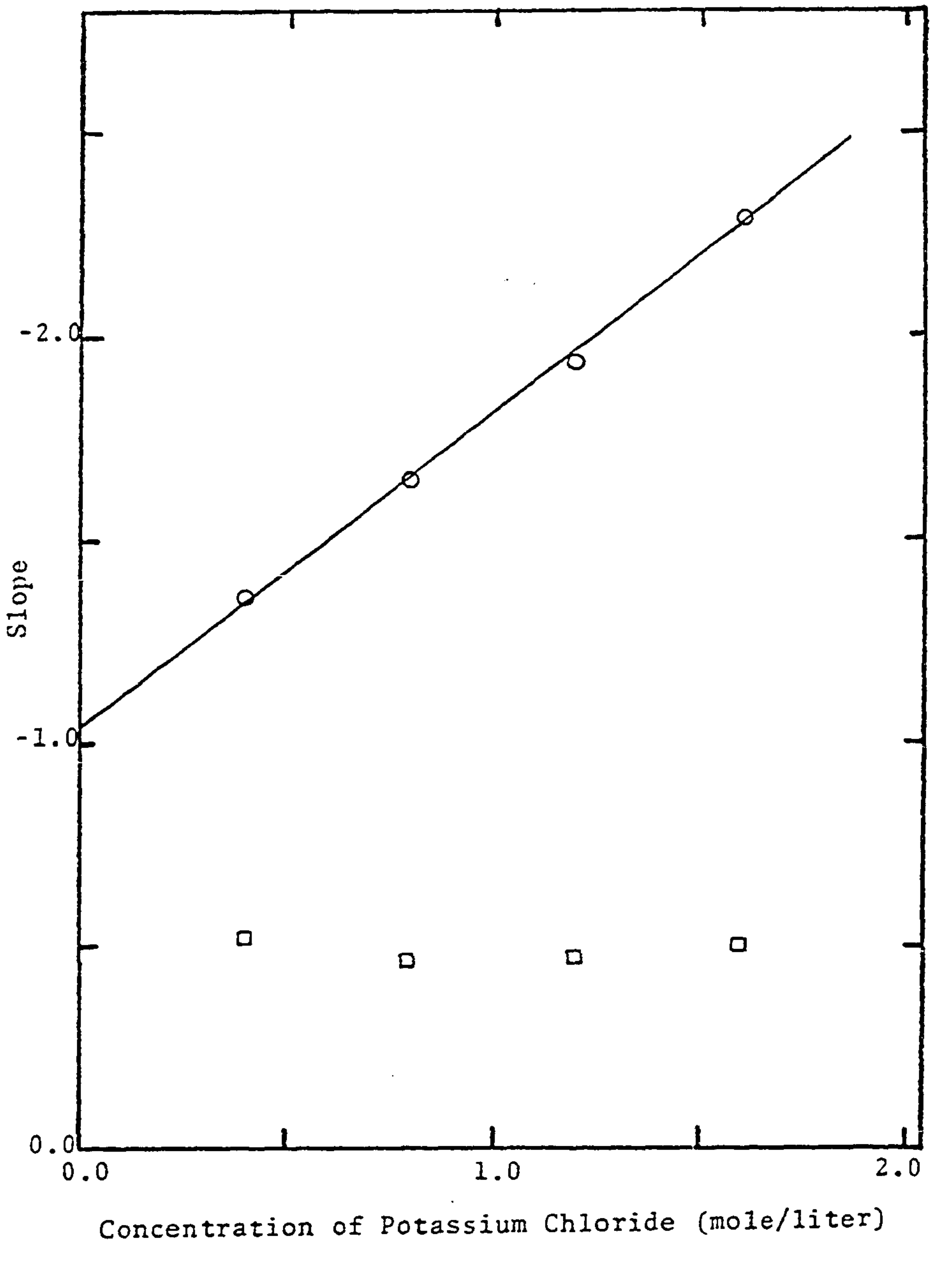

800
400
0
-400
$10^{-pH} - K_w/10^{-pH}$ (x 10^{-6}eq./l.)
200
600
1000
b/V
(x 10^{-6}eq./l.)

Figure 10. Effect of the concentration of potassium chloride on the slope before and after the equivalence-point in the titration of hydrochloric acid

○ Slope before the equivalence-point

☐ Slope after the equivalence-point


-2.0
-1.0
0.0
Slope
0.0
1.0
2.0
Concentration of Potassium Chloride (mole/liter)

with the value of b/V at the equivalence-point when the correction factors, $slope_1$ and $slope_2$, were applied are given in Table 4. The value of b/V calculated by the Yan method is also included in Table 4. The values of b/V at the equivalence-point for the titration of hydrochloric acid in Table 4 calculated by the different methods were in good agreement. These values are imprinted on the titration curve (pH versus b/V) of hydrochloric acid in 1.0 M potassium chloride given in Figure 11. An error of 1×10^{-6} eq./l. in the value of b/V in Figure 11 would cause an error of 3 p.p.m. in an eight hour titration of hydrochloric acid.

There is no advantage in using the graphical method over the use of the Yan method in the determination of the equivalence-point. The Yan method is more rapid because the titration data are used directly to calculate the point of inflection. The graphical method requires that the function, $10^{-pH} - K_w/10^{-pH}$ be calculated and that the temperature of the solution being titrated be known to obtain the value of K_w.

D. Failure of the Koch, Poe and Diehl Method of Locating the Points of Inflection in the Titration of Perchloric Acid

Both the Yan method (90) and the method of Koch, Poe and Diehl (48) for locating the point of inflection of a

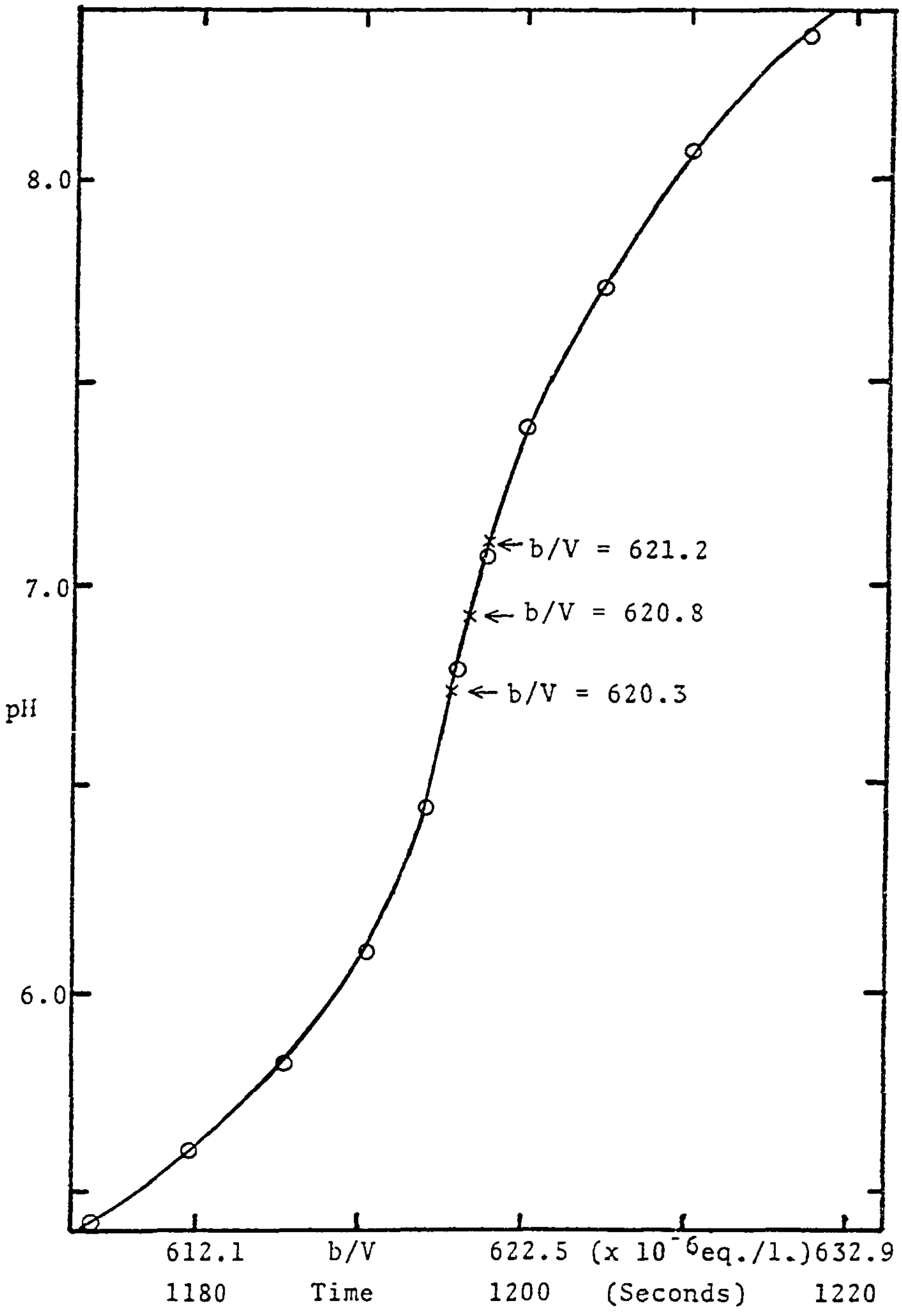


Figure 11. Plot of pH versus titrant added expressed as time of constant current and as microequivalents per liter for the coulometric titration of hydrochloric acid in 1.0 M potassium chloride

titration curve are based on the application of a cubic equation to the data. The cubic equation is the simplest polynomial having an inflection-point and it is symmetrical about the point of inflection. Problems arise in the use of these two methods because actual titration curves are not symmetrical. The titration of a strong acid with a strong base such as the titration of perchloric acid with sodium hydroxide is not symmetrical about the point of inflection as shown in a figure in Diehl's textbook (20, p. 134, Figure 10-1). The titration curve from the coulometric titration of hydrochloric acid given in Figure 11 is also unsymmetrical about the point of inflection.

Koch, Poe and Diehl tried to fit a third order polynomial to the data from the coulometric titration of perchloric acid with the aid of a computer but failed. The titration curve of perchloric acid used by Koch (44, pp. 115 and 118) was unsymmetrical over the pH range used, 2.9 to 9.1. A fifth order polynomial also failed and the Yan method was used to determine the inflection-point.

The Yan method uses only the four data points in the immediate vicinity of the point of inflection. Over this very limited region, the titration curve appears symmetrical as in Figure 11. When more data points over a broad pH range are considered, the titration curve is actually unsymmetrical about the point of inflection (see Figure 11).

The titration curves for the coulometric titration of a strong acid are very sharp; the change in the pH near the point of inflection per equivalent of base generated at the cathode is substantial. In Table 5, the change in the pH at the point of inflection and the amount of chemical produced at the working electrode to produce the pH change are given for the titration of some strong acids along with the slope of the titration curve at the inflection-point. Because of the large change in the pH at the inflection-point during the titration of strong acids, a small error in the pH of one of the four data points used to calculate the point of inflection by the Yan method would cause only a minor error, the determination of the inflection-point.

On the other hand, the change in the pH at the inflection-point during the coulometric titration of the weak bases, 4-aminopyridine and tris(hydroxymethyl)aminomethane titrated by Koch (44) were as little as 0.04 pH units between slugs of current generating about 1.4 microequivalents of hydrogen ions at the anode (see Table 5). A small error in one of the four data points used to calculate the inflection-point by the Yan method would cause a large error. The computer program of Koch, Poe and Diehl, used from 14 to 20 data points over a broad region of the titration curve and a small error in one or more pH values would only cause a minimal error to the determination of the

Table 5. Sharpness of the titration curve at the inflection-point

Sample	ΔpH	Titrant generated μeq.	Slope pH/μeq.	Reference
Perchloric acid	0.8	0.7	1.1	Koch, Ref. 44
Perchloric acid	0.3	0.1	3.0	This work
Hydrochloric acid	0.3	0.1	3.0	This work
Hydrochloric acid in 30 per cent methanol	0.3	0.9	3.3	This work
4-Aminopyridine and tris(hydroxymethyl)-aminomethane	0.14[a]	1.4	0.1	Koch, Ref. 44
	0.04[b]	1.4	0.03	Koch, Ref. 44
Potassium hydrogen phthalate	0.2	0.7	0.3	This work
Benzoic acid in 30 per cent methanol	0.18	0.4	0.5	This work
Furoic acid	0.2	0.2	1.0	This work
Furoic acid in 30 per cent methanol	0.2	0.2	1.0	This work

[a] Cathodic titration of excess perchloric acid.

[b] Anodic titration using hydrazine-platinum electrode.

inflection-point. In this case, the method of Koch, Poe and Diehl would be the more precise method.

The method of Koch, Poe and Diehl worked well for the titration of the weak bases because the titration curves were symmetrical. In fact, the titration curves for the anodic titration of 4-aminopyridine and tris(hydroxymethyl)-aminomethane using the hydrazine-platinum anode were almost straight lines (44, pp. 109 and 112). The pH range of the titration curve was from 4.7 to 3.7. The titration curves from the cathodic titration of the excess perchloric acid added to the weak bases had a somewhat better defined inflection in the curve; the titration curve covered a pH range of 4.0 to 5.5 (44, pp. 103 and 106). In both cases, the part of the titration curve used by Koch, Poe and Diehl to determine the point of inflection appeared to be symmetrical.

The question arises, which method, the Yan method or the Koch, Poe and Diehl method should be used in the present work for the determination of the inflection-point of the titration of the weak acids, potassium hydrogen phthalate, benzoic acid and furoic acid. The slope of the titration curves near the point of inflection for these acids are given in Table 11. Since the change in the pH per amount of base generated at the cathode is fairly large for these acids, the Yan method was chosen.

IV. MIGRATION OF IONS THROUGH POROUS MEMBRANES

A. Introduction

During the course of conducting coulometric titrations of various primary standard acids, National Bureau of Standards SRM 84d Potassium Hydrogen Phthalate was titrated several times using the coulometric titration cell used by Koch, Hoyle and Diehl (47) in their work on the determination of a value for the faraday. The working, titration compartment of this cell was separated from the intermediate compartment by a porous membrane of unfired Vycor. The results on potassium hydrogen phthalate were invariably low, from 0.1 to 0.5 per cent, and the precision poor. Changing the supporting electrolyte from 1.0 M sodium perchlorate to 1.0 potassium chloride did not improve the results. On switching to an intermediate compartment (called the "shield tube" in the paper of Koch, Hoyle and Diehl) fitted with a glass frit membrane, excellent results were obtained. The fritted glass membrane was more porous and the supporting electrolyte flowed through it more readily than through the unfired Vycor. It appeared, therefore, that the low results were probably caused by loss of hydrogen phthalate anion by migration from the cathode compartment to the intermediate compartment. This prompted a close look at the design of coulometric titration cells and an inquiry into how it happened that Koch, Hoyle and Diehl were successful in the titration of 4-aminopyridine with unfired Vycor.

In the first of the high-precision coulometric titrations, those by Taylor and Smith (84), a four-compartment cell was used, the two center compartments serving to separate the end compartments, which housed the cathode and the anode. Porous plugs of fritted-glass were used to separate the successive compartments. Toward the end of each titration, the intermediate chambers were emptied into the compartment containing the working electrode (cathode compartment in case an acid was being titrated). Taylor and Smith were successful in titrating SRM 84d Potassium Hydrogen Phthalate; see Table 9 and the text of Chapter V. The same cell was later used by Marinenko and Taylor (62) for the titration of the primary standards benzoic acid and oxalic acid.

The cell of Eckfeldt and Shaffer (24) represented a considerable advance. In it, a single intermediate compartment took the form of a tall tube, closed at the bottom by a porous membrane of fritted glass; this tube was dipped into the solution in the compartment housing the working electrode (titration compartment). The counter electrode was placed in another tube, of smaller diameter, also closed at the bottom by a fritted-glass membrane; this tube was placed inside the larger tube and the latter filled with supporting electrolyte to such a level that the supporting electrolyte flowed, at a rate of a few milliliters per hour, from the intermediate compartment into both working and counter electrode compartments. That no migration of acid being titrated from titration compartment to intermediate compartment occurred during a titration was tested by inserting a glass electrode into the intermediate compartment; no change in pH of the unbuffered supporting electrolyte was observed. Eckfeldt and Shaffer also titrated SRM 84d successfully; see Chapter V.

The Eckfeldt and Shaffer cell was used by Knoeck and Diehl (43) for the high-precision titration of potassium dichromate and ammonium hexanitratocerate; in a later paper (42), they titrated potassium dichromate as an acid, finding it necessary to devise a new cell to avoid reduction of the chromate at the cathode. In the new cell, the alkali necessary to titrate 99.9 per cent of the sample was generated in a separate "generation compartment" and this alkali then transferred to the reaction compartment; the titration was then completed by the addition of alkali from an external, "drip" electrode. The titration of potassium dichromate as an acid was successfully carried out with this cell and the cell was employed successfully also to the titration of SRM 84d; see Chapter V for a summary of the results on 84d.

The work of Koch, Hoyle and Diehl (47) and of Koch and Diehl (46) dealt with the coulometric titration of 4-aminopyridine in an effort to establish a new value for the faraday. The titration was made two ways: (a) directly at the anode using a newly devised hydrazine-platinum anode (39) to generate the hydrogen ions, and (b) indirectly at the cathode by adding excess perchloric acid and titrating the excess perchloric acid and standardizing the perchloric acid with hydroxyl ion generated at the cathode. In both titrations, the three-compartment Eckfeldt and Shaffer cell with some minor modification was used. Toward the end of the work of Koch and Diehl, the intermediate chamber carrying the fritted-glass membrane was replaced by one with a membrane of unfired Vycor. Obviously good results were obtained and it is difficult to explain their success in the titration of 4-aminopyridine and the complete failure in the present work with the unfired Vycor membrane in the titration of potassium hydrogen phthalate.

Eckfeldt and Shaffer identified three mechanisms by which material could be lost through a membrane: diffusion, electrical migration, and electro-osmotic flow of solution. Obviously, all three would be circumvented by sufficient flow of supporting electrolyte from the intermediate chamber into the electrode compartments. The most difficult to counteract would be the electromigration of the hydrogen ion and the hydroxyl ion owing to their very high mobility.

Steps were taken by earlier workers to prevent the accumulation of hydrogen ion when the counter electrode was the anode (as in the titration of a weak acid at the cathode). Taylor and Smith (84), Marinenko and Taylor (62), and Eckfeldt and Shaffer (24) all used an anode of silver, and the supporting electrolyte being a solution of potassium chloride, the anode reaction was the dissolution silver and the formation of insoluble silver chloride and the formation of hydrogen ion was thus obviated; Yoshimori and Matsubara (92) used a platinum anode but added barium carbonate to absorb the hydrogen ion generated. In the work of Koch and Diehl, in those titrations involving perchloric acid, the acid generated at the anode was allowed to accumulate and sole reliance was on the flow of supporting electrolyte from the intermediate compartment to the anode compartment; they did, during a eight-hour titration, several times remove some of the analyte, by suction; apparently the flow rate was fairly high. Conversely, when the 4-aminopyridine was titrated, with the hydrazine-platinum anode, hydroxyl ion was allowed to accumulate in the counter-electrode compartment, but again with occasional, partial removal of the catholyte. An unfired Vycor membrane was not used for separating the intermediate and counter electrode compartments at any time during the Koch and Diehl work.

