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ELECTROCHEMICAL ANALYSIS: STUDIES OF ACIDS, BASES, AND SALTS BY EMF, CONDUCTANCE, OPTICAL, AND KINETIC METHODS JULY 1965 TO JUNE 1966

Edited by Roger G. Bates

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

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Edited by Roger G. Bates
Electrochemical Analysis Section
Analytical Chemistry Division
Institute for Materials Research

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FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964, reorganization. It consists at present of nine sections and about 100 technical personnel encompassing some 45 different analytical competences from activation analysis and atomic absorption to vacuum fusion and X-ray spectroscopy. These competences, and in turn the sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is highly important. In addition, however, it has been our experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information. At the National Bureau of Standards such publications fit logically into the category of a Technical Note. In 1966 we plan to issue these summaries for all of our sections. The following is the second annual report on progress of the Electrochemical Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

This is the second in a series of annual progress reports of the Electrochemical Analysis Section of the Analytical Chemistry Division. The report covers the fiscal year 1966, which began on July 1, 1965, and ended on June 30, 1966.

Many of the processes and reactions of analytical interest take place in solutions, and a large fraction of these involve ionized solutes. If the research programs of the Electrochemical Analysis Section were to be placed in a single broad category, undoubtedly "Solution Electrochemistry" would be a fair choice, with primary emphasis on acid-base phenomena, solvent effects on the behavior of electrolytes, and potentiometry with reversible electrodes. Competence in polarography and coulometry exists elsewhere in the Analytical Chemistry Division; hence, these areas are not a part of the research activity of the Electrochemical Analysis Section. In line with a uniform policy of the Division, the Section's programs have both research and sample aspects. During the fiscal year just ending, about 70 percent of the total effort was devoted to research, while 20 percent was devoted to programs on Standard Reference Materials and 10 percent to Other-Agency programs.

The outstanding event of the present year was the long-awaited move to the excellent new facility at Gaithersburg, Md. The move and the attendant loss of time during resettlement have inevitably left their mark on the Section's activity. More serious, however, has been a shortage of personnel. Two project leaders, Dr. Robert Gary and Dr. Richard K. Wolford, were chosen as Science and Technology Fellows and were assigned elsewhere in the Department of Commerce for 10 months of the reporting period.

A third, Dr. Marion M. Davis, retired from the Section on December 31, 1965. On the other hand, Dr. Paul W. Schindler spent nine months in the Section as a guest worker supported by the Swiss National Foundation.

The purpose of this report is to summarize the broad program of the Electrochemical Analysis Section and to convey also the manner in which the individual projects contribute to the whole. An attempt is made to set forth in a rather complete way the entire year's activity of the Section and to reveal the ways in which this specialized group contributes to the missions of the Division and Institute of which it is a part.

In order to specify adequately the procedures, it has been necessary occasionally to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

The assistance of Mrs. Rosemary Maddock and Mrs. Marguerite Raudenbush in the preparation of this report is gratefully acknowledged.

Roger G. Bates, Chief
Electrochemical Analysis Section

Washington, D.C.
June , 1966

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ABSTRACT

This survey of the activities of the Electrochemical Analysis Section, Analytical Chemistry Division, covers the period July 1965 to June 1966. An attempt is made to summarize a year's progress on the technical projects of the Section in such a way as to stress the program and capabilities of the organizational unit as a whole. A description of facilities and equipment is presented and the directions of new programs are indicated. Brief summaries of the several lines of work now under way are given. The main areas include the study of acidity measurement in water, deuterium oxide, and methanol-water solvents, along with the development and certification of standard reference materials with which acidity scales in these media can be defined. Solvent effects and isotope effects are being studied, and equilibrium data for certain systems of analytical interest have been obtained. Progress on a conductometric method for determining traces of water is reported, and the thermodynamic properties of some salt mixtures have been measured by a vapor pressure method. Kinetic methods for trace analysis have been examined, and a new lot of potassium hydrogen phthalate (Standard Reference Material 84h) has been certified for use as an acidimetric standard. The survey concludes with lists of the members of the Section staff, publications and manuscripts produced during the year, talks given by the staff, and committee assignments.

1. FACILITIES AND EQUIPMENT

A. The Gaithersburg Laboratories

On March 23, 1966, the Electrochemical Analysis Section began the move to its assigned quarters at the Bureau's Gaithersburg site. By the end of the same month most of the equipment had been moved and the job of reconstructing apparatus and of adapting to the new surroundings had begun.