All of the primary standard acids (potassium hydrogen phthalate, benzoic acid, furoic acid) are weak acids and all of the primary standard bases (4-aminopyridine, tris-hydroxymethylaminomethane) are weak bases. Two consequences of this follow. First, during the titration of an acid at the cathode, the concentration of hydroxide ions in the solution in the cathode compartment is low and it would appear that no exceptionally high flow of supporting electrolyte should be necessary. Also, during the titration of a base at the anode, the concentration of hydrogen ions in the solution in the anode compartment is low. An exception to the above statements is the titration of benzoic acid; benzoic acid is relatively insoluble and dissolves slowly during the titration so that considerable hydroxide ion accumulates temporarily in the cathode compartment during the titration. The second consequence of the fact that the primary standard acids and bases are weak electrolytes is that the untitrated acid or untitrated base is present in the solution for the most part (the undissociated material) as a noncharged species and therefore does not undergo electromigration during a coulometric titration. The exception to this is potassium hydrogen phthalate, which is ionized completely in the solution and the acid part of which, the hydrogen phthalate ion, is subject to electromigration throughout the coulometric titration. This is undoubtedly the explanation for the puzzling discrepancy in the titration reported above for potassium hydrogen phthalate.

The work described in the present chapter was directed to learning more precisely the rate of flow of supporting electrolyte needed to counteract electromigration, attention being paid to the effect of the size of the electric current passing, the effect of the concentrations of hydrogen ion, hydroxyl ion and hydrogen phthalate anion, and the effect of the concentration of potassium chloride in the supporting electrolyte. The migration was followed by: (a) measurement of pH of the unbuffered supporting electrolyte in the intermediate compartment, either with a glass-electrode or with acid-base indicators; and (b) observing the absorption in the ultraviolet to detect the hydrogen phthalate anion.

B. Theory of Electrolytic Conduction of Current

Electrical conductance through a solution containing a supporting electrolyte is accomplished by the migration of cations toward the cathode and anions toward the anode. The conductivity of a solution is a measure of the amount of current that can pass through the solution by the migration of ions. The conductance of a solution depends on the charge of the ions, the concentration of the ions and the mobility of the ions.

The mobility of ions in solution vary greatly. Hydrogen ions and hydroxide ions have the greatest mobility, 36.2×10^{-4} cm.^{2}/(sec.-volt) and 20.5×10^{-4} cm.^{2}/(sec.-volt) respectively (31). The mobilities of the ions used in the supporting electrolytes employed in coulometry are: potassium, 7.61×10^{-4}; sodium, 5.19×10^{-4}; chloride, 7.91×10^{-4}; perchlorate 7.05×10^{-4} cm.^{2}/(sec.-volt). The velocity with which an ion moves through the solution is proportional to the mobility of the ion and the potential gradient to which it is subjected.

The rate of migration of an ion through a cross section, commonly called flux, $N_{mig,i}$, is proportional to the transference number, t_i, the current, I, the value of the faraday, F, and the absolute value of the charge on the ion, z_i, as given in equation (30)

$$N_{mig,i} = t_i I/F|z_i| \tag{30}$$

The transference number for an ion "i" is defined as the fraction of the total current carried by the migration of ion "i". The transference number is defined in equation (31)

$$t_i = \frac{|z_i|U_i C_i}{\sum_i |z_i|U_i C_i} \tag{31}$$

where U_i is the ionic mobility of the ion and C_i is the concentration of the ion.

Transference numbers are determined experimentally using an apparatus similar to coulometric titration cells; the compartments containing the working and counter electrodes are separated by one or more intermediate compartments (78). Transference numbers are determined by the analysis of the solution in the compartments for enrichment of the cation over the anion or vice verse after the passage of direct current through the cell. Currents between one and 100-mA are used (78). The generation of hydroxide ions and hydrogen ions are avoided because of their high mobilities.

During the passage of current through a three compartment titration cell using potassium chloride as the supporting electrolyte, potassium ions migrate from the intermediate compartment to the compartment containing the cathode and an equal amount of potassium ions enter the intermediate compartment from the compartment containing the anode. In the opposite direction, chloride ions migrate toward the compartment containing the anode. The concentration of potassium ions and chloride ions in the intermediate compartment remains constant because equal amounts of these ions enter the intermediate compartment as leave. The cathode-compartment becomes enriched in potassium ions and the anode-compartment becomes enriched in chloride ions.

If hydroxide ions are present in the compartment containing the cathode, they will migrate toward the anode even at low concentrations because of the high mobility of the ion (equation (31)). The hydroxide ions will migrate into the intermediate compartment and eventually into the compartment containing the anode. The same is true when hydrogen ions are present in the compartment containing the anode except the direction of migration is toward the cathode. Also the hydrogen phthalate anion, when present in the compartment containing the cathode would be attracted toward the anode during the passage of current. From equations (30) and (31), the concentration hydrogen ions, hydroxide ions, and hydrogen phthalate anions and their mobilities determine if migration between the compartments of the titration cell will occur. A high concentration of supporting electrolyte and a positive flow of supporting electrolyte from the intermediate compartment into the compartments containing the electrodes help to minimize the migration of the ions other than the ions of the electrolyte.

C. Experimental Work. Apparatus

The experiments on electromigration were performed on the same apparatus used for the coulometric titrations, Chapter II. The experiments involved three different intermediate compartments, differing in the nature of the porous membrane at the bottom (used to separate the intermediate compartment from the working-electrode compartment:

(a) ultrafine glass frit; (b) fine glass frit; (c) unfired Vycor. The two glass frits were each 2 mm. thick by 18 mm. diameter and were sealed to the glass tube by fusion of the glass: the unfired Vycor rod measuring 3 mm. thick by 14 mm. diameter was attached to the glass tube by Silicone Rubber Seal.

The working electrode was a coil of platinum wire having a surface area of 20 cm.^{2}. The spray trap surrounding the platinum working electrode described in Chapter II was not used in these studies.

A combination pH-reference electrode, Corning Scientific Instruments, Catalog Number 476115, was placed in the intermediate chamber about 3.5 cm. above the membrane. This electrode was first wrapped with Parafilm (American Can Company) to tightly seal the filler hole of the electrode and also the connection of the electrode to the shielded cable running from it. This electrode was connected to the modified Hach pH meter described in Chapter II. The 100-mV per pH unit output from the Hach pH meter was recorded by a Hewlett-Packard strip chart recorder. The solution in the intermediate compartment was stirred by a Teflon-covered micro stirring bar. The top of the intermediate compartment was closed by a rubber stopper through which passed the shielded cable from the pH electrode, a Teflon tube for the introduction of nitrogen, and another for venting the nitrogen.

With the Teflon tube lowered into the solution in the intermediate compartment, nitrogen could be bubbled through the solution. This served two purposes: (a) removal of carbon dioxide dissolved in the solution; and (b) mixing of the solution. After each time the current was passed through the titration cell, nitrogen was bubbled through the solution to mix the solution well to insure a steady pH reading. Also, the pH of the solution in the intermediate compartment was adjusted to a pH near 7.0 by adding either acid or base through the Teflon tube and bubbling nitrogen through the solution to mix the solution well. The acid and base used was either hydrochloric acid, perchloric acid, potassium hydroxide or sodium hydroxide depending on which supporting electrolyte was used. The Teflon tube was raised to prevent the bubbling of nitrogen and the agitation of the solution when the current was turned on.

D. Experimental Work. Measurement of Flow Rate through Membranes

The flow rate of water across the glass frits sealed to the bottom of the intermediate compartment was measured in the following manner. Water was added to the compartment to bring the level of 25 cm. above the glass frit. A dry, 50-ml. beaker containing a piece of absorbing tissue paper was weighed. A rubber ring (used normally in conjection with porous bottom filtering crucibles and 60° funnels) was placed on the top of the beaker and the intermediate compartment was inserted through the rubber ring so that the bottom of the compartment reached to within 3 cm. of the bottom of the beaker. After two hours, the bottom of the intermediate compartment was wiped clean with the absorbing paper and the beaker and paper weighed. Such experiments gave

Ultrafine glass frit number 1	1.3 cm.^{3}/hour
Ultrafine glass frit number 2	5.2 cm.^{3}/hour
Fine glass frit (10 minute run)	136.0 cm.^{3}/hour

The flow rate through the unfired Vycor membrane was measured by filling the intermediate compartment with water and sealing the top with a rubber stopper through which passed a 1.00-ml. pipet. The pipet was filled with water and sealed at the top with Parafilm to prevent evaporation. The height of the water in the pipet was 45 cm. The level of the water was recorded and again after 24 and 48 hours.

Unfired Vycor	1.3 μl./hour

E. Experimental Work. Migration of Ions Across a Membrane of Ultra Fine Fritted Glass, Potassium Chloride as Supporting Electrolyte

In the following experiments, Experiments 1 through 3, the apparatus used was that described in Section C, above.

The intermediate compartment with the ultra fine fritted glass membrane, flow rate 1.3 cm.^{3}/hour was used. The supporting electrolyte in the intermediate compartment and the working-electrode compartment consisted of 100 cm.^{3} of 1.0 M potassium chloride solution. The solution in the counter-electrode compartment consisted of 0.1 M potassium dihydrogen phosphate saturated with potassium sulfate, pH 7.0.

Before the experiments began, the solution in the intermediate compartment was bubbled with nitrogen to remove the dissolved carbon dioxide. The pH of the solution in the intermediate compartment was adjusted as close to 7.00 as possible.

1. Experiment 1. Migration of hydrogen ions

Hydrogen ions were found to migrate from the solution in the working-electrode compartment, through the fritted-glass membrane and into the solution in the intermediate compartment under the following conditions: (a) the pH of the solution in the working-electrode compartment was acidic, pH 2.8; and (b) the 100-mA current was passing through the titration cell with the working electrode as the anode. In this experiment, the pH of the solution in the working-electrode compartment was 2.8. During the passage of the current through the titration cell with the working electrode as the anode, there was an initial time period where the pH of the solution in the intermediate compartment remained constant but the pH soon began to decrease and continued to do so until the current was turned off. After mixing the solution well, the pH of the solution in the intermediate compartment decreased by 0.70 pH units after the passage of 100 seconds of the 100-mA current. On reversing the direction of the current, the pH of the solution in the intermediate compartment remained constant during the passage of the current.

2. Experiment 2. Migration of hydroxide ions

Hydroxide ions were found to migrate into the solution in the intermediate compartment when: (a) the pH of the solution in the working-electrode compartment was basic, pH 11.0; and (b) the 100-mA current was passing through the titration cell with the working electrode as the cathode. In this experiment, the pH of the solution in the working-electrode compartment was 11.0. During the passage of the 100-mA current with the working electrode as the cathode, the pH of the solution in the intermediate compartment started to increase after the current was on for 130 seconds and continued to increase until the current was turned off. The pH increased by 0.5 pH units after the passage of 200 seconds of the 100-mA current. No pH change was detected when the current was reversed.

3. Experiment 3. Migration of hydrogen phthalate anions

No hydrogen phthalate anions were detected in the solution in the intermediate compartment after the passage of the 100-mA current with the working electrode as the cathode. This experiment was carried out with 1.0-g., 2.0-g. and 4.0-g. samples of potassium hydrogen dissolved in the solution in the working-electrode compartment along with a saturated solution of potassium hydrogen phthalate. The pH of these solutions were 4.0. The pH of the solution in the intermediate compartment did not change after the passage of the 100-mA current for 800 seconds with each of the samples of potassium hydrogen phthalate. With the 1.0-g. sample, the current was turned on for an addition 2100 seconds without any change in the pH of the solution in the intermediate compartment; the ultraviolet transmittance spectra of the solution in the intermediate compartment given in Figure 12 was negative for the hydrogen phthalate anion.

F. Experimental Work. Migration of Ions Across a Membrane of Unfired Vycor, Potassium Chloride as the Supporting Electrolyte

In the following experiments, Experiment 1 and 2, the intermediate compartment with the attached unfired Vycor membrane was used. The supporting electrolyte in the

Figure 12. Ultraviolet transmittance spectra of potassium hydrogen phthalate and the solution from the intermediate compartment in 0.1 M hydrochloric acid

1-cm. quartz cells

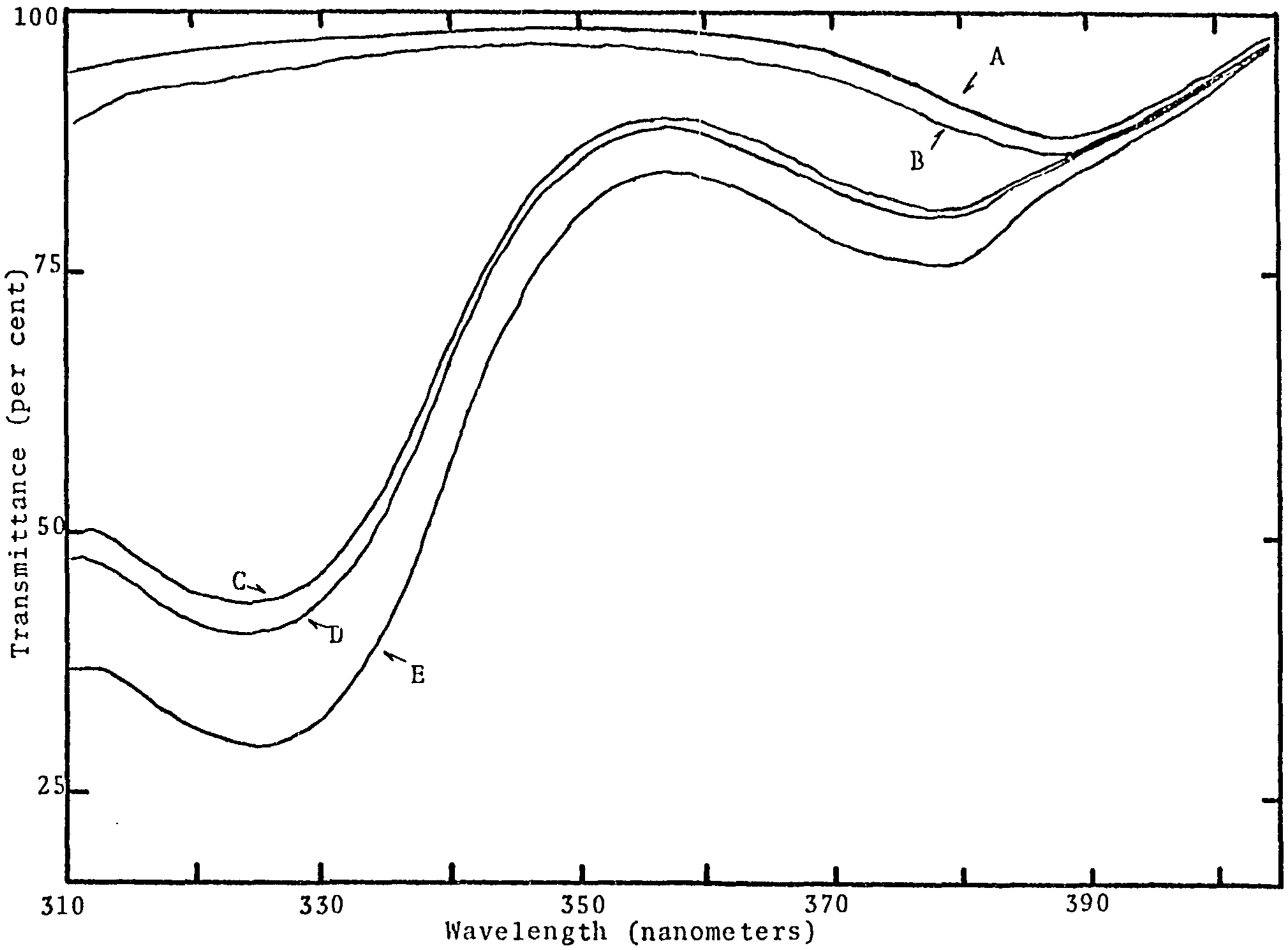
A) Blank containing 1.0 M potassium chloride

B) Solution from the intermediate compartment with the fritted-glass membrane; Experiment 3, Section E

C) 5×10^{-5} M potassium hydrogen phthalate and 1.0 M potassium chloride

D) 5×10^{-5} M potassium hydrogen phthalate

E) Solution from the intermediate compartment with the unfired Vycor membrane; Experiment 2, Section F


100
75
50
25
Transmittance (per cent)
310
330
350
370
390
Wavelength (nanometers)
A
B
C
D
E

working-electrode compartment and in the intermediate compartment consisted of 100 cm.^{3} of 1.0 M potassium chloride. The solution in the counter-electrode compartment consisted of 0.1 M potassium dihydrogen phosphate saturated with potassium sulfate, pH 7.0. Before the experiment began, nitrogen was bubbled through the solution in the intermediate compartment to remove any dissolved carbon dioxide and the pH of this solution was adjusted as close to a pH of 7.0 as possible.

1. Experiment 1. Migration of hydrogen ions

Hydrogen ions were found to migrate from the solution in the working-electrode compartment, through the unfired Vycor membrane and into the solution in the intermediate compartment when: (a) the pH of the solution in the working-electrode compartment was acidic, pH 2.8; and (b) the 100-mA current was passing through the titration cell with the working electrode as the anode. The pH of the solution in the working-electrode compartment was 2.8 in this experiment. During the passage of the 100-mA current with the working electrode as the anode, the pH of the solution in the intermediate compartment began to decrease after about 500 seconds. After a total of 1000 seconds, the current was turned off; the pH decreased by 0.3 pH units. Upon turning the current on again, the pH started to decrease immediately; apparently, the membrane was saturated with hydrogen ions causing the immediate decrease in the pH. The flow rate through the unfired Vycor membrane is so slow that hydrogen ions were not washed from the membrane.

2. Experiment 2. Hydrogen phthalate anions

Hydrogen phthalate anions were found to migrate across the unfired Vycor membrane and into the solution in the intermediate compartment when the 100-mA current was passing through the titration cell with the working electrode as the cathode. In this experiment, a 1.0-g. sample of potassium hydrogen phthalate was dissolved in the solution in the working-electrode compartment having a pH of 4.0. There was no change in the pH of the solution in the intermediate compartment during the passage of the 100-mA current for 800 seconds; however, during the passage of an additional 800 seconds of the current, the pH started to decrease after 400 seconds; the total change was 0.88 pH units. The current was turned on for an additional 3200 seconds after which the pH decreased by 1.21 pH units; the pH started to decrease immediately after the current was turned on. The ultraviolet transmittance spectra in Figure 12 of the solution in the intermediate compartment was identical to the spectra for potassium hydrogen phthalate also in Figure 12.

G. Experimental Work. Hydroxide Ion Migration Across Fritted-Glass Membranes. Effect of Flow Rates, pH, and Current Intensity on Migration

In the following experiments, Experiments 1 through 3, intermediate compartments having fritted-glass membranes with the 1.3, 5.2 and 136 cm.^{3}/hour flow rates were used. The solution in the working-electrode compartment and the intermediate compartment consisted of 1.0 M potassium chloride. The solution in the counter-electrode compartment consisted of 0.1 M potassium dihydrogen phosphate saturated with potassium sulfate, pH 7.0. The pH of the solution in the intermediate compartment was adjusted to a pH as close to 7.0 as possible.

The electrical circuit described in Figure 1 of Chapter II was modified slightly to provide a current between zero and 100 mA. to the titration cell. A Leeds & Northrup resistance box was connected between the two wires leading from the box containing the switches, in Figure 1, to the titration cell; the resistance box and the titration cell were connected in parallel. The Data Precision Digital Multimeter was connected between the resistance box and the working electrode to measure the current going through the titration cell. Currents from zero to 100 mA. could be delivered to the titration cell by adjusting the resistance of the resistance box between zero and 9999 ohms. With the multimeter in the 100-mA mode, the currents could be measured to within ± 0.01 mA.

1. Experiment 1. 136 $cm.^3$/hour flow rate

No hydroxide ions were found to migrate across the fritted-glass membrane with the 136 $cm.^3$/hour flow rate during the passage of the 100-mA current with the working electrode as the cathode. The pH of the solution in the working-electrode compartment was 12.4. The pH of the solution in the intermediate compartment did not change during the passage of the 100-mA current for 300 seconds.

2. Experiment 2. 5.2 $cm.^3$/hour flow rate

In this experiment, hydroxide ions were found to migrate across the fritted-glass membrane with the 5.2 $cm.^3$/hour flow rate during the passage of current with the working electrode as the cathode. The time required for hydroxide ions to traverse the membrane was found to depend on: (a) the pH of the solution in the working-electrode compartment; and (b) the size of the current. The experiment was carried out with the solution in the working-electrode compartment having a pH of 11.6, 12.4 and 13.0 and currents from 50 to 100 mA. The results are given in Table 6. Included in Table 6 are: (a) the response time, time of current passage for the first detectable increase in the pH of the solution in the intermediate compartment; (b) the total time that the current was on; (c) the change in the pH; and (d) the rate of migration (the change in pH divided by the difference between the total time and the response time).

Table 6. Hydroxide ion migration across a glass frit
Flow rate: 5.2 cm.^{3}/hour
Electrolyte: potassium hydroxide

Current mA	Working Chamber pH	Response Time Seconds	Total Time Seconds	ΔpH	Rate pH/sec.
100.0	11.6	800	1500	+0.09	0.0001
100.0	12.4	140	250	+0.12	0.0011
75.0	12.4	360	650	+0.20	0.0007
50.0	12.4	---	1600	0.00	---
100.0	13.0	98	150	+0.18	0.0035

3. Experiment 3. 1.3 cm.^{3}/hour flow rate

In this experiment, the migration of hydroxide ions across the fritted-glass membrant with the 1.3 cm.^{3}/hour flow rate was found to depend on: (a) the size of the current when the working electrode was the cathode; and (b) the pH of the solution in the working-electrode compartment. This experiment was carried out with the pH of the solution in the working-electrode compartment varied between 10.5 and 13.0. Starting with the 100-mA current, the size of the current was decreased until no hydroxide ions were detected entering the solution in the intermediate compartment in a reasonable amount of time. The results are given in Table 7.

Table 7. Hydroxide ion migration across a glass frit
Flow rate: 1.3 cm.^{3}/hour
Electrolyte: potassium chloride

Current	Working Chamber	Response Time	Total Time	ΔpH	Rate
mA	pH	Seconds	Seconds		pH/sec.
100.0	10.5	---	600	-0.03	---
100.0	11.4	130	200	+0.32	0.0046
75.0	11.4	190	270	+0.20	0.0025
50.0	11.4	321	470	+0.10	0.0007
25.0	11.4	---	900	-0.02	---
100.0	11.9	70	110	+0.32	0.0080
75.0	11.9	94	140	+0.22	0.0047
50.0	11.9	190	280	+0.14	0.0015
25.0	11.9	---	1000	-0.02	---
100.0	12.4	40	65	+0.58	0.023
75.0	12.4	52	80	+0.45	0.016
50.0	12.4	100	150	+0.30	0.006
25.0	12.4	310	430	+0.12	0.001
100.0	13.0	26	42	+0.88	0.055
75.0	13.0	38	55	+0.72	0.042
50.0	13.0	57	85	+0.74	0.026
25.0	13.0	175	250	+0.30	0.004
10.0	13.0	---	900	-0.01	---

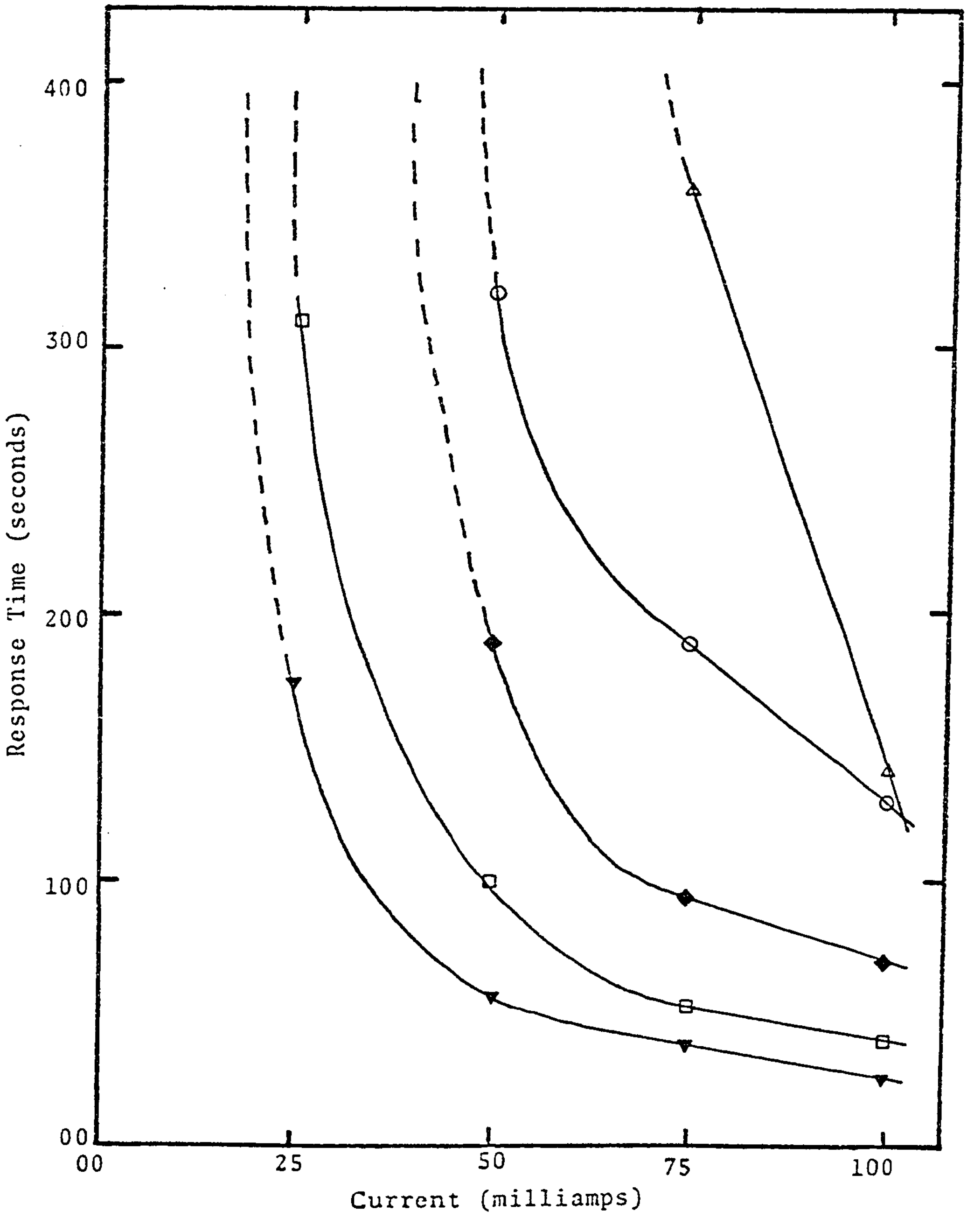
4. Discussion

The flow of the supporting electrolyte solution across the fritted-glass membrane had a great effect on the migration of hydroxide ions through the membrane. The flow of electrolyte solution and the migration of hydroxide ions were in the opposite direction. As the flow rate increased, the time required for hydroxide ions to traverse the membrane increased along with a decrease in the rate of migration. In some cases, no hydroxide ions crossed the membrane.

The migration of hydroxide ions was dependent on the size of the constant current flowing through the titration cell. When using the same glass frit membrane, as the size of the current increased, the time required for hydroxide ions to traverse the membrane decreased. This effect is apparently due to the increase in the potential applied to the electrodes to maintain the constant current as the size of the current increases. On increasing the size of the current, the potential applied to the electrodes increases and the velocity that the hydroxide ion travels through the solution increases. This relationship is represented in Figure 13 where the time required for hydroxide ions to traverse the membrane in relation to the size of the current is plotted. The "response time" is linear with respect to the size of the current except at low currents. At lower currents, no hydroxide ions migrate across the membrane.

Figure 13. Plot of response time against the size of the current

- △ pH of the solution in the working-electrode compartment: 11.40
  flow rate: 5.2 cm.^{3}/hour
- ○ pH of the solution in the working-electrode compartment: 11.40
  flow rate: 1.3 cm.^{3}/hour
- ◆ pH of the solution in the working-electrode compartment: 11.90
  flow rate: 1.3 cm.^{3}/hour
- □ pH of the solution in the working-electrode compartment: 12.40
  flow rate: 1.3 cm.^{3}/hour
- ▼ pH of the solution in the working-electrode compartment: 13.00
  flow rate: 1.3 cm.^{3}/hour


Response Time (seconds)
400
300
200
100
00
00
25
50
75
100
Current (milliamps)

At the membrane, there are two forces acting in opposition to each other; the flow of electrolyte solution and attraction of hydroxide ions toward the anode. At high currents, the velocity of the migrating hydroxide ions is greater than the flow of electrolyte solution; the plot of "response time" is linear with respect to the size of the current. At very low currents, the flow rate of the electrolyte is greater than the velocity of the migrating hydroxide ions and migration does not occur. At the intermediate currents, the two forces are nearly equal and the plot of "response time" against the size of the current is not linear.

Once migration of hydroxide ions across the membrane occurs, the rate of migration is dependent on the size of the current and the concentration of hydroxide ions in the working-electrode compartment. The concentration of hydroxide ions is involved in the equation for transference number, equation (31). The rate of migration is related to the flux in equation (30). The rate of migration increased as the size of the current increased and as the concentration of hydroxide ions in the solution in the working-electrode compartment increased (see Tables 6 and 7).

H. Experimental Work. Effect of the Concentration of the Supporting Electrolyte, Potassium Chloride, on the Migration of Hydroxide Ions Across Fritted-Glass Membranes

In the following experiments, the time of current passage to detect the first change in the pH of the solution in the intermediate compartment along with the rate of hydroxide ion migration was found to be dependent on the concentration of the supporting electrolyte, potassium chloride. Only the 100-mA current was used and the working electrode was the cathode.

The intermediate compartment with the 1.3 cm.^{3}/hour flow rate was used. The concentration of the potassium chloride supporting electrolyte in both the intermediate compartment and the working-electrode compartment was 0.6, 1.5 and 2.0 M in Experiments 1, 2 and 3, respectively. The data for the 1.0 M potassium chloride supporting electrolyte was taken from Experiment 3 of Section G, above.

1. Experiment 1. 0.6 M Potassium chloride

In Experiment 1, the supporting electrolyte consisted of 0.6 M potassium chloride. The 100-mA current was passed through the titration cell while the pH of the solution in the working-electrode compartment was 11.4, 11.9, 12.4 and 13.0. The data from this experiment are given in Table 8.

Table 8. Effect of concentration of potassium chloride on the migration of hydroxide ions

Current: 100-mA

Concentration of KCl moles/l.	Working Chamber pH	Response Time Seconds	Total Time Seconds	ΔpH	Rate pH/sec.
0.6	11.4	100	130	+0.28	0.0093
0.6	11.9	43	65	+0.38	0.0173
0.6	12.4	25	40	+0.60	0.0400
0.6	13.0	18	30	+0.90	0.0750
1.0	11.4	130	200	+0.32	0.0046
1.0	11.9	70	110	+0.32	0.0080
1.0	12.4	40	65	+0.58	0.0230
1.0	13.0	26	42	+0.88	0.0550
1.5	11.4	205	300	+0.30	0.0032
1.5	11.9	145	230	+0.42	0.0049
1.5	12.4	61	90	+0.48	0.0170
1.5	13.0	40	60	+0.82	0.0410
2.0	11.4	380	550	+0.20	0.0012
2.0	11.9	165	250	+0.18	0.0021
2.0	12.4	85	130	+0.18	0.0040
2.0	13.0	57	80	+0.50	0.0217

2. Experiment 2. 1.5 M Potassium chloride

In Experiment 2, the supporting electrolyte was 1.5 M potassium chloride. This experiment was performed in the same manner as Experiment 1, above. The results are given in Table 8.

3. Experiment 3. 2.0 M Potassium chloride

In Experiment 3, the supporting electrolyte consisted of 2.0 M potassium chloride. This experiment was performed in the same manner as the two preceding experiments. The results are given in Table 8.

4. Discussion

The time required for hydroxide ions to traverse the fritted-glass membrane increased as the concentration of the potassium chloride electrolyte increased. In Figure 14, this relationship is given in a plot of the "response time" against the concentration of potassium chloride. With an increase in the concentration of potassium chloride, the resistance of the titration cell decreases along with the potential applied to the electrodes to maintain the 100-mA current. Thus, the velocity of the hydroxide ions migrating across the membrane also decreased. The curvature in the line in Figure 14 could be due to effect of the flow rate across the membrane when the velocity of hydroxide ions decreased to a low value.

The rate of hydroxide ion migration decreased as the concentration of potassium chloride increased. The plot of the rate of migration against the concentration of potassium hydroxide is given in Figure 15. Since an increase in the concentration of potassium chloride would decrease the transference number of hydroxide ions in equation (31), the

Figure 14. Plot of response time against the concentration of potassium chloride

Current: 100 mA
Flow rate: 1.3 cm.^{3}/hour

○ pH of the solution in the working-electrode compartment: 11.40

□ pH of the solution in the working-electrode compartment: 11.90

◇ pH of the solution in the working-electrode compartment: 12.40

△ pH of the solution in the working-electrode compartment: 13.00

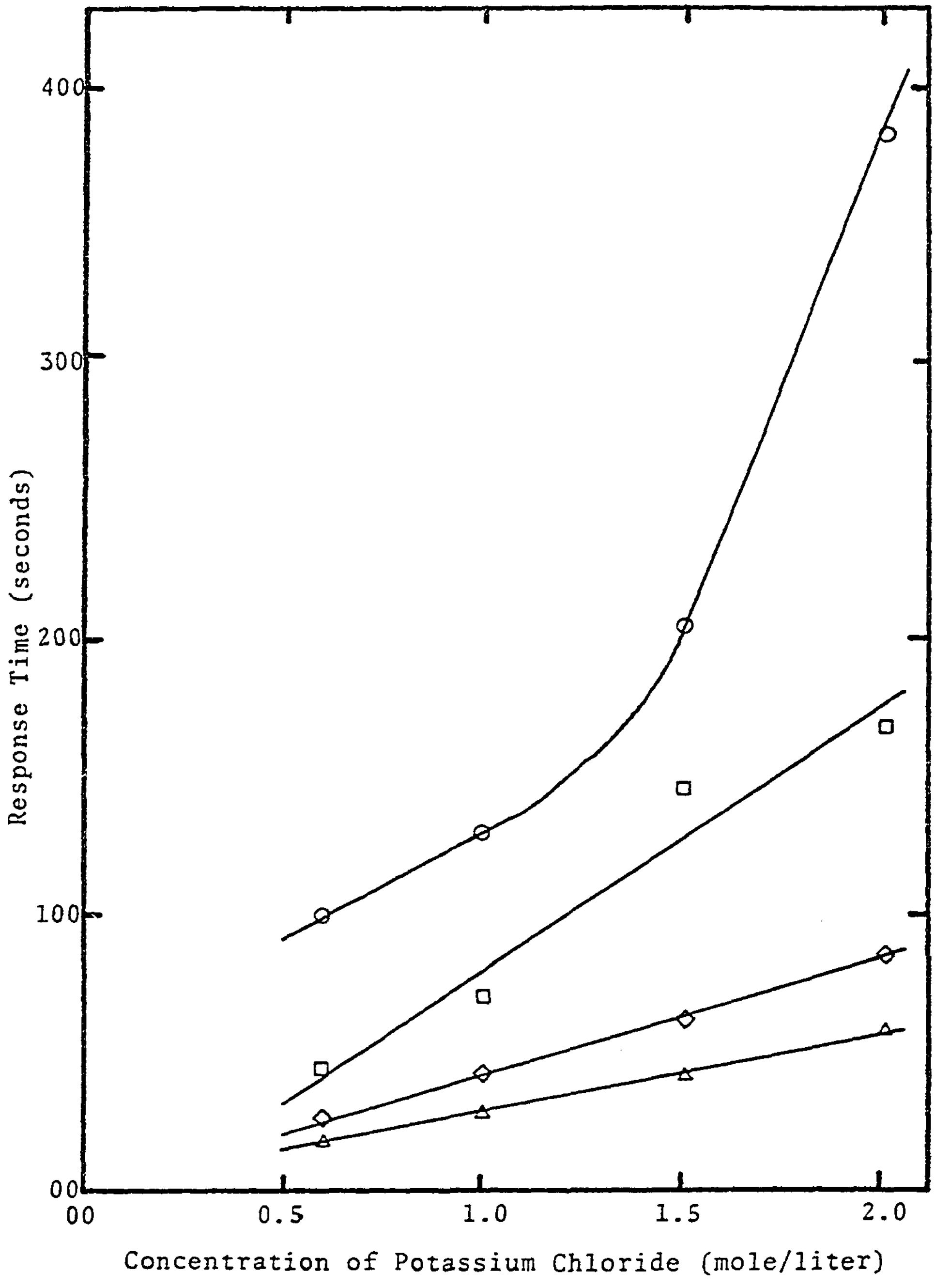

Response Time (seconds)
400
300
200
100
00
00
0.5
1.0
1.5
2.0
Concentration of Potassium Chloride (mole/liter)

Figure 15. Rate of hydroxide migration across a fritted-glass membrane with varying concentration of the potassium chloride supporting electrolyte

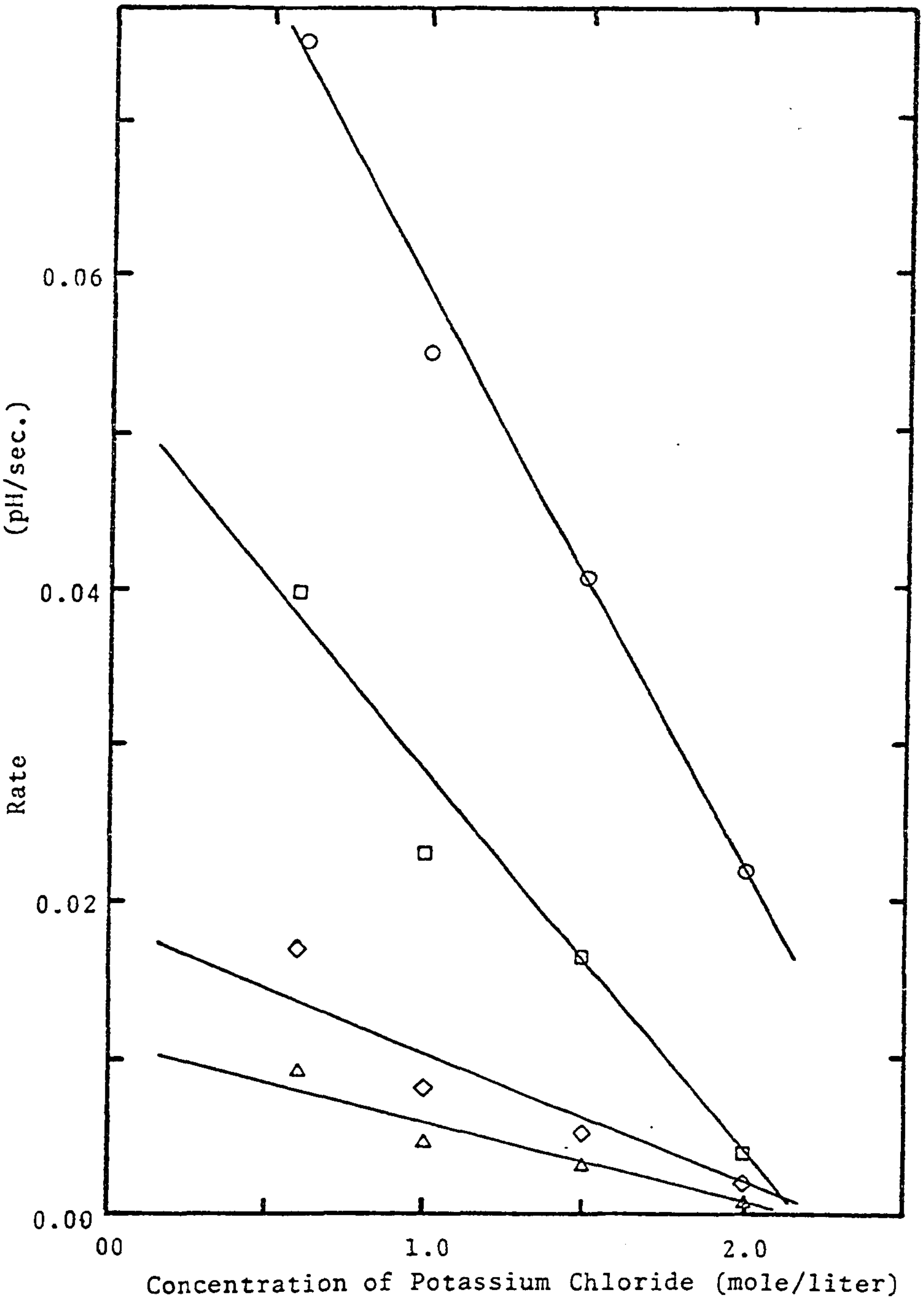
Current: 100 mA
Flow rate: 1.3 cm.^{3}/hour

○ pH of the solution in the working-electrode compartment: 13.00

□ pH of the solution in the working-electrode compartment: 12.40

◇ pH of the solution in the working-electrode compartment: 11.90

△ pH of the solution in the working-electrode compartment: 11.40


0.00
0.02
0.04
0.06
Rate (pH/sec.)
00
1.0
2.0
Concentration of Potassium Chloride (mole/liter)

flux would also decrease in equation (30). The flux in equation (30) is related to the rate of hydroxide ion migration in Table 8.