The Section was assigned space on a single corridor of the Chemistry Building, one of the seven general-purpose laboratory buildings. Twelve modules of general laboratory space and seven smaller modules (with north light) devoted to offices and limited laboratories fell to the Section. The total area provided for the Section was a little more than 3,600 square feet of which slightly less than 300 square feet were given over to the activities of the Section Office.

Four of the larger laboratory modules are temperature-controlled, nominally to ± 1 °F. In these laboratories will be carried out those measurements where precise temperature control (to ± 0.001 °C) will be required. All other offices and laboratories are controlled nominally to ± 2 °F.

The Section has more hood space at the new site than at the old. Against three hoods at the old quarters in Washington, the Section now has seven hoods, with provision for three elephant-trunk hoods in the larger general-purpose modules. The elephant-trunk hoods are expected to be suspended over oil thermostats which may be operated at high temperatures.

The equipment available for use in conductometric, spectrophotometric, isopiestic, and potentiometric measurements remains essentially the same as that described in last year's progress report [1]. The equipment for the precise measurement of emf has, however, been augmented by the addition of a Radiometer pH M4 high-impedance electrometer. Furthermore, the constant-temperature baths used on the three emf assemblies are being replaced by new ones. These are of stainless-steel construction with built-in refrigeration. Temperature control is provided by external electronic controllers of the proportional type, provided with thermistor sensors.

It is anticipated that a fourth emf assembly will be added to the inventory of the Section. The new instruments will be devoted principally to the study of the behavior of electrolytes dissolved in mixed media consisting of water and organic solvents.

(V. E. Bower)

B. Plans and Needs

The measurement of acidity has been a major activity of the Section for many years, and it is here that the Section's competence has been developed to the highest level. However, the concept of a practical acidity scale for partially aqueous and nonaqueous solvents has only recently been developed, despite the fact that techniques for acidity measurements are critically needed for many media of fixed composition. It is hoped therefore to continue and accelerate this aspect of the program. With the acquisition of new constant-temperature baths, the facilities for studies with hydrogen and deuterium electrodes are excellent. Research with the glass electrode, to which little attention has been given in the past, should be expanded, and for this purpose a precision high-impedance electrometer of the vibrating-reed or dynamic-condenser types is needed. Measurements in sea water have taken on a new significance with the recent emphasis on oceanographic research, and studies of acid-base behavior in this medium will shortly be initiated.

The establishment of a new acidity scale and the selection of reference materials needed to define it require an extensive series of emf measurements over a range of solute concentrations, solvent compositions, and temperatures. A completely automated system which would program the temperature changes, monitor the approach of the cells to equilibrium, and record all of the essential data has been designed. It was described in the annual progress report for 1964-65 [1]. As the broad program of acidity studies takes form, this type of facility will prove indispensable and should be constructed soon.

The need for accurate pH measurements at high temperatures and pressures is increasingly being felt. No standards of reference are at present available for temperatures above 95 °C. The construction of equipment for precise emf measurements of solutions under pressure in the range 100 to 200 °C should be undertaken in the Section in the near future.

The Section now has competence in thermodynamic studies of solution equilibria, in the conductance of electrolytic solutions, and in the study of the rates of homogeneous reactions in solution. There is a need to supplement these studies with direct calorimetric measurements of the enthalpies of solution reactions. Furthermore, calorimetric measurements are assuming a role of increased importance in analytical chemistry. The Division would, for example, benefit from the development of competence in enthalpimetric titrimetry. Furthermore, the new technique of microcalorimetry is revealing exciting new possibilities in rapid analysis and in the investigation of reactions in biological systems for which conventional methods of analysis are completely unsuitable. To begin work in this new area, we should acquire equipment for microcalorimetric studies in the near future.

(R. G. Bates)

2. MEASUREMENT OF ACIDITY

A. Concepts and Program

Studies performed in the Section over a period of more than two decades have led to the establishment of the NBS conventional activity scale of pH. This scale has five fixed points represented by aqueous solutions of the standard reference materials issued by the National Bureau of Standards. The development of this pH scale has been described in detail elsewhere [2].

In establishing a useful pH scale, one comes face to face with the dilemma that the experimental methods for acidity measurement do not yield quantities of exact physical definition, whereas the hydrogen ion concentration and other exactly defined quantities cannot be measured accurately in solutions of unknown composition. The emf cell with hydrogen electrode and a calomel reference electrode, or the modern counterpart of this cell, the glass electrode pH meter, develops an emf that is a function of the acidity of the solution. This hydrogen ion response depends on the activities of the substances in the solution but is not clearly related to the activity of the hydrogen ion. Indeed, the activity of a single ionic species is not uniquely defined by thermodynamics. It is still possible, however, to establish a conventional scale of hydrogen ion activity through the arbitrary choice of a numerical scale for the activity coefficient of a single species of ions.

The NBS pH scale, which is gaining favor gradually throughout the world, has its experimental base in accurate emf measurements of cells without liquid junction of the type

$$H_2(g.\ 1\ atm),\ Buffer\ soln.,\ Cl^-,\ AgCl;Ag$$

The standard emf of this cell is known accurately from 0 to 60 °C and with reduced accuracy to 95 °C; other measurements have extended as high as 270 °C. By the strict application of thermodynamics, therefore, it is possible to determine the acidity function $p(a_H\gamma_{Cl})$ in buffer-chloride solutions and, by an extrapolation procedure, in the chloride-free buffer solution, if need be. The standard values of the hydrogen ion activity (pa_H) are easily derived by the relationship

$$pa_H = p(a_H\gamma_{Cl}) + \log \gamma_{Cl} \qquad (1)$$

provided an estimate of γ_{Cl} can be made. This is accomplished through the adoption of a non-thermodynamic convention. For this purpose, representatives of the British and American groups engaged in pH standardization have agreed to accept a particular form of the Debye-Hückel equation relating γ_{Cl} to the ionic strength, I [3]:

$$-\log \gamma_{Cl} = \frac{AI^{1/2}}{1 + \rho I^{1/2}} \qquad (2)$$

where A is a constant of the Debye-Hückel theory and ρ has the value 1.5 in water at 25 °C.

It must be recognized that, in theory, there is no single scale of hydrogen ion activity. An arbitrary or conventional scale defined in this way will, however, meet all of the practical requirements. Coupled with the scale of single-ion activity coefficients fixed by the convention adopted above (eq. 2), experimental pH values determined under ideal conditions are completely consistent with ionization constants and other thermodynamic data for the acid-base systems which fix the pH. It is evidently of primary importance that the same conventional scale be adopted by everyone who measures and records pH values. For this reason, it is imperative that procedures for pH standardization be recommended by a national standardizing body such as the National Bureau of Standards or by an authoritative international standards group such as the International Standards Organization (ISO) or the International Union of Pure and Applied Chemistry (IUPAC). The NBS approach to a standard scale of pH has received the endorsement of the IUPAC and of the American Society for Testing Materials (ASTM).

There is a persistent demand on the part of science and industry for practical scales of acidity in nonaqueous solvents and in mixtures of water and organic solvents. During the past few years, some effort has been directed by the Section's staff to providing a useful experimental scale for acidity in alcohol-water media and in heavy water. The glass electrode has been found to respond satisfactorily to deuterium ions in heavy water and to hydrogen ions in aqueous methanol and aqueous ethanol, at least in solvents containing no more than 90 wt. percent of the organic component. It remained to show that the liquid-junction potential between an aqueous calomel reference electrode and a nonaqueous or partly aqueous buffer solution was not a function of the acidity of the latter. Satisfactory evidence of the constancy of the liquid junction was obtained for methanol-water mixtures containing as much as 70 wt. percent methanol [4].

These studies made it clear that the glass electrode pH meter is capable of yielding values for the <u>relative</u> hydrogen ion activity of two solutions both of which have the same solvent composition. To set up a scale, therefore, one or more reference points are needed. For practical reasons, the pH unit pa_H^* was chosen. This quantity is defined as follows:

$$pa_H^* = -\log m_H \cdot {}_s\gamma_H \qquad (3)$$

where m is molality and ${}_s\gamma_H$ is the molal activity coefficient based on the standard state in the nonaqueous or partly aqueous solution (s); in other words, ${}_s\gamma_H$ becomes equal to unity at infinite dilution in each particular solvent or solvent mixture in question. The procedures used for the establishment of standard values of pH can be easily extended to yield standard values of pH*. To do so, the convention which furnishes numerical values of ${}_s\gamma_{Cl}$ is entirely similar to that used for γ_{Cl} in aqueous solutions, namely eq. 2. Appropriate changes in the constants A and ρ are made to reflect the different dielectric constants and densities of the solvents.