I. Experimental Work. Migration of Hydroxide Ions and Hydrogen Phthalate Anions in Sodium Perchlorate Supporting Electrolyte

In the following experiments, Experiments 1 through 3, sodium perchlorate was used as the supporting electrolyte. The pH of the solution in the intermediate compartment was not measured with a pH electrode because of difficulties with the measurement when the current was on. Instead, an acid-base indicator, phenol red was added to the solution in the intermediate compartment in Experiment 1. This indicator changed from a yellow color at a pH of 6.8 to a red color at a pH of 8.2. The solution in the counter-electrode compartment consisted of 0.1 M sodium hydrogen phosphate and 1.0 M sodium perchlorate, pH 7.00.

1. Experiment 1. Migration of hydroxide ions

In this experiment, the migration of hydroxide ions across the fritted-glass membrane was found to occur in sodium perchlorate electrolytes. The intermediate compartment carrying the fritted-glass membrane with the 1.3 $cm.^3$/hour flow rate was used. The solution in the working-electrode compartment and intermediate compartment consisted of 1.2 M sodium perchlorate. The pH of the solution in the intermediate compartment was adjusted to yield a yellow color from the indicator. The pH of the solution in the working-electrode compartment was 11.8. During the passage of the 100-mA current with the working electrode as the cathode, a pink color appeared in the solution in the intermediate compartment in the vicinity of the glass frit and the pink color moved slowly up the solution toward the counter-electrode compartment. After the passage of 200 seconds of the current, the solution was entirely pink in color.

2. Experiment 2. Migration of hydrogen phthalate anions across fritted glass membranes

In this experiment, the hydrogen phthalate anion was detected in the solution in the intermediate compartment after the passage of current. The intermediate compartment with the fritted-glass membrane having the 1.3 $cm.^3$/hour flow rate was used. The solution in the working-electrode compartment consisted of 1.0 g. of potassium hydrogen phthalate dissolved in 0.2 M sodium perchlorate, pH 4.0. The solution in the intermediate compartment consisted of 1.5 M sodium perchlorate. After passing the 100-mA current through the titration cell with the working electrode as the cathode for 2000 seconds, the ultraviolet transmittance spectra of the solution in the intermediate compartment was taken. As shown in Figure 16, the spectra for the solution in the intermediate compartment were identical to the spectra of the potassium hydrogen phthalate standard.

3. Experiment 3. Migration of hydrogen phthalate anions across unfired Vycor membranes

The hydrogen phthalate anion was detected in the solution in the intermediate compartment with the unfired Vycor membrane after the passage of current through the titration cell. This experiment was identical to Experiment 2, above, except the intermediate compartment with the unfired Vycor membrane was used. The ultraviolet transmittance spectra of the solution in the intermediate compartment after the passage of 2000 seconds of the 100-mA current is shown in Figure 16. The spectra of this solution were identical to the spectra of a potassium hydrogen phthalate standard in Figure 16.

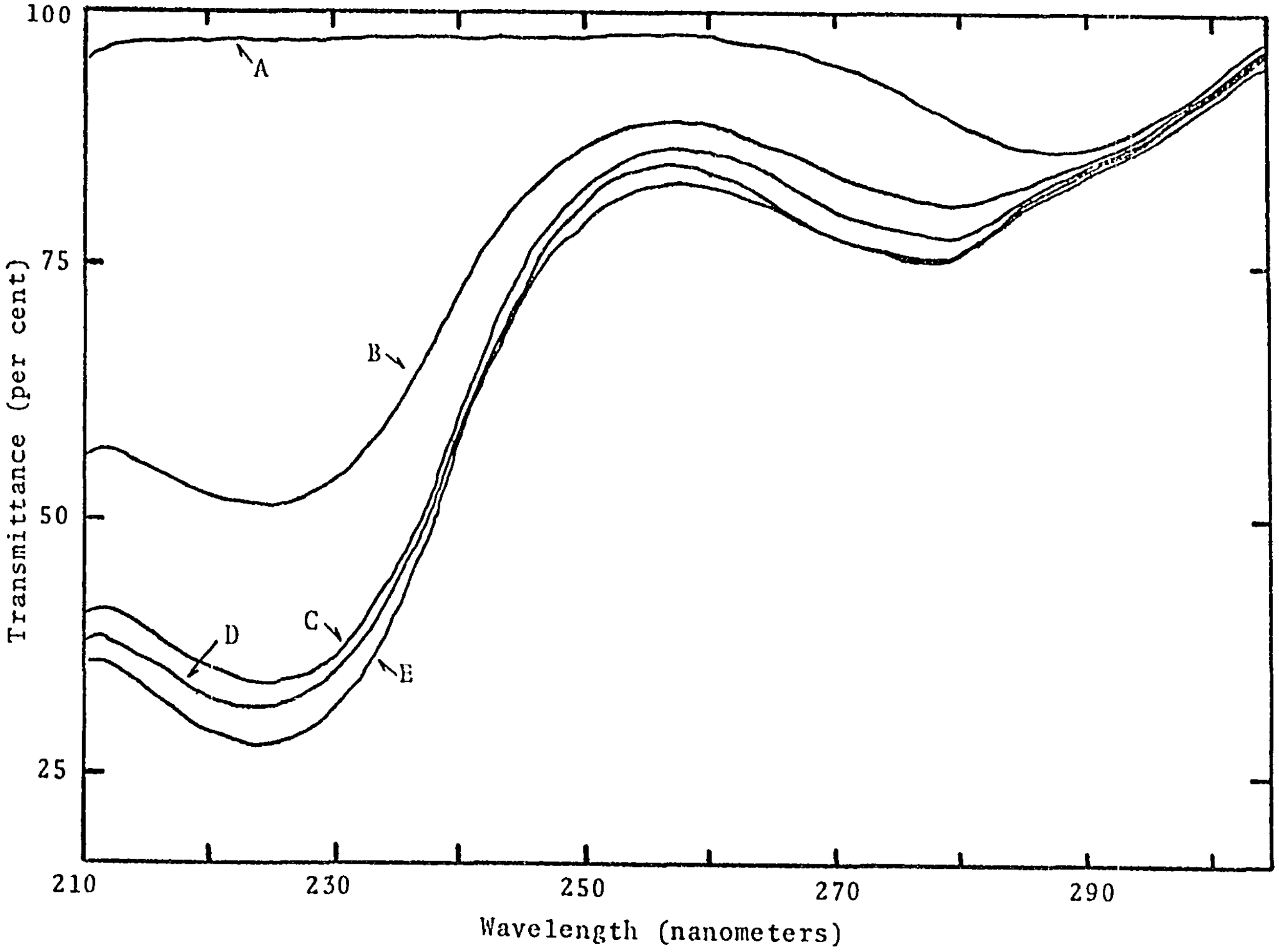
4. Discussion

In Experiment 1, the migration of hydroxide ions across a fritted-glass membrane was confirmed in a sodium perchlorate electrolyte. The migration was followed by the change in the color of the indicator in the solution in the intermediate compartment. The progress of the migration of hydroxide ions up the solution in the intermediate compartment

Figure 16. Ultraviolet transmittance spectra of potassium hydrogen phthalate and the solutions from the intermediate compartment in 0.1 M perchloric acid

1-cm. quartz cells

A) Blank containing 1.0 M sodium perchlorate
B) Solution from the intermediate compartment with fritted-glass membrane; Experiment 2, Section I
C) 5 x 10^{-5} M potassium hydrogen phthalate
D) 5 x 10^{-5} M potassium hydrogen phthalate and 1.0 M sodium perchlorate
E) Solution from the intermediate compartment with the unfired Vycor membrane; Experiment 3, Section I


100
75
50
25
Transmittance (per cent)
210
230
250
270
290
Wavelength (nanometers)
A
B
C
D
E

was observed visually by the dramatic color change from yellow to pink as the hydroxide ions progressed up the intermediate compartment.

The hydrogen phthalate anion was detected in the intermediate compartment with the fritted-glass membrane when sodium perchlorate was used as the electrolyte but not when potassium chloride was used in Section E. It must be pointed out that 7.0 M sodium perchlorate is usually used as the electrolyte solution in the intermediate compartment rather than 1.5 M sodium perchlorate. The 0.2 M sodium perchlorate solution was used in the working-electrode compartment to prevent the precipitation of potassium perchlorate when potassium hydrogen phthalate was added.

V. TITRATION OF POTASSIUM HYDROGEN PHTHALATE

A. Potassium Hydrogen Phthalate as a Primary Standard

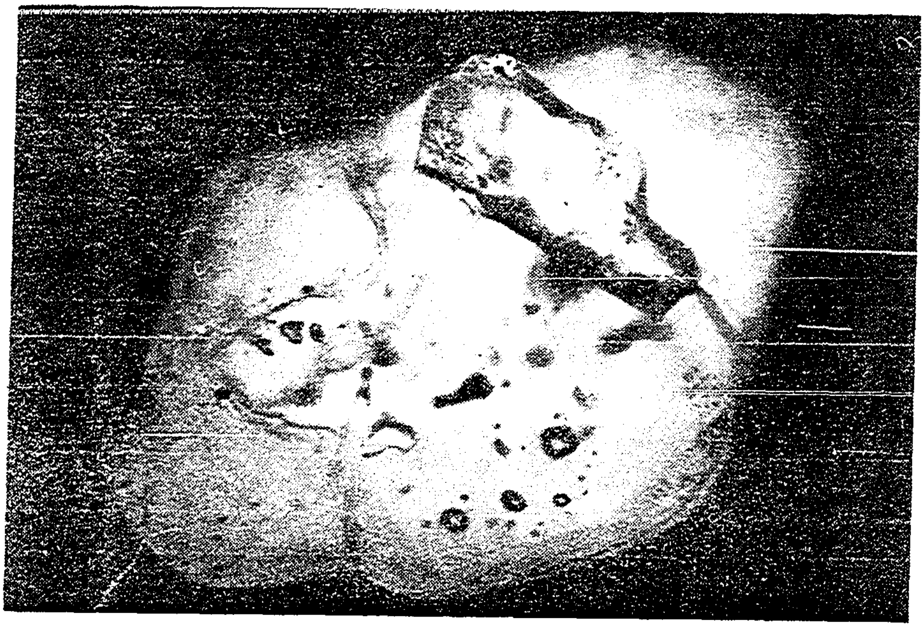
Potassium hydrogen phthalate is easily obtained in highly pure form, it is a white, free-flowing, crystalline solid, it dissolves readily in water, and it is the most widely used of all primary standards. In practice, throughout the chemical world it has been the only primary standard acid used during the past fifty years. It was quite natural then that this material was used as a reference standard in the course of the development of high-precision coulometry, beginning with the work of Taylor and Smith (84) in 1959 and continuing through the present work. Concerning this high-precision work with potassium hydrogen phthalate, however, there have always been two reservations: the atomic weight of potassium has not been accurately known and there has been no way to insure the absence of water from the crystals of the material. The first of these difficulties has now been overcome, by the brilliant determination of the atomic weight of potassium by the mass spectrophotometric method by Garner, Murphy, Gramlich, Paulsen and Barnes (28). Because of the nature of potassium acid phthalate, it can neither be melted without decomposition nor sublimed, the problem of the occluded water will probably never be solved; that the nature of this problem can be properly grasped, photomicrographs prepared by Professor Donald L. Biggs of the Department of Earth Sciences, Iowa State University, of the standard sample of the National Bureau of Standards (NBS), SRM 84d Potassium Hydrogen Phthalate, are given in Figure 17.

Five earlier workers had made high-precision analyses of potassium hydrogen phthalate and it was in order, therefore, to use potassium hydrogen phthalate to check the improved coulometric titration apparatus described in Chapter II of the present work. The four earlier studies and the present study were all made on the same lot of material, National Bureau of Standards SRM 84d Potassium Hydrogen Phthalate. This, itself, is unusual inasmuch as the six studies have extended over a period of twenty-five years, during which time the National Bureau of Standards has marketed to exhaustion three more lots of the material (the current lot is numbered 84h).

Of the five earlier analyses of potassium hydrogen phthalate, the first is a purely chemical analysis, the other four all coulometric titrations: Bates and Wichers (2), 1957; Taylor and Smith (84), 1959; Eckfeldt and Shaffer (24), 1965; Knoeck and Diehl (42), 1969; and Yoshimori and Matsubara (92), 1970. The Bates and Wichers work is a comparison of SRM 84d and two other preparations of

Figure 17. Photomicrographs of crystals of SRM 84d Potassium Hydrogen Phthalate, showing cavities and inclusions of the solution from which the material was crystallized. Magnification 100X

Top photo: focal plane 23 μm. below surface



potassium hydrogen phthalate with "single crystal" benzoic acid by differential titration using solid sodium carbonate as an intermediate alkali and the hydrogen electrode as the device for locating the equivalence-point. In each of the four coulometric titrations, the purpose of analyzing the potassium hydrogen phthalate was to prove the efficacy of one or another feature of the coulometric titration technique: Taylor and Smith, the first of the high-precision titration studies, that their four-chambered cell functioned poorly; Eckfeldt and Shaffer that their simplified electrical apparatus and simpler titration cell made high-precision coulometric titrations available to all serious workers; Knoeck and Diehl, that a cell in which the reagent was generated electrically externally to the titration cell worked efficiently, and Yoshimori and Matsubara that the equivalence-point could be located amperometrically with an antimony electrode. The problem of occluded water was met head on by Bates and Wichers but it was either ignored or left as a possible source of otherwise unexplained discrepancies, by the others, although Marinenko (60) in 1969 went to the trouble of calculating a value for the atomic weight of potassium from the data of Bates and Wichers to bolster the argument of basing their value for the faraday on single-crystal benzoic acid. The results of the various analyses of potassium acid phthalate, fortunately most have been done on the same lot of material, SRM 84d, are summarized in Table 9.

Before analyzing, Bates and Wichers (2) crushed SRM 84d Potassium Hydrogen Phthalate to a fine powder and dried at 100°. They stated that they felt that this treatment eliminated any occluded water. Two analyses of this material, designated lot 1P, and two similar analyses of benzoic acid lot 2B (also designated as "single crystal benzoic acid"; see Chapter VI of the present dissertation for details) were made by a differential titration method using solid sodium carbonate as an intermediate alkali. Assuming the benzoic acid 2B to be 100.0000 per cent pure, the purity obtained for SRM 84d was 99.9870 per cent; Table 9.

In another preparation of potassium hydrogen phthalate, cleavage plates from large crystals grown from water were analyzed; the purity found, 99.9958 per cent, indicated that this material was purer than the crushed SRM 84d. In a still further selection, material in which the cleavage plates of lot 2P were selected to avoid ragged edges, material designated lot 3P, was obtained. Two titrations of this material gave for the purity 99.9998 per cent, again in terms of benzoic acid 2B taken as 100.0000 per cent.

Bates and Wichers state that in calculating their results, the molecular weights were calculated using atomic weights taken from the 1955 Table of Atomic Weights; they do

Table 9. High-precision analyses of potassium hydrogen phthalate

Source of Lot Number	Method of Analysis	Purity in Per Cent Range (R) or Standard Deviation (σ)	Author. Location. Year. Reference.
SRM 84d Potassium Hydrogen Phthalate. Lot 1P.[a]	Differential titration using sodium carbonate as intermediate alkali.[b]	99.9870 R = 0.0036[c] (= 36 p.p.m.) 99.9867[d]	Bates and Wichers. NBS. 1957. Ref. 2.
Selected cleavage plates. Lot 2P.[e]	Same.	99.9958 R = 0.0102[f] (= 102 p.p.m.) 99.9955[d]	Same.

---

[a] The material, National Bureau of Standards SRM 84d, was crushed to a powder and dried at 100°.

[b] Using the hydrogen electrode as indicating device.

[c] Range of the three determinations reported; Bates and Wichers give for the standard deviation 0.0018 per cent potassium hydrogen phthalate.

[d] Recalculated using the g.-eq.-wt. of potassium acid phthalate 204.224,95 and for benzoic acid 122.124,67 (carbon-12 basis, atomic weight of potassium 39.098,034 (28).

[e] Selected cleavage plates from crystals grown from water.

[f] Range of the two determinations reported.

Table 9. (Continued)

Source of Lot Number	Method of Analysis	Purity in Per Cent Range (R) or Standard Deviation (σ)	Author. Location. Year. Reference.
Specially selected cleavage plates. Lot 3P.[g]	Differential titration using sodium carbonate as intermediate alkali.[b]	99.9998 R = 0.0012[f] (= 12 p.p.m.) 99.9995[d]	Bates and Wichers. NBS. 1957. Ref. 2.
SRM 84d.[a]	Coulometric titration.	99.9764[h] σ = 0.0031[i] (= 31 p.p.m.) 99.989[j] 99.9901[k]	Taylor and Smith. NBS. 1959. Ref. 84.

---

[g] Specially selected cleavage plates of lot 2P.

[h] Using for g.-eq.-wt., 204.216 and for the faraday 96,495.6 coulombs per g.-eq.-wt.

[i] Standard deviation of the individual result; all 10 analyses reported, 9 degrees of freedom.