Thus far the solvents selected for study have been chosen because of their practical importance and freedom from undesirable side reactions with the hydrogen electrode or the silver-silver chloride electrode which would impair the accuracy of the measurements. It is planned to extend the work to other alcohol-water mixtures and to aqueous ketones and aqueous amides in the order of the importance of these solvents in acid-base studies. Attention will then be directed to certain acidic or basic solvents such as acetic acid and ethylenediamine. The procedures will become more laborious when an attempt is made to study solvents with dielectric constants below the range 30 to 40. Under these circumstances, supplementary measurements, possibly by conductance methods, of ion-pair association constants will be necessary.

These procedures are most likely to be successful when the solvents are amphiprotic. At the present time it seems unlikely that methods based on emf measurements will succeed with aprotic (inert) media, where the dielectric constant is usually low and ionization is slight. Nevertheless, the measurement of acidity in media of this sort is of very real practical importance. At the present time it appears that a different approach to the establishment of acidity scales in aprotic media will have to be found.

(R. G. Bates)

B. pH Standards

1. Redetermination of the pH of Potassium Hydrogen Phthalate, Primary pH Standard.

a. Method. The assignment of standard values of pH to the NBS primary standard buffers consists essentially of four steps. The first of these is the determination of the acidity function $p(a_H\gamma_{Cl})$ by measurement of the emf of hydrogen-silver, silver chloride cells without liquid junction, containing the buffer solution and three or more different concentrations of soluble chloride. This function is calculated by

$$p(a_H\gamma_{Cl}) = \frac{(E - E°)\,F}{RT \ln 10} + \log m_{Cl} \qquad (4)$$

in which a is activity, γ the molal ionic activity coefficient, E the measured emf, E° standard emf of the cell, F the faraday, and m molality. These values of $p(a_H\gamma_{Cl})$ are then extrapolated to zero chloride concentration to obtain the quantity $p(a_H\gamma_{Cl})°$. The pa_H is then computed by the relationship

$$pa_H = p(a_H\gamma_{Cl})° + \log \gamma_{Cl} \qquad (5)$$

The Bates-Guggenheim convention is used to evaluate $\log \gamma_{Cl}$ (see eq. 2, section 2.A). Finally, the standard reference value pH(S) is identified with the conventional pa_H value of the buffer.

b. Procedures. Except for a few changes in technique, the usual procedures for emf measurements were followed. As is the usual practice, hydrogen electrodes coated with palladium black were used to avoid reduction of the phthalate by hydrogen in the presence of platinum black. Several different palladium solutions were used, including one prepared from palladium of exceptionally high purity. No differences in behavior were observed among electrodes prepared from the different solutions. The potassium hydrogen phthalate used was NBS Standard Reference Material 185d.

The cells were measured first at 25 °C, then from 0 to 35 °C at five-degree intervals in one series. A different set of cells was then measured at 25 °C and from 40 to 60 °C. Final checks were always made at 25 °C. All of the cells contained 0.05 m potassium acid phthalate and either 0.005, 0.010, or 0.015 m potassium chloride.

c. Results. The linear extrapolation of values of $p(a_H\gamma_{Cl})$ to obtain the quantity $p(a_H\gamma_{Cl})^\circ$ at each temperature was carried out by the method of least squares. The ionic strengths, I, were computed from table 2 of the paper of Hamer, Pinching, and Acree [5]. The values of pH(S) obtained as described were fitted by the method of least squares to an equation of the form

$$\mathrm{pH(S)} = \frac{A}{T} + B + CT + DT^2 \qquad (6)$$

with $A = 2042.45$, $B = -13.0228$, $C = 0.044210$, $D = -3.3761 \times 10^{-5}$. The standard deviation of the calculated values at the 13 temperatures is 0.0010.

The results are shown in table 1. Values of pH(S) now in use, based on the experimental data of Hamer and Acree [5,6] are given in the last column for comparison.

Table 1. Standard pH values of 0.05 m potassium hydrogen phthalate.

t °C	$p(a_H\gamma_{Cl})^\circ$	$-\log \gamma_{Cl}$	pa_H	^{a}pH(S)	^{b}pH(S)
0	4.096_0	0.084	4.012	4.012	4.003
5	4.089_9	.085	4.005	4.005	3.999
10	4.087_5	.086	4.002	4.002	3.998
15	4.087_6	.086	4.001	4.001	3.999
20	4.089_9	.087	4.003	4.003	4.002
25	4.096_3	.088	4.009	4.008	4.008
30	4.102_3	.088	4.014	4.014	4.015
35	4.109_4	.089	4.020	4.023	4.024
40	4.124_0	.090	4.034	4.033	4.035
45	4.135_6	.091	4.045	4.045	4.047
50	4.149_9	.091	4.059	4.058	4.060
55	4.165_5	.092	4.073	4.073	4.075
60	4.181_9	.093	4.089	4.089	4.091

a Calculated by eq. 6.

b Present NBS values.

(H. B. Hetzer)

2. Certification of a New Lot of Potassium Dihydrogen Phosphate

For acid-base studies, the equimolal aqueous mixture of potassium dihydrogen phosphate and disodium hydrogen phosphate provides a most useful reference solution. These two salts, packaged separately, are distributed as Standard Reference Materials by the National Bureau of Standards. A standard buffer solution prepared according to the directions on the certificate accompanying these materials provides an accurately defined reference point near the middle of the pH scale.

The chemicals which are used for these reference materials are analytical reagents of high grade, certified only for the pH value they yield when mixed and prepared according to directions. Because these salts are bought in rather large lots by the Bureau, recertification is only occasionally required. The high quality of these salts is an assurance that the pH value will change very little with change of lot. Nonetheless, because the pH standards are certified to the highest precision that present techniques and theory permit, minor variations in pH between lots occur, and a detailed restudy is required for certification of each new lot.

During the last year such a study was undertaken because a new lot of potassium dihydrogen phosphate had been acquired. The study shows that standard buffers prepared with the new lot will have a lower pH, by a few thousandths of a unit, than buffers made with the old material. The tentative results listed in table 2 show the change of pH that has been observed. The values given relate to the solution containing the two phosphates, each at molality of 0.025.

Confirmatory measurements are now under way, and the final results will be listed in the certificate issued with the new lot of potassium dihydrogen phosphate.

Table 2. Comparison of standard pH values, pH(S), for present phosphates with those for the newly certified materials.

t °C	pH(S), present materials	Tentative pH(S), new lot
0	6.984	6.982
5	6.951	6.949
10	6.923	6.922
15	6.900	6.897
20	6.881	6.876
25	6.865	6.862
30	6.853	6.849
35	6.844	6.840
40	6.838	6.834
45	6.834	6.831
50	6.833	6.831

(V. E. Bower)

3. Sodium Hydrogen Succinate, a New Standard Reference Material for pH Measurements

Sodium hydrogen succinate in aqueous solution provides useful buffer solutions with pH near 4.7. Mixed with either succinic acid or disodium succinate, it can be used to make buffers whose pH varies, according to the mixing proportions, from about 3.5 to about 6.0. The relative ease of purification of these three compounds and the pH range which they cover has led to their widespread use as reference buffers for the determination of the dissociation constants of weak acids.

For the standardization of the glass electrode in the slightly acid pH range, potassium hydrogen phthalate solutions (pH about 4) are very often used and are indeed among the most reliable standard buffers available. However, as a buffer medium in the spectrophotometric determination of dissociation constants or in spectrophotometric analysis, potassium hydrogen phthalate is of limited usefulness because it absorbs strongly in the ultraviolet region of the spectrum. Furthermore, potassium hydrogen phthalate is unstable in contact with the platinum-hydrogen electrode.

Solutions of sodium hydrogen succinate have pH values not greatly different from those of potassium hydrogen phthalate, yet they have the great advantage of stability in contact with hydrogen and finely-divided platinum. Inasmuch as succinate buffers are free of the difficulties outlined above, it was considered desirable to add this new pH standard to those which define the NBS conventional pH standard scale.

Samples of sodium hydrogen succinate were prepared and measurements begun this year. Preliminary results point to a stable well-behaved system capable of precise measurement.

The measurements of the kind required for the establishment of a pH standard are carried out on a potentiometric assembly such as that shown in figure 1. This arrangement is temporary, but the appearance of the permanent station will not differ greatly from that shown in the figure.