[j] Recalculation by Taylor, communicated to Eckfeldt and Shaffer and published by them (24), using for the g.-eq.-wt. 204.228 (carbon-12 basis, potassium 39.102) and for the faraday 96,490.0 coulombs per g.-eq.-wt. (Craig, Hoffman, Law and Hamer (15)).

[k] Using for g.-eq.-wt. 204.224,95 (carbon-12 basis, potassium 39.098,304 (Garner, Murphy, Gramlich, Paulsen and Barnes (28)) and for the faraday 96,486.57 1972 NBS coulombs per g.-eq.-wt. (Koch and Diehl (46)).

Table 9. (Continued)

Source of Lot Number	Method of Analysis	Purity of Per Cent Range (R) or Standard Deviation (σ)	Author. Location. Year. Reference.
SRM 84d.[a]	Coulometric titration.	99.9988[l] σ = 0.0027[m] (= 27 p.p.m.) 100.0009[k]	Eckfeldt and Shaffer. Leeds & Northrup Co. 1965. Ref. 24
SRM 84d.[a]	Same; external generation of titrant.	99.991[n] σ = 0.0049[o] (= 49 p.p.m.) 99.9874[k]	Knoeck and Diehl. Iowa State University. 1969. Ref. 42.

---

[l] Using for g.-eq.-wt. 204.228 and for the faraday 96,490.0 coulombs per g.-eq.-wt. (the then current value of Craig, Hoffman, Law and Hamer (15)).

[m] Standard deviation of the individual result; all 10 analyses reported, 9 degrees of freedom.

[n] Based on g.-eq.-wt. of 204.229 and for the faraday 96,487.0 coulombs per g.-eq.-wt.

[o] Standard deviation of the individual result; 6 analyses, 5 degrees of freedom.

Table 9. (Continued)

Source of Lot Number	Method of Analysis	Purity of Per Cent Range (R) or Standard Deviation (σ)	Author. Location. Year. Reference.
SRM 84g.[p]	Coulometric titration; amperometric end-point.	99.9955[q] σ = 0.0132 (= 132 p.p.m.)	Yoshimori and Matsubara. University of Tokyo. 1970. Ref. 92.
SRM 84d.[a]	Coulometric titration.	99.9930 σ = 0.0019 (= 19 p.p.m.)	Present author. Iowa State University. 1979. This dissertation.

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[p] The exact sample used, SRM 84g was identified in a later reference by Yoshimori (91). The certificate for SRM 84g states that the purity is 99.98 per cent potassium hydrogen phthalate.

[q] Average of all 12 results reported. Standard deviation of the individual result. Calculations based on the faraday equal to 96,487.2 coulombs per g.-eq.-wt. but the molecular weight not stated.

not give the actual values used. Presumably, the values used were: potassium hydrogen phthalate 204.232; benzoic acid 122.125. For the journal location of the 1955 Table of Atomic Weights, see Appendix. I have made a recalculation of the Bates and Wichers data on benzoic acid 2B and on the three lots of potassium hydrogen phthalate, using for the equivalent weights: potassium hydrogen phthalate, 204.224,95; benzoic acid, 122.124,67. The rationale for the selection of the values for the atomic weights used is given in Section B below. The results of the recalculations of the Bates and Wichers data are given in Table 9.

For an appreciation of the truly remarkable character of the work of Bates and Wichers, see the section immediately below dealing with atomic weights for the use made of the Bates and Wichers data on benzoic acid and potassium hydrogen phthalate by Marinenko (60) for a calculation of the atomic weight of potassium.

The coulometric titrations of Taylor and Smith, done at the National Bureau of Standards and reported in 1959 (84), yielded for the purity of SRM 84d Potassium Hydrogen Phthalate 99.9764 per cent. The calculations were based on a g.-eq.-wt. of 204.216 and a value for the faraday of 96,495.6 coulombs per g.-eq.-wt. (11). Recalculation using the present day values of 204.224,95 for the g.-eq.-wt. (carbon-12 basis; Garner and others (28) value for potassium

(1975), and 96,486.57 1972 NBS coulombs per g.-eq.-wt. (Koch and Diehl (46)) gives for the purity SRM 84d 99.9901 per cent (Table 9).

In checking out their coulometric titration apparatus employing the continuous counter flow partition, Eckfeldt and Shaffer (24) analyzed both potassium hydrogen phthalate and constant boiling hydrochloric acid. The potassium hydrogen phthalate was the same SRM 84d analyzed by Bates and Wichers and by Taylor and Smith and Eckfeldt and Shaffer were in communication with Taylor while the work was in progress. In the same manner, they prepared their SRM 84d by grinding and drying. The purity for SRM 84d found by Eckfeldt and Shaffer was some 224 p.p.m. higher than that of Taylor and Smith. Eckfeldt and Shaffer commented on and attempted to explain this discrepancy, but without success. My own recalculation of the Eckfeldt and Shaffer results using the recent values for the g.-eq.-wt. and the faraday brings the two values closer together but the discrepancy is still some 108 p.p.m. (Table 9).

The coulometric titration cell of Knoeck and Diehl (42), providing for external generation of titrant, was designed for the titration of acids which are reducible at the cathode concurrently with the reduction of the hydrogen ion (generation of hydroxyl for the titration of acids). Specifically, the cell was designed for the titration of potassium dichromate as an acid. The latter objective was achieved and SRM 84d was titrated as a further check on the efficiency of the cell. The purity obtained for SRM 84d was 99.991 per cent. This value was based on a g.-eq.-wt. of 209.229 (carbon-12 basis, but a high value for potassium) and for the faraday 96,487.0 coulombs per g.-eq.-wt. (the then current recalculated) value for the value of Craig and others (15). My recalculation to the present-day values for the g.-eq.-wt. and the faraday changes the purity to 99.9874 per cent, the lowest of the three coulometric titrations. The standard deviation is higher than that of the others.

The potassium hydrogen phthalate analyzed by Yoshimori and Matsubara (92) was identified as SRM 84g in a later paper by Yoshimori (91). The mean and standard deviation given in Table 9 are for all twelve results reported. The value used by Yoshimori for the faraday was 96,487.2 coulombs per g.-eq.-wt. but the value for the molecular weight is not given.

B. The Atomic Weight Tables. The Atomic Weights of Carbon, Hydrogen, Oxygen and Potassium. The Molecular Weights of Potassium Hydrogen Phthalate and Benzoic Acid

An unexpected difficulty in obtaining the molecular weight of potassium hydrogen phthalate and of benzoic acid arises from a change in the practice of the Commission on Atomic Weights of assessing and of reporting the uncertainties in the values for the atomic weights of the elements. In the 1971 table, Atomic Weights of the Elements (see Appendix for reference), the values in the 1961 table are rounded off for general chemical use. In the 1961 table and subsequent tables, the ± sign does not have the normal meaning of uncertainty in the accompanying value but represents the maximum reported in various studies for the effect resulting from natural variation in isotopic composition; this is clearly stated by Wichers in the 1961 table. Thus, Koch, Hoyle and Diehl (47), in calculating the molecular weight of 4-aminopyridine, found it necessary to go back to the 1961 table for values for carbon and hydrogen. I have followed this practice. The values used then are:

$C = 12.011{,}15 \pm 0.000{,}05$

$H = 1.007{,}97 \pm 0.000{,}01$

$O = 15.999{,}4 \pm 0.000{,}1$

and for potassium, the value of Garner, Murphy, Gramlich, Paulsen and Barnes (28):

$K = 39.098{,}304 \pm 0.000{,}57$

These values yield for

Potassium hydrogen phthalate, $KC_8H_5O_4$

molecular weight, 204.224,95; $\sigma_{m.w.} = 0.000{,}57$

($\delta = 2.8$ p.p.m.)

The uncertainties given in these molecular weights reflect the maximum range of variation in all measurements reported on the isotopes of the four elements involved and is not an uncertainty or probable error in the normal sense. They can be considered as a guide and they make it apparent that if the value for the faraday is ever to be made reliable to 1 p.p.m. that a determination of the ratios of the various isotopes in the particular lot of primary material used must be determined particularly the ratios for carbon and oxygen.

The atomic weight of potassium, which plays a significant role in the high-precision analyses of potassium hydrogen phthalate reported above, has undergone some interesting changes. The value 39.100 appearing in the 1957 table was based on three chemical determinations; that in the 1961 table, 39.102, was based only on mass spectrometric measurements. That the 1961 value is significantly different from the value 39.098 obtained by converting the 1957 chemical atomic weight (O = 16, K = 39.100) to the carbon-12 scale was pointed out by Marinenko (60), who then went on to use the data of Bates and Wichers (2) on single crystal benzoic acid (lot 2B) and single crystal potassium hydrogen phthalate (lot 3P) to calculate the atomic weight of potassium. The value obtained, 39.099±0.001, is close to the chemical value. Later, an exceptionally thorough measurement of the atomic weight of potassium was conducted at the National Bureau of Standards by Garner, Murphy, Gramlich, Paulsen and Barnes (28) who obtained 39.098,304±000,058. This is an astonishing confirmation of the remarkable experimental work of Bates and Wichers and attests to the insight into the general problem of high-precision analyses of Marinenko.

C. Experimental Work

1. Preparation of potassium hydrogen phthalate

The sample of National Bureau of Standards SRM 84d Potassium Hydrogen Phthalate was prepared by gently crushing about twelve grams of the acid in an agate mortar and drying the sample in the oven at 110° for eight hours. The dried sample was stored in a vacuum desiccator over anhydrous magnesium perchlorate until used.

Two lots of commercially available potassium hydrogen phthalate were crushed in the agate mortar and dried in an oven for eight hours at 110°. The two lots, Fisher Lot 732537 and Baker Lot 35397 were manufactured by the Fisher Scientific Company and the J. T. Baker Chemical Company, respectively. These two lots were used in preliminary titrations as a check on the titrations The purity of these samples as stated by the bottle containing the acids were 100.04 per cent for the Fisher Lot 732537 and 99.99 per cent for the Baker Lot 35397.

2. Apparatus

The titration apparatus was described in Chapter II of this dissertation. The intermediate compartment with the unfired Vycor membrane and the intermediate compartment with the fritted-glass membrane were used in the following titrations. The working electrode, used as the cathode in this case, was enclosed in the bubble shield to prevent the splashing of the electrolyte to the walls of the titration vessel by the hydrogen generated.

3. Procedure

The pH of the solution in the working-electrode compartment was lowered to a pH of 2.2 using either hydrochloric acid or perchloric acid depending on which salt was used as the electrolyte. Nitrogen was passed through the working-electrode compartment for one hour. A pretitration was then made. The bubble shield was lowered into the solution until only 1.5 cm. of the shield remained above the surface of the solution. The pretitration was performed by passing the 100-mA current through the titration cell until a pH of 10.0 was reached. Additional hydrochloric acid or perchloric acid was added to the solution in the working-electrode compartment to lower the pH to 2.2. The 100-mA current was turned on again until a pH of 3.4 was reached at which time the current was switched to the 5-mA range. The bubble shield was lowered to completely submerge the shield and the top of the shield was raised a few mm. to allow rapid mixing of the base generated at the cathode. Starting at a pH of about 4.0, the pH of the solution in the working-electrode compartment was recorded along with the time interval that the 5-mA current was turned on. The addition of small time intervals of the 5-mA current was continued until a pH of 10.0 was reached.

The bubble shield was raised until the top of the shield was about 1.5 cm. above the surface of the solution. The sample boat containing the sample was lowered into the solution in the working-electrode compartment and the sample was allowed to dissolve. The 100-mA current was turned on until approximately 99.5 per cent of the sample was titrated. The bubble shield was lowered as before and the titration cell was washed with water free of carbon dioxide. The pH was recorded and the 5-mA current was turned on for small time intervals with the pH recorded between each addition of the current. This was continued past the equivalence-point until a pH of 10.0 was reached.

4. Titration A. Sodium perchlorate electrolyte. Vycor membrane

The titration of the sample of NBS SRM 84d Potassium Hydrogen Phthalate was first performed using the 1.0 M sodium perchlorate supporting electrolyte in the working-electrode compartment and using the intermediate compartment carrying the unfired Vycor membrane. The electrolyte in the intermediate compartment consisted of 7.0 M sodium perchlorate, pH 7.0. During the titration, a white precipitate formed and remained through the titration. This precipitate did not dissolve on stirring overnight; presumably it was potassium perchlorate. A similar precipitate formed when 1.5 g. of potassium hydrogen phthalate was added to 100 $cm.^3$ of 1.0 M sodium perchlorate. At lower concentrations of sodium perchlorate, the precipitate did not form. A solution of 0.2 M in sodium perchlorate proved satisfactory for the supporting electrolyte in the working-electrode compartment. Several samples of the Fisher Lot 732537 and Baker Lot 35397 were titrated in 0.2 M sodium perchlorate; the results are given below.

5. Titration B. Potassium chloride electrolyte. Vycor membrane

The titration performed here was identical to the titration performed in Titration A except potassium chloride was used as the electrolyte. The solution in the working-electrode compartment consisted of 1.0 M potassium chloride. The solution in the intermediate compartment consisted of 2.0 M potassium chloride, pH 7.0. Several samples of Baker Lot 35397 were titrated. The results are given below.

6. Titration C. Potassium chloride electrolyte. Glass frit membrane

In this experiment, the intermediate compartment with the fritted-glass membrane having the 5.2 cm.^{3}/hour flow rate was used. The solutions in both the working-electrode compartment and the intermediate compartment consisted of 1.0 M potassium chloride. A pH electrode was inserted into the intermediate compartment to monitor the pH of the solution in the intermediate compartment. Before the titration began, nitrogen was bubbled through the solution in the intermediate compartment for 30 minutes. The pH of the solution in the intermediate compartment was adjusted to a pH of 7.00 at the beginning of the titration and did not deviate by more than 0.1 pH units from a pH of 7.00 during the titration. Two titrations on Baker Lot 35397 were performed as a check on this method. Six titrations of SRM 84d using 1.5 g. samples were made. The results are given in Table 10.

7. Density of potassium hydrogen phthalate

The density of potassium hydrogen phthalate used by Bates and Wichers (2) was 1.62 g./cm.^{3} and has been reported as high as 1.636 g./cm.^{3} (67). As a check on the densities of the acid reported in the literature, the density of potassium hydrogen phthalate was redetermined in this work. A ten-cm.^{3} pycnometer was used along with xylene saturated with potassium hydrogen phthalate as the transfer medium. The density of the National Bureau of Standards 84d Potassium Hydrogen Phthalate was found to be 1.6364 g./cm.^{3}.

D. Results and Discussion

The results were calculated as the per cent purity of potassium hydrogen phthalate using equations (2) through (9) of Chapter II. The equivalence-point was calculated by the Yan (90) method. The value of the faraday used 96,486.57 1972 NBS coulombs per g.-eq.-wt. calculated by Koch and Diehl (46) was used along with the g.-eq.-wt. 204.224,95 (Section B above). The density of potassium hydrogen phthalate used was 1.636 g./cm.^{3}.

The result of the titration of the NBS SRM 84d Potassium Hydrogen Phthalate by Titration A using 1.0 M sodium perchlorate, 99.016 per cent potassium hydrogen phthalate, was poor. The poor result of this titration was attributed to the precipitation of potassium perchlorate which occurred during the titration. The solubility of potassium perchlorate 0.78 g. per 100 ml. at 0° (67) was exceeded and the precipitate formed The use of 0.2 M sodium perchlorate as the electrolyte prevented the formation of the precipitate as long as the sample was not too large. The result of the titration of Fisher Lot 732537 in 0.2 M sodium perchlorate was 99.009, 99.038 and 99.247 per cent. The result of the titration of Baker Lot 35397 in the same electrolyte was 98.986 and 98.831 per cent. The results were disappointing.

The electrolyte was changed to 1.0 M potassium chloride and Baker Lot 35397 was titrated in Titration B. The results were 99.800, 99.544 and 99.693 per cent. Again, the results were quite poor. During an exhaustive investigation of the titration, potassium hydrogen phthalate was found to be present in the solution in the intermediate compartment. This led to the investigation of the migration of ions under the influence of an electrical field described in Chapter IV. The hydrogen phthalate anion was found to migrate through the Vycor membrane toward the anode in the counter-electrode compartment. Use of a membrane with a high flow rate was found to prevent this loss. The intermediate compartment having a glass frit membrane with a high flow rate was used in Titration C.

The results of the titration of Baker Lot 35397 in 1.0 M potassium chloride in Titration C were 99.977 and 100.003 per cent. With the method working, six titrations of NBS SRM 84d Potassium Hydrogen Phthalate were made in 1.0 M potassium chloride electrolyte with the intermediate compartment being that with a glass frit membrane. The results of the titration are given in Table 10.

The result of the titration of SRM 84d using the intermediate compartment with the glass frit agreed fairly well with the previous high-precision titrations in the same sample given in Table 9. The standard deviation in my titration of SRM 84d was slightly lower than the previous titrations of the same sample. Much of the difference in the results in Table 9 could be due to the amount of occluded solvent in the sample (see Figure 17). The occluded solvent is presumably also the reason that the sample is not 100.0000 per cent pure and that the standard deviation was higher than expected for the quality of the analyses made.

Table 10. Assay of SRM 84d Potassium Hydrogen Phthalate by coulometric titration

	Weight of Sample[a] g.	Purity Per Cent
	1.455095	99.9914
	1.489877	99.9916
	1.461044	99.9954
	1.325246	99.9947
	1.459466	99.9911
	1.702476	99.9940
Mean		99.9930
Standard Deviation		0.0019

[a] Weight after correction for buoyancy of air.

VI. COULOMETRIC TITRATION OF BENZOIC ACID IN WATER AND IN WATER-ALCOHOL MIXTURES

A. Introduction

Benzoic acid occupies a preeminent position among our primary standards. It has been adopted as the ultimate chemical standard against which other primary standards have been compared, by Bates and Wichers in 1956 (2), and has been used for the coulometric evaluation of the faraday, by Marinenko and Taylor in 1968 (62). In spite of such use and ready availability in pure form, it has never been popular with the analytical chemist, chiefly because of the low solubility and the slowness with which it dissolves in water.

In the present work, I have made use of benzoic acid in a further determination of the value of the faraday, with particular attention to the effect of alcohol and other water-miscible liquids added to the water in which the coulometric titration was performed. As explained later, I was never able to effect the coulometric titration of benzoic acid in a water solution, because of the solubility problem. This has been in spite of two earlier reports of high-precision coulometric titrations of benzoic acid (62,84). An important objective of the present work was the determination of the value of the faraday on the same material in water and in a nonaqueous solvent, and the failure in the present work to titrate benzoic acid successfully in water was indeed disappointing.

B. Physical and Chemical Properties

Benzoic acid is stable indefinitely at temperatures below 130° (76); the anhydride is formed only when the acid is heated above 130° in very dry air (76). The acid is stable also toward moist air and will only absorb water from an atmosphere of relative humidity above 90 per cent (70).

The freezing point of benzoic acid is 133.36±0.01° (76).

The solubility of benzoic acid in water is 3.4 g./liter at 25°. It is not wetted by water and crystals prepared by sublimation float almost indefinitely on water. The acid is much more soluble in ethanol than in water, the solubility being reported (67) to be 434 g./liter, presumably at room temperature.

The density of benzoic acid is 1.320 g./cm.^{3} (see experimental work below).

C. Purification

The benzoic acid used in the very early study of it as a primary standard by Morey (68) was purified by recrystallization from alcohol followed by sublimation in a vacuum.