(V. E. Bower)

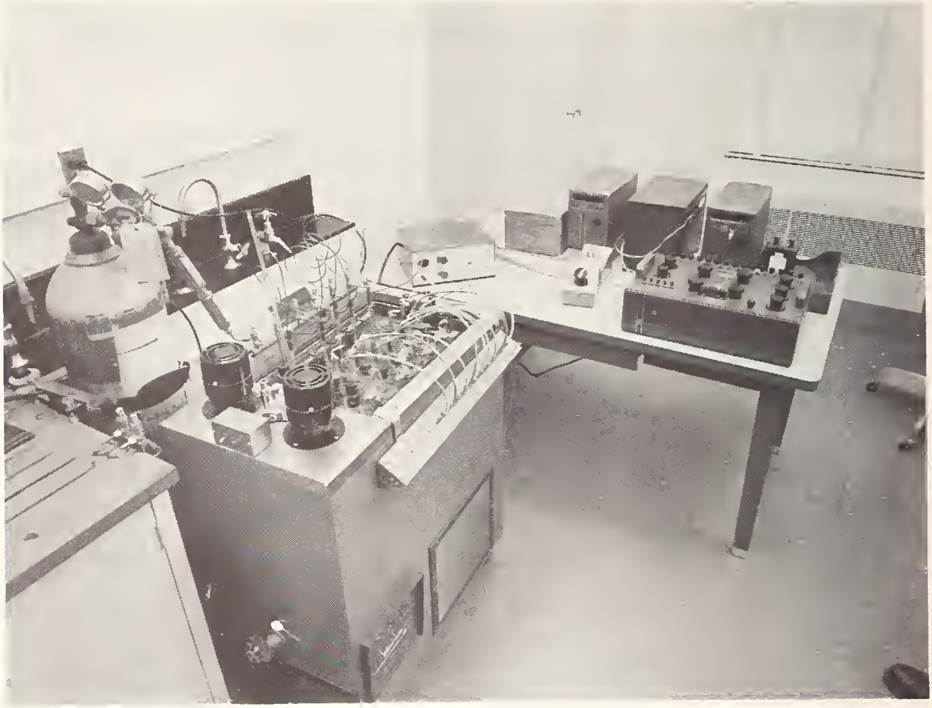


Figure 1. Equipment for the emf measurements on which pH standards in aqueous solution are based.

C. Standard pH* Values for 4-Aminopyridine Buffers in 50 Percent Methanol

As a continuation of the development and standardization of an acidity scale for amphiprotic media, pa_H^* values in 50 percent methanol were determined for a fifth buffer in this series, namely for a mixture of 4-aminopyridine and its hydrochloride. This buffer has found use in the pH range 8.5 - 9.5 in place of the borax buffer when the latter has undesirable side reactions. 4-Aminopyridine is a solid base which can easily be purified. It is moderately soluble in a variety of solvents such as water, alcohol, benzene, toluene, and chloroform. It has also been proposed as a primary acidimetric standard.

A method for determining standard values for pH measurements in aqueous buffer solutions has been developed in this laboratory, and the same general procedure was followed in 50 percent methanol medium for the five buffer systems that have been studied.

The 4-aminopyridine was the same material used for determining the dissociation constant of this base in water in this laboratory [7]. A stock solution of the 4-aminopyridine and standard hydrochloric acid was prepared in 50 percent methanol. This was diluted further with water and methanol to yield buffer mixtures with a total ionic strength varying from 0.1 to 0.01. The acidity function $p_s(a_H\gamma_{Cl})$ was measured over a temperature range from 10 to 40 °C with the aid of the cell

$$\text{Pt};H_2(\text{g., 1 atm.}),\ \text{Buffer in 50 percent methanol},\ \text{AgCl};\ \text{Ag}$$

It was calculated from the emf of this cell and the standard emf of the hydrogen-silver chloride cell in 50 percent methanol by the use of the eq. 4 of section 2.B.1. The standard emf, ${}_{s}E°$, in 50 wt. percent methanol has already been determined and the results published [8]. By using a convention for evaluation of the single-ion activity coefficient, ${}_{s}\gamma_{Cl}$, analogous to that used in water (eq. 2 of section 2.A), the pa_H^* values were obtained from the experimental acidity functions by the relationship

$$pa_H^* = p_s(a_H\gamma_{Cl}) + \log {}_{s}(\gamma_{Cl}) \qquad (7)$$

These pa_H^* values are given in table 3, where they are identified with pH*(S), the standard reference values in the operational definition of the pH* for alcohol-water solvents. These values can be used for practical measurements of pH* in 50 percent methanol by standardizing the pH meter with a reference solution of the same solvent composition as that of the test solution. This procedure avoids to some degree the variation of the asymmetry potential of the glass electrode due to changes in solvent composition when the electrode is transferred from one solution to another of different water content.