These and various other methods of preparing and purifying the acid were studied by Schwab and Wichers (76) who found their best preparations were obtained by repeated recrystallization from benzene, by hydrolysis of benzoyl chloride, and by fractional freezing; the purity of such preparations was 99.999 mole per cent as determined by the freezing range and by specific heat measurements. The apparatus used by Schwab and Wichers for the purification by freezing was described in detail (77); this technique is now called "zone refining by batch". The apparatus for the precision determination of the depression of the freezing point was also described in detail (75). The benzoic acid used by Bates and Wichers (2) as the ultimate chemical standard and later titrated coulometrically by Taylor and Smith (84) and by Marinenko and Taylor (62) was prepared by them (2) by fractional freezing (lot designated 1B), a small lot of this material being given a final purification by the slow growth of a single crystal (lot designated 2B and also as "single crystal benzoic acid").

D. Benzoic Acid as a Primary Standard

Benzoic acid was suggested as a primary standard by Phelps and Weed (71) in 1908. It was investigated carefully and then introduced as a primary standard by Morey at the National Bureau of Standards in 1912 (68). It was subjected to an intensive purification by Schwab and Wichers (76), and made the subject of a careful proof of purity (77). It was made the principal of all primary standards by Bates and Wichers (2) in 1957. It has been subjected also to three high-precision coulometric titrations, by Taylor and Smith (84), by Marinenko and Taylor (62), and later for the purpose of evaluating the faraday, and by Yoshimori and Matsubara (92). Since 1951, benzoic acid has been distributed as a primary standard by the National Bureau of Standards.

In any comparison of the results of these four high-precision analyses (2,62,84,92) care must be taken to put the results on the same basis as far as possible. Complicating this picture are: (a) the change in 1961 of the basis of the Table of Atomic Weights from oxygen to carbon-12; (b) a change in the nature of reporting the uncertainty in the values for the atomic weights in the Table of 1963 and again in a further change in the Table of 1977; (c) change in the value of the faraday, as reflected in successive recalculations of the 1960 value of Craig, Hoffman, Law and Hamer (15); (d) changes in the definition of the volt in 1969 and again in 1972; and (e) use of different definitions and methods of evaluating the standard deviation. In the following discussion and in Table 11, I have tried to clarify the reporting of the results of these analyses by recalculating certain of the data.

Table 11. Benzoic acid as a primary standard

Method of Purification. Source. Lot Number	Method of Analysis	Purity in Per Cent or Value Obtained for the Faraday[a]	Author. Year. Location. Reference
Recrystallization from benzene followed by sublimation in vacuum.	Titration versus constant boiling hydrochloric acid.		Morey. NBS. 1912. Ref. 68.
Various; zone refining by batch.	Depression of the freezing point.	99.999[b]	Schwab and Wichers. NBS. 1940-1944. Refs. 75,76,77.
Growth of a single crystal. Lot 2B, also called "single crystal benzoic acid".	Differential titration using sodium carbonate as intermediate alkali.	Assumed to be 100.000[c]	Bates and Wichers. NBS. 1957. Ref. 2.
Zone refining by batch. Lot 1B.	Same.	99.9957[d] $\sigma = 0.00126$[e] ($\delta = 12.6$ p.p.m.)	Same.

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[a] In coulombs per g.-eq.-wt.

[b] In mole per cent.

[c] Two analyses only: 100.0151, 100.182 per cent benzoic acid versus sodium carbonate equal to 100.0000; range 0.0032 per cent benzoid acid.

[d] Purity versus benzoic acid 2B.

[e] Standard deviation of the individual result, in terms of per cent benzoic acid; 8 analyses, calculation made using 7 degrees of freedom.

Table 11. (Continued)

Method of Purification. Source. Lot Number	Method of Analysis	Purity in Per Cent or Value Obtained for the Faraday[a]	Author. Year.	Location. Reference
Zone refining by batch. Lot 1B.	Coulometric titration.	99.9915[f] $\sigma = 0.0053$[g] (δ = 53 p.p.m.) 100.0112[h]	Taylor and Smith. NBS. 1958. Ref. 84.	

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[f] Recalculation, including all eleven results reported.

[g] Standard deviation of the individual result; 11 analyses, calculation using 10 degrees of freedom.

[h] Recalculation using for the g.-eq.-wt. 122.124,67 and for the faraday 96,486.57 1972 NBS coulombs per g.-eq.-wt. (Koch and Diehl (46)).

Table 11. (Continued)

Method of Purification. Source. Lot Number	Method of Analysis	Purity in Per Cent or Value Obtained for the Faraday[a]	Author. Year.	Location. Reference
Zone refining by batch.	Coulometric titration.	96,486.71[i] σ = 2.16[j] (δ = 22.4 p.p.m.) 96,487.30[k] (δ = 12 p.p.m.)[l]	Marinenko and Taylor. 1968.	NBS. Ref. 64.

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[i] Using for the g.-eq.-wt. 122.124,67.

[j] Standard deviation of the individual result; 19 analyses, calculation using 18 degrees of freedom.

[k] As recalculated by Cohen and Taylor (12).

[l] Standard deviation of the mean combined with systematic errors estimated at the 70 per cent confidence level.

Table 11. (Continued)

Method of Purification. Source. Lot Number	Method of Analysis	Purity in Per Cent or Value Obtained for the Faraday[a]	Author. Year.	Location. Reference
Not stated.	Coulometric titration.[m]	99.992 $\sigma = 0.0089$[n] (δ = 89 p.p.m.)	Yoshimori and Matsubara. University of Tokyo. 1970. Ref. 92.	

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[m] Amperometric end-point with antimony electrode. Titrations performed in 30 per cent ethanol.

[n] Standard deviation of the individual results; all 10 analysis, 9 degrees of freedom.

As mentioned in the preceding section, Lot 2B, the "single crystal benzoic acid" was assumed by Bates and Wichers (2) to be 100.0000 per cent pure and the purity of other primary standard acids was established by reference to it. The analytical method used to make the comparison was a differential titration employing solid sodium carbonate as an intermediate alkali and the hydrogen electrode as the device for indicating the equivalence-point. The weighed sample of benzoic acid and sufficient solid sodium carbonate to react with 99 to 99.5 per cent of it were added to water and the mixture heated to 90° to effect the reaction. The titration was then completed by the addition of sodium hydroxide delivered from a weight buret. Two analyses of 2B were made: 100.0151 and 100.0182 per cent benzoic acid versus sodium carbonate equal to 100.0000, the range thus being 0.0031 per cent benzoic acid or 31 p.p.m. The equivalent weight of benzoic acid used in the calculations was not given but presumably was calculated from values in the 1955 Table of Atomic Weights (see Appendix) and thus was 122.125. Eight analyses of benzoic acid 1B gave for the purity an average of 100.124 per cent assuming the purity of the sodium carbonate to be 100.0000 per cent.* The standard deviation of the mean of these results (seven degrees of freedom was 0.00126 per cent benzoic acid or 12.6 p.p.m. The purity of 1B converted from the basis of sodium carbonate to benzoic acid 2B (the two determinations reported just above) gives for the purity of 1B 99.9957 per cent. The eight analyses of benzoic acid 1B by Bates and Wichers are undoubtedly the most precise of all chemical analyses ever performed.

In the first of the papers in which the coulometric titration technique was employed in high-precision chemical analysis, Taylor and Smith (84) describe a cell and electrical measuring circuits adequate to the purpose and report the results of titrations of benzoic acid, potassium hydrogen phthalate, constant boiling hydrochloric acid, adipic acid, and sodium carbonate. The benzoic acid titrated was the lot 1B of Bates and Wichers. The results of fifteen analyses gave for the purity 99.9915 per cent, standard deviation of the individual result 0.0053 per cent benzoic acid equal to 53.0 p.p.m.

The results of Taylor and Smith just quoted were calculated using the g.-eq.-wt. of benzoic acid 122.112 and for the faraday 96,495.6 coulombs per g.-eq.-wt. (value of Cohen and DuMond (11)). I have recalculated the results to the basis of 122.124,67 (see note h, Table 11) for the g.-eq.-wt. and F = 96,486.57 1972 NBS coulombs per g.-eq.-wt. (value of Koch and Diehl (46), a calculation which gives for the purity 100.0112 per cent. This recalculation does not take into consideration the changes in the calibration of the Taylor and Smith electrical standard which would result if the various redefinitions of the volt and ampere made during the intervening years could be calculated and applied.

In the coulometric titration cell of Taylor and Smith (84), the titration compartment (Cathode compartment in the titration of benzoic acid) and the compartment carrying the counter electrode were separated by two intermediate compartments, each separation of compartments being by fritted glass membranes. Additional separation of the counter electrode (anode in the titration of benzoic acid) from the intermediate chambers was secured by placing a porous, agar plug against the nearest face of the nearest glass membrane. Provision was made for forcing, by nitrogen pressure, the electrolyte in the intermediate compartments into the titration compartment, thus returning to the titration solution any ions which may have migrated into the intermediate compartments during electrolysis. No problem with the slowness with which benzoic acid dissolves was mentioned by Taylor and Smith. A one-gram sample of the benzoic acid was added to the 1 N potassium chloride electrolyte and the mixture stirred for 30 minutes before the electrolysis was begun. Toward the end of the electrolysis, the electrolyte in the intermediate chambers was transferred to the cathode chamber and the wall of the cathode chamber washed down with 15 per cent ethanol to dislodge any crystals of benzoic acid clinging to the upper wall of the cell. Judging from my experience, the solution of Taylor and Smith must have become highly alkaline during the initial phases of the electrolysis, which was carried out with a relatively high current of 200 mA and considerable alkali must have diffused into the intermediate chambers; presumably all of this alkali was transferred back to the catholyte during the washing operation.

The benzoic acid analyzed by Marinenko and Taylor (62) by coulometric titration was also the lot 1B of Bates and Wichers. Nineteen titrations gave for this benzoic acid the average 1.265,715 mg. per coulomb, with a standard deviation of the individual results (18 degrees of freedom) 0.000,028,4, corresponding to 22.5 p.p.m. Using for the equivalent weight of benzoic acid the value 122.124,67 (1967 Table of Atomic Weights, carbon-12 basis), this gives for the faraday F = 96,486.71 coulombs per g.-eq.-wt. Marinenko and Taylor report the standard deviation as the standard deviation of the mean; this value when combined with an estimate of the systematic errors at the 70 per cent confidence level, gave a figure for the uncertainty in this measurement of the faraday of 12 p.p.m.

The Marinenko and Taylor (J. K. Taylor) value for the faraday was recalculated by Cohen and B. N. Taylor (12) taking into consideration the redefinitions of the ampere and volt made in 1969 and 1972, the value obtained being F = 96,487.30 1972 NBS coulombs per g.-eq.-wt. For a still more recent recalculation and resume of the current values proposed for the faraday, see B. N. Taylor and Cohen (82).

The coulometric titration cell of Marinenko and Taylor (62) was that of Taylor and Smith (84) with some modifications as to size. The solution was not stirred during the electrolysis and the electrolyte itself was used to wash the wall of the cathode chamber. Apparently no alcohol was used, nor was any difficulty reported in getting the benzoic acid to dissolve.

The question of the purity of benzoic acid lot 1B was a matter of some concern and Marinenko and Taylor used for the purity 99.9955 per cent obtained by recalculating to the 1967 Table of Atomic Weights, (carbon-12 basis) the purity of 99.9957 per cent of Bates and Wichers, this value being based on two analyses of benzoic acid 2B assumed to be 100.0000 per cent pure. Some further analyses of the sodium carbonate of Bates and Wichers against another specimen of single crystal benzoic acid is referred to by Marinenko and Taylor (62, p. 1647, paragraph 2) but it is not clear who made the analyses and how. In any case, the value of Marinenko and Taylor for the faraday is based on single crystal benzoic acid, and the work appears to have been done entirely in an aqueous solution.

Still another high-precision analysis of benzoic acid by the coulometric method was made, by Yoshimori and Matsubara (92). The objective of the work was to demonstrate that the equivalence-point in the titration could be determined amperometrically with an antimony electrode and to determine the most efficacious method of drying the sample (91,92). The benzoic acid was obtained from the Resources Research Institute (Japan) but unfortunately no information is given as to how it was purified. The standard deviation obtained was 89 p.p.m. The titrations of Yoshimori and Matsubara were performed in a solvent of 30 per cent ethanol-70 per cent water.

E. Experimental Work

1. Source and purification of benzoic acid

a) Preparation 1 National Bureau of Standards SRM 350 Benzoic Acid. Dated January 1958. Purity stated (70) to be 99.98 per cent. This material consisted of fine crystals. It was dried 24 hours in a vacuum desiccator over anhydrous magnesium perchlorate.

b) Preparation 2 National Bureau of Standards SRM 350 Benzoic Acid. Dated October 1975. Identical in all respects and treatment of Preparation 1. Purity also stated to be 99.98 per cent.

c) Preparation 3 Obtained from the Fisher Scientific Company, in the form of small flakes and large clumps. The large clumps could be dissolved only with great difficulty, even in a mixture of water and methanol. A preliminary titration gave a purity of 99.95 per cent.

d) Preparation 4 Preparation 3 was sublimed in a stream of dry nitrogen, the sublimation apparatus used by Koch, Hoyle and Diehl (47) for 4-aminopyridine being used. The benzoic acid was melted and poured into the pot of the sublimation vessel. The benzoic acid sublimed into the condensing tube to form long needles. Three lots were collected.

1) Preparation 4I First sublimate, from three successive starts, the temperatures of the pot and elbow being respectively 115° and 100°.

2) Preparation 4II Another first sublimate but formed at lower temperatures: pot 105°, elbow 95°.

3) Preparation 4III Obtained by the slow sublimation of 4I over a period of 4 hours, the temperatures being pot 110°, elbow 100°.

All three lots were stored in a vacuum desiccator over anhydrous magnesium perchlorate

e) Preparation 5 First, benzoic acid was sublimed by the method described in Preparation 4II. Next the sublimed benzoic acid was placed in a vacuum sublimation apparatus for the purpose of being fused under vacuum. The crystals of the sublimed benzoic acid were slowly heated to the melting point of benzoic acid with a vacuum applied to the apparatus. The sublimed benzoic acid remained melted for five minutes before the heat was removed and the acid allowed to cool. After the benzoic acid cooled to room temperature, the acid was again heated just enough to allow the chunk of fused benzoic acid to be removed from the apparatus. The benzoic acid was broken into small pieces and stored over anhydrous magnesium perchlorate in a vacuum desiccator.

2. Density of benzoic acid

The density of benzoic acid has been reported to be 1.32 g./cm.^{3} (62), 1.321 g./cm.^{3} (67) and 1.266 g./cm.^{3} (10). The density reported on the certificate of SRM 39g Benzoic Acid was 1.320 g./cm.^{3} (69). No density was reported on the certificate for the SRM 350 Benzoic Acid. Because of the large difference between the densities of 1.32 and 1.266, the density of Preparation 4II, sublimed benzoic acid, was determined by a 10 cm.^{3} pycnometer using water saturated with benzoic acid as the transfer material. Because the sublimed benzoic acid floated on water, this method was used only as a check on which of the reported densities was correct. Before the pycnometer containing the benzoic acid and the water saturated with benzoic acid was weighed, the pycnometer containing benzoic acid was filled half way with the water saturated with benzoic acid and placed in a vacuum desiccator. A vacuum was applied for 10 minutes to dislodge any air bubbles trapped between the crystals of benzoic acid. The density of benzoic acid calculated by this method was 1.328 g./cm.^{3} It was assumed that the value of the National Bureau of Standards was the best value, 1.320 g./cm.^{3}, and this value was used in this work.

3. Apparatus

The titration apparatus used in this work was described in Chapter II. The intermediate compartment with the unfired Vycor membrane was used except in Titration C where the intermediate compartment with the fritted-glass membrane was also used. The working electrode, or cathode in this case, was enclosed by the bubble shield.

4. Reagents

The titrations of benzoic acid in this chapter were performed in water, 30 per cent methanol-70 per cent water, 30 per cent 2-propanol-70 per cent water, 30 per cent acetone-70 per cent water, 50 per cent acetone-50 per cent water and 30 per cent acetonitrile-70 per cent water mixtures. The supporting electrolyte in the working-electrode compartment consisted of 1.0 M potassium chloride.

In preparing the solutions in the working-electrode compartment, the supporting electrolyte, potassium chloride, was first dissolved in the amount of water required and then the appropriate amount of the water miscible nonaqueous solvent was added to make the final concentration of potassium chloride 1.0 M and the concentration of the nonaqueous solvent that which was desired. In one case, Titration B, a nonaqueous titration in 2-propanol saturated with sodium perchlorate was tried.

All of the nonaqueous solvents were fractionally distilled before use. Acetonitrile was passed through a column containing a mixture of Dowex 50 x 8 cation exchange resin in the hydrogen form and Dowex 1 x 8 anion exchange resin in the hydroxide form to remove acidic and basic impurities before distillation (87).

The supporting electrolyte in the intermediate compartment consisted of 2.0 M potassium chloride except in Titration B where the solution was 7.0 M sodium perchlorate. Both solutions had a pH of 7.0. The solution in the counter-electrode compartment consisted of 0.1 M potassium dihydrogen phosphate saturated with potassium sulfate, pH 10.0. In the case of Titration B, the solution in the counter-electrode compartment consisted of 0.1 M sodium hydrogen phosphate and 1.0 M sodium perchlorate, pH 10.0.

5. Procedure

The pH of the solution in the working-electrode compartment was lowered to a pH of 2.2 by the addition of some 1.0 M hydrochloric acid. Nitrogen was passed over this solution for thirty minutes. The bubble shield containing the cathode was lowered into the solution until the top 1.5 cm. of the shield remained above the solution. A pretitration was performed by passing the 100-mA current through the titration cell until a pH of 10.0 was reached. The pH of the solution in the working-electrode compartment was lowered to a pH of 2.4 by the addition of some 1.0 M hydrochloric acid. The 100-mA current was turned on again until a pH of 3.4 was reached at which time the current was turned off and the bubble shield was lowered to completely submerge the shield. The top of the shield was raised a few mm. to allow rapid mixing of the titrant generated at the cathode. The sides of the titration cell was rinsed with a few cm.^{3} of water free of carbon dioxide to wash down any solvent creeping up the walls of the titration cell. The current was switched to the 5-mA range and the current was turned on until a pH of 3.8 was reached and the current was turned off. The pH was recorded and the current was turned on for small time intervals; the pH was recorded after the current was turned off. The 5-mA current was added in small time intervals until a pH of 10.0 was reached.

The bubble shield was raised with the top of the shield being 1.5 cm. above the surface of the solution. The sample boat containing the sample of benzoic acid was lowered into the solution in the working-electrode compartment. The 100-mA current was turned on until 99.5 per cent of the sample was titrated. The bubble shield was lowered to completely submerge the bubble trap and the sides of the titration cell were washed with water. The 5-mA current was passed through the titration cell in small time intervals with the pH being recorded each time the current was turned off. This was continued past the equivalence-point until a pH of 10.0 was reached.

a) Titration A. Titration of benzoic acid in water The sample of National Bureau of Standards SRM 350, Benzoic Acid (Preparation 2) and the sublimed benzoic acid, Preparation 4III, were titrated coulometrically in water. The samples of benzoic acid, especially the sublimed benzoic acid sample floated on top of the water solution and did not dissolve. The crystals of the acid clung to the sides of the glassware and were hard to dislodge. The 100-mA current was turned on in the hope that the base generated at the cathode would aid in dissolving the sample. After a few minutes, all of the sample that was dissolved was neutralized and the pH of the solution increased rapidly. When the pH reached 10, the current was turned off to prevent hydroxide ions from migrating out of the working-electrode compartment. The rate of electrolysis was faster than the rate that the sample dissolved and the solution quickly became alkaline.