(M. Paabo)

Table 3. Values of pH*(S) for buffer solutions composed of 4-aminopyridinium chloride (m) and 4-aminopyridine (m) in 50 percent methanol.

m	10 °C	25 °C	40 °C
0.02	9.048	8.629	8.262
0.04	9.088	8.668	8.305
0.06	9.116	8.695	8.332
0.08	9.137	8.715	8.353
0.10	9.155	8.732	8.368

D. Standards for a pD Scale in Deuterium Oxide

The procedures described in earlier sections of this report, which have led to standard reference data for a pH scale in water and a pH* scale in alcohol-water solvents, can readily be adapted to the definition of a pD scale for deuterium oxide (heavy water). The cell used for measurements of this type is

$$\mathrm{Pt;D_2(g,\ 1\ atm.),\ Buffer\ soln.\ containing\ Cl^-\ in\ D_2O,\ AgCl;\ Ag}$$

The acidity function $p(a_D\gamma_{Cl})$ in the buffer solution can be determined, inasmuch as E°, the standard emf of the cell, is known [9]. The convention for γ_{Cl}, needed to derive pa_D from $p(a_D\gamma_{Cl})$, is that proposed by Bates and Guggenheim [3] see eq. 2 of section 2.A), in which A and ρ are modified to reflect the difference between the dielectric constants and densities of ordinary water and heavy water.

It is thus possible to define a pa_D scale for solutions in deuterium oxide. For this purpose, pa_D has already been established over a range of temperatures for the equimolal mixture of potassium dideuterium phosphate (0.025 m) and disodium deuterium phosphate (0.025 m) in deuterium oxide as solvent [10].

A further pa_D standard has now been established -- the equimolal mixture of acetic acid (0.05 m) and sodium acetat (0.05 m) in deuterium oxide [11]. Measurements of the above cell with this buffer solution and a deuterium gas electrode gave values of $p(a_D\gamma_{Cl})$, and extrapolations to zero chloride concentration gave $p(a_D\gamma_{Cl})^\circ$. Using values of A and ρ in the Bates-Guggenheim convention for log γ_{Cl} appropriate to the density and dielectric constant of heavy water and to the temperature, values of pa_D were calculated. These are given in table 4. They may be regarded, along with those for the phosphate and acetate buffers, as standard values, pD(S), for an operational scale of pD in deuterium oxide.

Table 4. pa_D values of the buffer solution 0.05 m acetic acid, 0.05 m sodium acetate in heavy water.

t °C	pa_D	t °C	pa_D
5	5.265	30	5.227
10	5.254	35	5.226
15	5.243	40	5.227
20	5.236	45	5.230
25	5.230	50	5.236

(R. A. Robinson)

E. A Scale of Acid Strengths in Benzene

Benzene is the most important of the hydrocarbon solvents. Work on this project has been directed to developing methods and standard reference materials for determining relative strengths of acids and bases in benzene, as well as for determining the total acid and base content of benzene solutions. The results of these studies have considerable generality; for example, they are applicable to other hydrocarbon media as well as to halogenated hydrocarbons. Such media are often referred to as "inert" or "aprotic" (the latter term signifying that they have little or no ability to accept or donate protons); another adjective often applied to them is "differentiating".

A paper was prepared, based on unpublished experimental work by M. M. Davis and M. Paabo and bearing the title "Comparative Strengths of Aliphatic Acids and Some Other Carboxylic Acids in Benzene at 25°"; it has been accepted for publication by the Journal of Organic Chemistry. Excerpts from the abstract and discussion follow.

1. Experimental

In continuation of earlier measurements by Davis and Hetzer [12] the strengths of the following acids (HA) in benzene were determined: all of the straight-chain aliphatic acids containing from 2 to 20 carbon atoms except the 15- and 19-carbon acids; isobutyric and trimethylacetic (pivalic) acids; and *o*-benzoylbenzoic, trans-cinnamic, 2,4- and 2,5-dimethyl-2-furoic, and 1- and 2-naphthoic acids. Like most other procedures for comparing strengths of Brønsted (hydrogen) acids in aprotic solvents, the method requires the use of a standard reference base and a standard indicator acid; it differs from other methods in the choice of reference base and reference acid and also in the treatment of data.