After 30 minutes of stirring the solution containing the sample, the pH of the solution was low enough to continue the titration. The 100-mA current was passed through the titration cell again but, after a few minutes, the pH of the solution increased to a pH of 10 and the current was turned off again to allow the sample to dissolve. This procedure was repeated numerous times until 99 per cent of the sample was titrated. As the titration of benzoic acid progressed, the time that the 100-mA current was passed before the solution being titrated became alkaline decreased and the time required for more of the sample to dissolve increased. Near the end of the titration, only about 200 seconds of the current was passed before the current was turned off and the sample allowed to dissolve for an additional one to three hours until enough dissolved to continue the titration. The titration of benzoic acid required an extreme amount of time and the results were poor. The results from the titration of SRM 350 Benzoic Acid are given below. The titrations of the sublimed benzoic acid were never completed because of the trouble of dissolving the sample.

b) Titration B. Titration in nonaqueous solvent A coulometric titration using 2-propanol saturated with sodium perchlorate as the solution in the working-electrode compartment was tried. The intermediate compartment with the unfired Vycor membrane was used. The solution in the intermediate compartment consisted of 7.0 M sodium perchlorate. Several attempts were made to pass the 100-mA current through the titration cell but the resistance of the titration cell was too high at the maximum voltage output of the current source. Adding a trace of water did not decrease the resistance of the titration cell. There were also problems with the Vycor membrane cracking. The titration using 100 per cent nonaqueous solvents was abandoned.

c) Titration C. Titration of SRM 350 Benzoic Acid in methanol-water solvent Below 30 per cent methanol the solubility of benzoic acid was too low to be useful; above 30 per cent methanol creeping of the electrolyte up the sides of the vessel became a serious problem, because a film of solid material was left by the rapid evaporation of the methanol. This film could be washed down into the electrolyte solution but some parts of the working-electrode compartment were hard to wash. The methanol content was kept as low as possible to minimize the creeping. Another alcohol, 2-propanol, was found to creep up the sides of the glassware even more than methanol.

The National Bureau of Standards SRM 350 Benzoic Acid, Preparation 1 and 2, were titrated in the 30 per cent methanol-70 per cent water solution. In the titration of Preparation 2, three titrations were performed using the intermediate chamber with the Vycor membrane and three titrations were performed using the intermediate chamber with the glass frit. The results of the titrations are given in Table 12. Preparation 1 was titrated two times and the results are given below.

d) Titration D. Sublimed benzoic acid in alcohol-water solvent Preparation 4II was titrated in 30 per cent methanol-70 per cent water and in 30 per cent 2-propanol-70 per cent water solutions. Samples of 0.5 g. were titrated, this being the capacity of the sample boat for the bulky crystals of the sublimed acid. The results of the titrations of Preparation 4II are given in Table 13.

Preparation 4III was titrated in the 30 per cent methanol-70 per cent water solution. Samples weighing 0.5 g. were titrated. The results of these titrations are given below.

e) Titration E. Fused benzoic acid in alcohol-water solvent   A titration of Preparation 5, fused benzoic acid, was tried in a 30 per cent methanol-70 per cent water solution. A sample weighing 1.0 g. did not dissolve in the methanol-water solvent even when the solution was left stirring over night. On increasing the methanol content to 50 per cent, the acid still did not dissolve and methanol-water solvents for fused benzoic acid was abandoned. The sample also did not dissolve in water containing 30 per cent 2-propanol.

f) Titration F. Fused benzoic acid in acetonitrile-water solvent   Preparation 5, fused benzoic acid, was found to dissolve readily in a 30 per cent acetonitrile-70 per cent water mixture. Two titrations of 1-g. samples were made in this solvent; the equivalence-point appeared much sooner than predicted. The results of this titration are given below.

g) Titration G. Fused benzoic acid in acetone-water solvent   Preparation 5, fused benzoic acid, was found to dissolve in 30 per cent acetone-70 per cent water solutions. One-gram samples of fused benzoic acid were titrated in this solution. Titrations were also made in solutions containing up to 50 per cent acetone. Acetone did not creep up the wall of the glassware during these titrations. The results of these titrations are given in Table 14.

F. Results and Discussion

1. Calculation of results

The results of the titrations of benzoic acid were calculated as the per cent purity of benzoic acid using equations (2) through (9) of Chapter II. The inflection-point of the titration curve was calculated by the Yan method (90). The value of the faraday used was 96,486.57 1972 NBS coulombs per g.-eq.-wt. (Koch and Diehl (46)). The molecular weight of benzoic acid, calculated using the atomic weights taken from the 1961 Table of Atomic Weights (see Appendix for reference), was 122.124,67 g./mole with the uncertainty in the molecular weight being 0.000,41 g./mole (molecular weight and uncertainty calculated in Chapter V, Section B). The density of benzoic acid used in equation (2) was 1.320 g./cm.^{3}.

2. Titration of NBS SRM 350 Benzoic Acid

The result of the titration of Preparation 2, National Bureau of Standards SRM 350 Benzoic Acid in water, Titration A were poor, the purity found being 99.94, 100.76 and 101.27 per cent. The low value could have been the result of some sample remaining undissolved at the end of the titration. The high results probably resulted from the loss of hydroxide ions by migration during the long period required for the titrations.

Preparations 1 and 2, National Bureau of Standards SRM 350 Benzoic Acid, were titrated in 30 per cent methanol-70 per cent water solution, Titration C. Preparation 1 was found to be 99.91 per cent pure; insoluble black particles were present in the solution at the end of the titration. Preparation 2 was found to have a purity 99.9901 per cent, slightly higher than the certificate value of 99.98 per cent (70). The standard deviation of the six results was 0.0054 per cent. Results of the titration of Preparation 2 are given in Table 12. The difference in the mean of the titrations using the Vycor and glass frit membranes was only 0.0018 per cent; apparently either membrane can be used in the titration of benzoic acid.

Table 12. Assay of National Bureau of Standards SRM 350 Benzoic Acid by coulometric titration in 30 per cent methanol

Weight g.	Purity per cent	Membrane Used
0.439252	99.9965	Vycor
0.417938	99.9872	Vycor
0.475399	99.9838	Vycor
0.409664	99.9862	Glass frit
0.497841	99.9902	Glass frit
0.400176	99.9967	Glass frit
Mean	99.9901	
Standard Deviation	0.0054	

3. Titration of sublimed benzoic acid

The results of the titration of Preparation 4II using 30 per cent methanol in water and 30 per cent 2-propanol in water, Titration D, are given in Table 13. The mean of the titration using 30 per cent methanol was only 0.0022 per cent greater than the mean of the titration using 30 per cent 2-propanol. The standard deviation of the results when 30 per cent 2-propanol was used were higher than the standard deviation for the 30 per cent methanol titration.

Table 13. Assay of sublimed benzoic acid, Preparation 4II, by coulometric titration in 30 per cent methanol and in 30 per cent 2-propanol

	30 Per Cent Methanol Purity (Per Cent)		30 Per Cent 2-Propanol Purity (Per Cent)
	100.0038		99.9888
	99.9990		99.9993
	100.0132		100.0134
	100.0047		100.0100
	100.0052		99.9981
	100.0000		
Mean	100.0041	Mean	100.0019
Standard Dev.	0.0056	Standard Dev.	0.0099

The results of the individual titrations of Preparation 4III in 30 per cent methanol were 99.9935, 100.0068, 99.9902, 100.0002 and 100.0207 per cent. The mean of the first four results is 99.9978 per cent with a standard deviation of 0.0074 per cent. The value, 100.0207 was not used in the calculation of the mean or standard deviation because of the large difference between 100.0207 per cent and the rest of the results. The purity of this material was somewhat lower than Preparation 4II.

4. Titration of fused benzoic acid

The large chunks of fused benzoic acid, Preparation 5, did not dissolve in a reasonable time in 30 per cent methanol, 50 per cent methanol or 30 per cent 2-propanol. It did dissolve in 30 per cent acetonitrile but the results of the titration were poor, the purity found, two titrations being less than 98 per cent.

Successful titrations of the fused benzoic acid were obtained in 30 per cent acetone, Titration G, Table 14. The results of a titration in 50 per cent acetone are also given in Table 14. The mean of the results of the titration in 30 per cent acetone was 0.0026 per cent lower than the titration in 50 per cent acetone. The standard deviation of the results in 30 per cent acetone was almost identical to the standard deviation from the titration of Preparation 4II in 30 per cent 2-propanol, Table 13. The standard deviation of the titration in 50 per cent acetone was very high compared to the other titrations of benzoic acid.

Table 14. Assay of fused benzoic acid, Preparation 5, by coulometry in acetone-water solvents

	30 Per Cent Acetone Purity (Per Cent)		50 Per Cent Acetone Purity (Per Cent)
	100.0099		100.0133
	99.9915		99.9875
	99.9919		99.9922
	100.0090		100.0213
	100.0029		
Mean	100.0010	Mean	100.0036
Standard Dev.	0.0089	Standard Dev.	0.0163

It is unfortunate that this work did not yield results for the high-precision titration of benzoic acid in water which could be compared with those obtained in the alcohol-water and acetone-water mixtures. Thus, it has not been possible to reach one of the goals of the project, one of making such a comparison as a possible lead into the nature of the discrepancy in the existing values for the faraday. The large uncertainties in the titrations in the mixed solvents makes it appear unlikely that a successful determination of a value for the faraday can be obtained from a titration in an alcohol-water or acetone-water mixture.

VII. PURIFICATION AND TITRATION OF FUROIC ACID

A. Introduction

Furoic acid was first proposed as a primary standard chemical by Kellog and Kellog (41) in 1934. Kellog and Kellog stated that the acid could be easily purified by sublimation. They found that the purity of the sublimed furoic acid compared favorably with standard samples of benzoic acid and potassium hydrogen phthalate issued by the National Bureau of Standards. Between 1934 and 1977, furoic acid appears to have been littled used as a primary standard although Welcher (89, pp. 22,23) and Kolthoff and Stenger (49, Chapter 3) mention it and refer back to the work of Kellog and Kellog. In the course of my work for the degree of Master of Science (34), I did extensive work in the purification of furoic acid and performed a few preliminary titrations of the purified acid to determine the purity. Furoic acid was found to be less than 100.0000 per cent pure and the impurities at that time were thought to result from decarboxylation of the acid during sublimation.

Ostensibly, furoic acid has all of the properties of a good primary standard such as 4-aminopyridine. The acid will sublime into long, clear needles at temperatures near 100° (34). The molecular weight of the acid is high, 122.1 g.-eq.-wt. The acid is nonhygroscopic and in one test gained only 0.04 per cent moisture after exposure to the atmosphere for three months (41). The acid readily dissolves in water and the dissociation constant as an acid is 6.855×10^{-4} at 25° (54). The acid has been reported to decarboxylate at temperatures above 158°, forming furane (30).

In the present work, furoic acid was purified by sublimation and the purity of the sublimed acid was determined by coulometric titration. The overall objective was to determine the feasibility of using furoic acid in a determination of a value for the faraday. The titrations were made in water and then repeated in a solvent consisting of 30 per cent methanol and 70 per cent water, and then again in a solvent consisting of 30 per cent acetone and 70 per cent water.

B. Experimental Work

1. Purification of furoic acid

Furoic acid was purified by first dissolving the acid in hot water and adding activated charcoal to the hot solution. The hot solution was filtered to remove the charcoal and cooled to crystallize the acid. The acid was again recrystallized and then sublimed. The sublimation apparatus used was the apparatus of Koch, Hoyle and Diehl

(47). An atmosphere of nitrogen was maintained in the apparatus. During the sublimation, the temperature of the pot of the sublimation apparatus was held at 120° and that of the elbow at 110°. The material from the first sublimation was resublimed, the temperature of the pot being 110° and that of the elbow 100°. In the second sublimation, the acid was collected after the sublimation had gone on for 15 hours. The crystals collected were well-formed, large needles. This acid was stored in a vacuum desiccator over anhydrous magnesium perchlorate.

2. Apparatus

The titration apparatus used is described in Chapter II. The intermediate compartment with the unfired Vycor membrane was used. The bubble shield described in Chapter II was used to prevent the electrolyte and acid from being carried away by the bubbles of hydrogen produced at the cathode.

3. Reagents

The solution in the working-electrode compartment consisted of 100 $cm.^3$ of 1.0 M potassium chloride when furoic acid was titrated in water. When furoic acid was titrated in 30 per cent methanol or 30 per cent acetone, the solution in the working-electrode compartment consisted of 7.5 g. of potassium chloride dissolved in 75 $cm.^3$ of water to which 40 $cm.^3$ of either methanol or acetone was added. The methanol and acetone were purified before use by fractional distillation. The solution in the intermediate compartment was 2.0 M potassium chloride, pH 7.00. The solution in the counter-electrode compartment consisted of 0.1 M potassium dihydrogen phosphate saturated with potassium sulfate, the pH of this solution was 10.0.

a) Titration A. Furoic acid titrated in water

Furoic acid was titrated in the 1.0 M potassium chloride solution. With the pH of the solution in the working-electrode compartment (cathode compartment) at 2.8, nitrogen was passed over the solution for 30 minutes. A pretitration was performed by passing the 100-mA current through the titration cell until a pH of 10.0 was reached. Some 1.0 M hydrochloric acid was added to the solution in the working-electrode compartment to lower the pH to 2.8. A second pretitration was carried out until the pH of 3.6 was reached at which time the current was switched to the 5-mA range and the current was passed until a pH of 4.0 was reached. The current was turned off and the bubble shield surrounding the working electrode was lowered to completely submerge the shield in the solution as described in Chapter II, Section F. The 5-mA current was turned on for small time intervals after which the current was turned off and the pH was recorded. The addition of small time increments of current and the recording of the pH was continued past the equivalence-point until a pH of 10.0 was reached. The bubble shield was raised so that the top of the shield was about 1.5 cm. above the surface of the solution.

At this time, the sample boat containing the weighed sample of furoic acid was lowered into the solution in the working-electrode compartment and the sample was allowed to dissolve. The 100-mA current was turned on until 99.8 per cent of the sample was titrated after which the bubble trap was lowered to completely submerge the trap. The sides of the working-electrode compartment were washed with water. The titration was completed by using the 5-mA current turned on for small time intervals and recording the pH after each addition of the current until a pH of 10.0 was reached. Five coulometric titrations of the sublimed furoic acid was performed on samples weighing between 0.8 to 1.0 g. The results of the titrations are given in Table 15.

b) <u>Titration B. Furoic acid titrated in water-methanol solvent</u> Furoic acid was titrated in the 30 per cent methanol-70 per cent water mixture. The same procedure as used in Titration A above was used here. Five coulometric titrations of the sublimed furoic acid were performed on samples weighing between 0.8 and 0.9 g. The results of the titrations are given in Table 15.

c) Titration C. Furoic acid titrated in water-acetone solvent Furoic acid was titrated in the 30 per cent acetone-70 per cent water mixture. The same procedure as used in Experiment A above was used here. The results of three titrations are given below. The size of the sample was 0.6 g.

C. Results and Discussion

The results of the titrations of furoic acid were calculated as the per cent purity using 96,486.57 1972 NBS coulombs per g.-eq.-wt. (46) for the value of the faraday in equation (4) and the value of the faraday was calculated by rearranging equation (4) and assuming the purity of furoic acid was 100.0000 per cent. The density of furoic acid used in equation (2) was 1.496 g./cm.^{3} (34). The molecular weight of furoic acid was calculated using values taken from the 1961 Table of Atomic Weights (see Appendix of this dissertation for the reference), the atomic weights used being

$$C = 12.01115 \pm 0.00005$$
$$H = 1.00797 \pm 0.00001$$
$$O = 15.9994 \pm 0.0001$$

Using the empirical formula of $C_5H_4O_3$ for furoic acid, the molecular weight of furoic acid is:

$$5(12.01115) + 4(1.00797) + 3(15.9994) = 112.08583$$

The uncertainty in the molecular weight, σ, was calculated by

$$\sigma^2 = (5\sigma_C)^2 + (4\sigma_H)^2 + (3\sigma_O)^2$$

$$\sigma^2 = 1.51 \times 10^{-7}$$

$$\sigma = 0.000393 \quad (3.5 \text{ p.p.m.})$$

The results of Titration A, sublimed furoic acid in 1.0 M potassium chloride, are given in Table 15; the mean of the five titrations calculated as the per cent purity was 99.9964 per cent and the relative standard deviation was 19 p.p.m. The purity of furoic acid was slightly lower than expected; the calculation involves the faraday of which the correct value is in question. The decarboxylation of a small percentage of the acid during sublimation was suspected to be the reason and the sublimation was repeated at a lower temperature under vacuum. Only a small amount of material was collected when a vacuum sublimation apparatus was tried. The sublimation apparatus of Koch, Hoyle and Diehl (47) was also tried for the sublimation of furoic acid under a vacuum but no product was obtained; nitrogen flowing through the apparatus was required to carry the subliming acid through the apparatus.

The other method of reporting the results assumes that the purity of furoic acid is 100.0000 per cent and a value for the faraday is calculated, Table 15. The value of the faraday obtained from the mean of the five titrations was 96,483.10 1972 NBS coulombs per g.-eq.-wt. with a relative standard deviation of 19 p.p.m. An independent method of determining the purity of furoic acid such as freezing point depression is needed to verify the purity of the acid before the value of the faraday calculated from the titration of furoic acid can be used.

The results of the titration of the sublimed furoic acid in 30 per cent methanol are given in Table 15. The mean of the results of the titration agrees with that of the titrations in water, but the standard deviation was over three times greater. The standard deviation of the titration in 30 per cent methanol is in the same range as the titrations of benzoic acid in water-alcohol mixtures in Chapter VI.

The results from the coulometric titration of sublimed furoic acid in the 30 per cent acetone were 100.0156, 99.9882 and 100.0045 per cent furoic acid with a mean of 100.0028 and a range of 0.0274 per cent. The mean is thus 0.0192 per cent higher than the results in water and in 30 per cent methanol and the scatter (range 274 p.p.m.) among the individual results much greater.

Table 15. Assay of furoic acid by coulometric titration in water and in water-methanol solvents

Titration in Water			Titration in 30 Per Cent Methanol		
Weight[a] g.	Purity[b] Per Cent	Faraday[c]	Weight[a] g.	Purity[b] Per Cent	Faraday[c]
0.875926	99.9988	96,485.41	0.878059	99.9883	96,475.28
1.108229	99.9943	96,481.07	0.821305	100.0022	96,488.69
1.018105	99.9973	96,483.96	0.926804	99.9929	96,479.71
0.926442	99.9947	96,481.46	0.852816	99.9946	96,481.36
0.980731	99.9969	96,483.58	0.764986	100.0051	96,491.49
Mean	99.9964	96,483.10	Mean	99.9966	96,483.31
Standard Deviation	0.0019	1.82	Standard Deviation	0.0069	6.65

[a] Weight corrected for buoyancy of air.

[b] Per cent purity of furoic acid using 96,486.57 1972 NBS coulombs per g.-eq.-wt. for the value of the faraday.

[c] Value of the faraday assuming the purity of furoic acid to be 100.0000 per cent. In units of 1972 NBS coulombs per g.-eq.-wt.

VIII. PURIFICATION AND TITRATION OF ADIPIC ACID

A. Introduction

Hexanedioic acid, commonly known as adipic acid, is used commercially in the manufacture of nylon. Adipic acid is prepared by the oxidation of cyclohexanol with concentrated nitric acid (89) or by oxidizing cyclohexanone with potassium permanganate (27). Adipic acid was first proposed as an acidimetric standard by Van Voorst (88) in 1928 because the acid was easily purified by recrystallization. Kolthoff and Stenger (49) and Welcher (89) later in their texts recommended adipic acid as a primary standard. Taylor and Smith (84) apparently made the first real test of the material, in the course of their development of the coulometric titration procedure for high-precision work.

Adipic acid is fairly soluble in water, 1.44 g./cm.^{3} (67), presumably at room temperature. The two replaceable hydrogens on the acid are titrated simultaneously and there is only one point of inflection in the titration curve ($k_1 = 3.9 \times 10^{-5}$ and $k_2 = 5\ 6 \times 10^{-6}$) (67). The melting point of the pure acid is 152.05° (88) and the boiling point is 337.5° at 760 mm. of mercury (67). The 50th edition of the "Chemical Rubber Company Handbook of Chemistry and Physics" (10) reported that adipic acid will sublime but a further search of the literature uncovered no additional information about sublimation.

Adipic acid was purified by Van Voorst (88) by recrystallization two times from water, and was dried at 130°. The acid was titrated by dissolving the sample in hot water and titrating with alkali to the phenolphthalein end-point. Taylor and Smith (84) used material prepared by Delmo Enagonio of the National Bureau of Standards by recrystallization from the melt. The purity for this acid found by Taylor and Smith was 99.945 per cent adipic acid with a relative standard deviation of 70 p.p.m. The sample was recrystallized a second time from the melt by Taylor and Smith; the purity was better, 99.984 per cent adipic acid, relative standard deviation, 40 p.p.m.

In the present work, commercial adipic acid was purified by sublimation. This purified acid was titrated coulometrically.

B. Experimental Work

1. Purification of adipic acid

Commercial adipic acid, purchased from the Aldrich Chemical Company, was stated to have a purity of 99+ per cent. A preliminary coulometric titration of the dried sample yielded for the purity 99.843 per cent. This commercial acid was sublimed in the apparatus used by Koch, Hoyle and Diehl (47) for the sublimation of 4-aminopyridine. The temperature of the pot was 190° and of the elbow was 180°. The sublimation was performed under an atmosphere of nitrogen. The acid condensed as a very fine powder on the bottom of the collection tube and several attempts to produce large crystals failed. It was necessary to hold the flow of nitrogen down to prevent the sublimed powder from leaving the collection tube through the exit slit.

The fine powder of acid collected from the sublimation was fused under vacuum using a vacuum sublimation apparatus. The powder was slowly heated until a temperature of 160° was reached by which time the acid had melted. This temperature was held for 5 minutes and the acid was then allowed to cool to room temperature. A vacuum was applied to the apparatus during the entire fusion process. The acid was broken into small pieces and stored in a vacuum desiccator over anhydrous magnesium perchlorate.

2. Titration of adipic acid

Adipic acid was titrated coulometrically in 1.0 M potassium chloride using the apparatus described in Chapter II. Because adipic acid has two replaceable hydrogen atoms, the intermediate compartment carrying the glass frit membrane was used; this was necessary to prevent the migration of the hydrogen adipate anion through the membrane.

The flow rate of the electrolyte through the membrane was 5.2 cm.^{3}/hour. The bubble shield was attached to the cathode to prevent loss of material by entrapment in the bubbles of hydrogen. The titration procedure was the same procedure described in Chapter VII, Section B. The results of titration of 0.8-g. samples of the sublimed adipic acid are given below.

C. Results and Discussion

The purity of adipic acid was calculated using equations (2) to (9) in Chapter II. The density of adipic acid used in the calculation was 1.366 g./cm.^{3} (67). The molecular weight of adipic acid was calculated from the 1961 Table of Atomic Weights (see Appendix for reference). The atomic weights used were

$$C = 12.01115 \pm 0.00005$$

$$H = 1.00797 \pm 0.00001$$

$$O = 15.9994 \pm 0.0001$$

Using the empirical formula for adipic acid, $C_6H_{10}O_4$, the molecular weight is

$$6(12.01115) + 10(1.00797) + 4(15.9994) = 146.14420$$

The equivalent weight of adipic acid is 73.07210 and the uncertainty σ was calculated by

$$\sigma^2 = (6\sigma_C)^2 + (10\sigma_H)^2 + (4\sigma_O)^2$$

$$\sigma^2 = 2.6 \times 10^{-7}$$

$$\sigma = 0.00051 \quad (3.5 \text{ p.p.m.})$$

The purity of the adipic acid purified by sublimation obtained by the coulometric titration were 99.870, 99.911, 99.803 and 99.796 per cent adipic acid. The mean of the results is 99.845 per cent and the range is 0.115 per cent adipic acid. Thus, little improvement resulted from the sublimation. The acid is an excellent one to titrate, however; the solubility is good and the inflection-point sharp. The failure to effect a real purification at NBS by zone refining by batch, and here by sublimation, indicate that the purification may be a serious problem.

IX. SUMMARY

A survey has been made of the high-precision coulometric titrations which have been performed during the past two decades and the interconnection of such titrations to the fundamental constant, the faraday, has been discussed.

The history of recent work on the faraday has been reviewed and a tabulation of recent values for the faraday has been made. Emphasis has been placed on the continuing discrepancy between the experimental and calculated values for the faraday.

The sources of uncertainty in the experimental, electrochemical value for the faraday have been reviewed and several lines of attack proposed for reducing the uncertainty: improvements in the electrical circuits and measuring equipment used in coulometric titrations; reducing loss by electromigration during a coulometric titration; use of pure acids as primary chemicals; and use of mixtures of water and miscible organic liquids as media for coulometric titrations.

New apparatus has been assembled for high-precision coulometric titrations by which the uncertainties in the physical manipulations and measurements, with the possible exception of the measurement of mass, can be made with an uncertainty less than one part per million (1 p.p.m.).

A constant current source, based on the Kroeger-Rhinehart circuit, delivering 100 milliampere (mA) and 5 mA, and stable to a few parts in 10^7, has been designed, built and installed.

New, standard 10-ohm resistors have been obtained and calibrated (National Bureau of Standards (NBS)), and uncertainties in the values being a few parts in 10^8. The electrical circuit has been modified so that a constant current passes through the resistors at all times, passing through a dummy load when a titration is not in progress; thus, the temperature of these resistors has been maintained constant at a temperature a few hundreds of a degree above the oil bath in which they are immersed.

A bank of standard, Weston saturated cells in a constant temperature box has been obtained. These cells have been calibrated at NBS, the uncertainties in the respective potentials being only a few parts in 10^7. The working cells, standard unsaturated Weston cells, have been calibrated against the new bank of standard cells.

The 100-mA current has been measured by measuring the potential drop over a standard, 10-ohm resistor two ways: (a) directly with a Leeds & Northrup Company Type K potentiometer, and (b) by opposing the potential drop to a standard cell and measuring the difference in potential with a Honeywell Microvolt Potentiometer. By the second procedure, the K-5 potentiometer had been eliminated and uncertainties from the calibration of it obviated.

A new, electronic, digital readout timing device, reliable to a few parts in 10^8, has been obtained and the calibration of it checked against the NBS time signals from Station WWV.

The Hach pH meter has been modified for digital readout, greated reproducibility on shifting scales, and continuous recording.

A three-compartment titration cell, based on earlier cells but with certain improvements, has been made. In the new cell, washing of the upper walls toward the close of a titration is easier and more thorough. A bubble trap has been perfected which eliminates loss of electrolyte by entrapment in the gases released at the working electrode.

The titration cell, the various electrical measuring devices, and the auxiliary equipment have been assembled in a constant temperature room. Considerable attention has been paid to grounding, shielding, elimination of ground loops, and otherwise reducing the pick-up of electromagnetic radiation. Noise has been reduced to less than 1 μV.

A survey has been made of the literature of the various methods of handling the titration data in the determination of the equivalence-point. The determination of the equivalence-point has been identified as one of the largest sources of errors in high-precision coulometric titrations.

The basic equations describing the coulometric titration of a strong acid has been derived. The second derivation of the equation describing the coulometric titration of a strong acid has been determined and set equal to zero. The inflection-point of the titration curve has been found to coincide with the equivalence-point.

Two strong acids, perchloric acid and hydrochloric acid have been titrated coulometrically in various concentrations of sodium perchlorate and potassium chloride supporting electrolyte. Perchloric acid has been titrated volumetrically in various concentrations of sodium perchlorate.

The titration data from the titrations of the strong acids have been analyzed by a graphical method using the theoretical equation for the titration of strong acids. The plot of the data using the graphical method has been found to be somewhat dependent on the concentration of the supporting electrolyte. An attempt has been made to correct the plot of the data for the concentration of the supporting electrolyte. The graphical method and the Yan method of determining the end-point in the titration of perchloric acid and of hydrochloric acid have been compared.

The failure of the Koch, Poe and Diehl method of determining the inflection-point of the titration of perchloric acid has been determined. The advantage of the Yan method over the method of Koch, Poe and Diehl with respect to the sharpness and symmetry of titration curve has been determined.

The results of the coulometric titration of potassium hydrogen phthalate at the cathode have been found to depend on the rate of flow of the electrolyte from the intermediate compartment to the compartment containing the sample. The low results in the titration of potassium hydrogen phthalate has been speculated to be caused by electromigration of the undissociated hydrogen phthalate anion into the intermediate compartment.

A review has been made on the role of the design of the titration cell with particular attention to the loss of the sample being titrated due to electromigration.

The theory of ionic migration during electrolysis has been given with emphasis on the effect of the size of the current and the concentration of the ions in solution. The high mobilities of hydrogen ions and hydroxide ions have been found to increase the probability that these ions will migrate during coulometric titration.

Hydrogen ions have been found to migrate from the compartment with the anode, across the membrane and into the intermediate compartment during coulometric titrations when: (a) the pH of the solution in the working-electrode was acidic, pH 2.8; and (b) the 100-mA current was passing through the titration cell with the working electrode as the anode.

Hydroxide ions have been found to migrate across the membrane and into the intermediate compartment when: (a) the pH of the solution in the working-electrode compartment was alkaline, pH 11.0; and (b) the 100-mA current was passing through the titration cell with the working electrode as the cathode.

No migration of the hydrogen phthalate anion into the intermediate compartment has been detected during titrations of potassium hydrogen phthalate at the cathode when using the intermediate compartment carrying the fritted-glass membrane with potassium chloride was the supporting electrolyte. However, migration of the hydrogen phthalate anion into the intermediate compartment has been observed during the titration of potassium hydrogen phthalate at the cathode when the intermediate compartment carrying the unfired Vycor membrane was used. Migration of hydrogen phthalate anions have also been observed in sodium perchlorate electrolyte when both types of membrane was used.

The migration of hydroxide ions across the fritted-glass membrane has been found to be affected by: (a) the flow rate of the supporting electrolyte solution across the membrane; (b) the size of the current; (c) the pH of the solution in the working-electrode compartment (cathode compartment in this case); and (d) the concentration of the potassium chloride supporting electrolyte. Conditions have been found where hydroxide ions will not cross the fritted-glass membrane.

The intermediate compartment carrying the fritted-glass membrane has been chosen in the titrations involving potassium hydrogen phthalate because the high flow of supporting electrolyte through the membrane prevents the loss of hydrogen phthalate anions by migration. The intermediate compartment carrying the unfired Vycor membrane has been found to work satisfactorily in titrations which do not involve samples of undissociated acids which are already in the ionic form such as potassium hydrogen phthalate.

A survey has been conducted of the acids which could possibly be used as primary chemicals for a determination of the value of the faraday by a high-precision coulometric titration. Three acids have been selected for a definitive review of the literature of the physical and chemical characteristics, and for experimental study: potassium hydrogen phthalate, benzoic acid, and furoic acid. Potassium hydrogen phthalate was selected principally as a check on the functioning of the titration apparatus and cell developed for the present work, and because it has been widely used and extensively studied as a primary standard acid; however, it was known in advance that it would not be suitable for the faraday work because it can be neither fused nor sublimed and thus provides no way of insuring the absence of trapped solvent of crystallization. Benzoic acid was selected because it has occupied the number one position among primary standard chemicals as attested by extensive literature covering all phases of purification, proof of purity, and high-precision assay, and even application as a primary chemical for the evaluation of the faraday; it was known in advance that difficulty would probably arise in using it in the present work owing to the low solubility. Furoic acid, for which the literature is scanty, was selected because it appeared to have all the properties desired: ease of purification and sublimation, good solubility in water, satisfactory strength as an acid. Some belated attention, unfortunately begun too late in the work, has been given also to adipic acid, an acid which may ultimately become the acid of choice for the faraday work.

A survey has been made of the uses of potassium hydrogen phthalate as a primary standard acid. The history of the high-precision analyses which have been made of the National Bureau of Standards material, SRM 84d, together with a critique of the methods of analysis, the fundamental constants used in the calculations, and the results reported, has been offered.

The results which have been reported earlier on analyses made of NBS SRM 84d Potassium Hydrogen Phthalate have been recalculated taking into account changes in the value of the faraday, the shift of the basis of the atomic weight table to carbon-12, and a molecular weight computed from more select values for the atomic weights of carbon, hydrogen and oxygen and a recent value for the atomic weight of potassium.

Potassium hydrogen phthalate has been titrated coulometrically with the new titration equipment developed for the present work and using sodium perchlorate as the supporting catholyte. Very unsatisfactory results were obtained and the difficulties have been traced to the precipitation of potassium perchlorate during the titration and to loss of potassium hydrogen phthalate by electromigration of the hydrogen phthalate anion through the unfired Vycor membrane used to isolate the catholyte. Satisfactory results have been obtained by reducing the concentration of sodium perchlorate in the catholyte and by using potassium chloride as the supporting catholyte, and by replacing the membrane with a more porous one of fritted glass.

NBS SRM 84d Potassium Hydrogen Phthalate has been titrated coulometrically. The results obtained, mean 99.9930 per cent potassium hydrogen phthalate, relative standard deviation of the individual result (6 titrations) 19 p.p.m., agrees with earlier values as recalculated. With respect to precision, these titrations are among the very best of all coulometric titrations made to date.

The impurity present in NBS SRM 84d is undoubtedly mostly water and proof of this has been offered in the form of photomicrographs which show cavities in the crystals, some with meniscuses. Because potassium hydrogen phthalate can be neither fused nor sublimed to eliminate this water, this primary standard, far and away the most widely used of all primary standard acids, cannot be used as a primary chemical for the evaluation of the faraday.

A detailed review has been made of the several high-precision analyses which have been made in the past of benzoic acid, the principal of all primary standard chemicals and the primary chemical in one evaluation of the faraday. The methods of purifying, of establishing the total impurity present in the final material, of effecting the analysis (both volumetric and coulometric), and a detailed treatment of the respective results, as offered and as they have been affected during the past two decades by changes in the fundamental standards, have been present.

A lot of benzoic acid has been purified by sublimation.

National Bureau of Standards SRM 350 Benzoic Acid has been titrated coulometrically using the high-precision equipment described above and employing 1 M potassium chloride in water as the supporting electrolyte. Very poor results were obtained owing to the low solubility and the slow rate of dissolution of benzoic acid. Although benzoic acid has been titrated coulometrically successfully earlier, it has been concluded that the titration cannot be made in a water solution with the particular titration cell developed for the present work.

SRM 350 Benzoic Acid has been titrated successfully, however, in a mixture of 30 per cent methanol-70 per cent water. A value for the purity has been obtained, 99.9901 per cent benzoic acid (relative standard deviation of the individual result (6 titrations) 54 p.p.m.), which agrees with the NBS certificate value, 99.98 per cent benzoic acid, and very well with an internal NBS value of 99.9957 per cent for a lot of benzoic acid prepared by zone refining by batch, of which none remains and of which SRM 350 may or may not have been a part.

Values for the purity of the benzoic acid purified by sublimation have been obtained by titration in 30 per cent methanol (100.0041 per cent benzoic acid, relative standard deviation (5 titrations) 56 p.p.m.) and in 30 per cent 2-propanol (100.0019 per cent, relative standard deviation (5 analyses) 99 p.p.m.).

To circumvent the difficulties of handling the large bulk of the sublimed crystals of benzoic acid, benzoic acid has been fused and the frozen material analyzed. Dissolution of the fused benzoic acid in alcohol-water mixtures has been found so slow as to make titration impracticable but titrations have been effected successfully in 30 per cent acetone (100.0010 per cent benzoic acid, relative standard deviation (5 titrations) 89 p.p.m.) and in 50 per cent acetone (100.0036 per cent benzoic acid, relative standard deviation (4 analyses) 163 p.p.m.).

Although the characteristics of benzoic acid made it impossible to obtain high-precision values for titration in water for comparison with titrations in water-alcohol mixtures, the large standard deviations in the results of the titrations in mixed liquids has made it appear unlikely that a high-precision determination of the value for the faraday can be effected in a miscible liquid-water solvent. The agreement which has been found between the averages of the four sets of titrations in miscible-liquid-water mixtures (range 100.0010 to 100.0041 per cent benzoic acid) is remarkable and attests to the high merit of the coulometric titration method.

A lot of furoic acid has been prepared and purified. The final stage of the purification has been by sublimation in an atmosphere of nitrogen to insure the absence of trapped solvent of crystallization.

High-precision coulometric titrations of the sublimed furoic acid have been made in water in a 30 per cent methanol-70 per cent water mixture. The averages of the two sets of results agreed within two parts per million but the relative standard deviation of the individual result, σ, in the titrations in 30 per cent methanol is some 2.5 times greater than that for the titrations in water:

	Purity Per Cent	σ p.p.m.	Number of Titrations
Water	99.9964	19	5
30 per cent methanol	99.9966	67	5

The precision among the titrations made in water is about the best ever obtained by the coulometric titration method but the low purity found has proved disconcerting.

It has been concluded that this lot of furoic acid cannot be used for a determination of a value for the faraday. It has been concluded further, as was concluded above from the results on sublimed benzoic acid, that the large scatter among results obtained in 30 per cent methanol makes it unlikely that a value for the faraday can be obtained from a coulometric titration in a mixture of a miscible liquid with water.

A lot of adipic acid has been purified by sublimation and the sublimed material has been fused under vacuum. This lot of fused adipic acid has been analyzed by coulometric titration in water. The purity of the acid was disappointingly low, 99.845 per cent adipic acid, range 0.115 per cent (4 titrations). Little improvement in the purity of the acid has been made by the sublimation. The purification of adipic acid has been a problem.

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XII. APPENDIX: ATOMIC WEIGHTS OF THE ELEMENTS

A. Location of Successive Reports by the Commission on Atomic Weights of the International Union of Pure and Applied Chemistry

Year	Publication	Editor
1951	J. Am. Chem. Soc., 74, 2447 (1952)	E. Wichers
1955	J. Am. Chem. Soc., 78, 3235 (1956)	E. Wichers
1957	J. Am. Chem. Soc., 80, 4121 (1958)	E. Wichers
1961	J. Am. Chem. Soc., 84, 4175 (1962)	A. E. Cameron and E. Wishers
1963	Anales Real Soc. Espan. Fis. Quim. Ser. B, 60, 3 (1964)	J. Gueron
1967	Pure and Appl. Chem., 18, 571 (1969)	E. Wichers
1969	Pure and Appl. Chem., 21, 95 (1970)	H. S. Peiser
1971	Pure and Appl. Chem., 30, 639 (1972)	H. S. Peiser
1973	Pure and Appl. Chem., 37, 591 (1974)	H. S. Peiser
1975	Pure and Appl. Chem., 47, 75 (1976)	H. S. Peiser
1977	Pure and Appl. Chem., 51, 405 (1979)	H. S. Peiser