2. Discussion

In the method developed, the comparative strengths of acids are denoted by values of equilibrium constants (K_{BHA}) for the 1:1 association of acid (symbolized by HA) and reference base (symbolized by B). The association product is believed to consist of hydrogen-bonded ion pairs. The logarithm of K_{BHA} is regarded as being the analog of the corresponding pK_a value for an aqueous solution of the acid. (In the past, a more usual practice was to express comparative acidities in aprotic solvents as ratios, taking acetic acid or benzoic acid as the basis for comparison.)

The reference base adopted, 1,2-diphenylguanidine, is stronger than the reference bases ordinarily used. For example, it associates readily with carboxylic acids, commonly giving equilibrium constants in the range 10^4 to 10^7. By comparison, the extent of other hydrogen bonding reactions under the experimental conditions used is slight and can be neglected. However, slightly more accurate association constants can be obtained by correcting for the carboxylic acid present as the dimer (double molecules), and in the process of correction, a monomer-dimer equilibrium constant for the carboxylic acid can be deduced; dimerization constants thus deduced compare favorably with results by other methods.

The reference indicator acid employed, 3',3",5',5"-tetrabromophenolphthalein ethyl ester ("bromophthalein magenta E") is well suited for determining the strengths of aliphatic and aromatic carboxylic acids in aprotic solvents, because it matches them well in strength.

The results of this investigation are in harmony with the previous results, whose validity was indicated by clear-cut linear relationships between log K_{BHA} values (B = diphenylguanidine, solvent = benzene) and aqueous pK_a values (and also acidic strengths in alcohols and partly aqueous solvents). Figure 2 shows the separate linear correlations obtained in the latest work for meta-substituted and ortho-substituted benzoic acids. _o_-Benzoylbenzoic acid is an interesting exception to the general behavior in that it conforms to the "normal" (meta-) relationship instead of to the special relationship found for the other ortho-substituted acids; this exceptional behavior of _o_-benzoylbenzoic acid has not yet been explained.

This method of determining acidities in benzene is applicable to varied chemical types of acids and is also useful for acids that are difficultly soluble, scarce in amount, or unstable toward moisture.

(M. M. Davis)

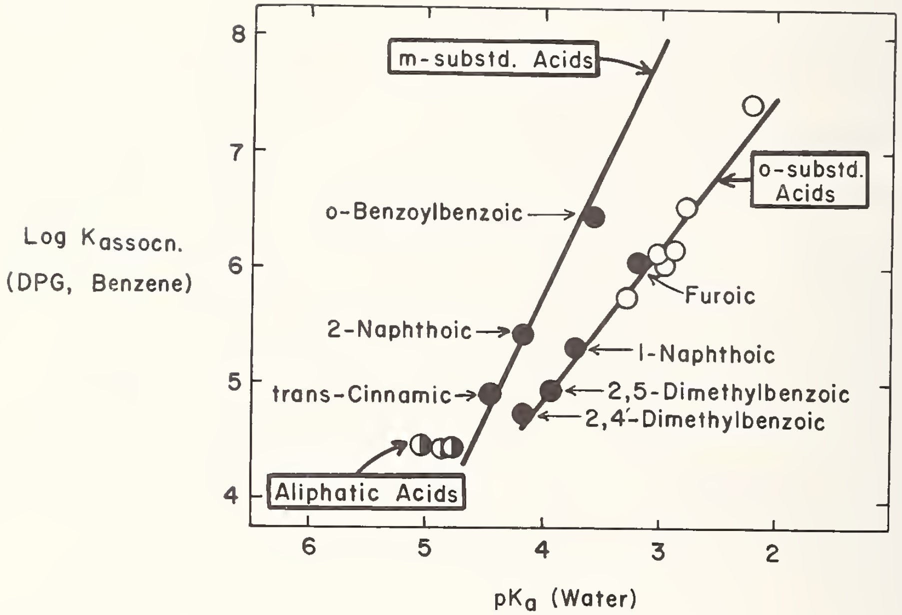


Figure 2. Relative acidic strengths in benzene and water at 25 °C. The strength in benzene is expressed as the value of log K for 1:1 association of the acid (HA) with 1,3-diphenylguanidine (DPG).

Open circles, results from previous work
Half-filled circles, values for three aliphatic acids (acetic, isobutyric, trimethylacetic), this work
Filled circles, this work

3. SOLVENT EFFECTS ON ACID-BASE PROCESSES

A. Dissociation of Positively-Charged Acids in Methanol-Water Solvents

The process by which a cationic weak acid dissociates is one of particular interest. A positively charged acid such as ammonium ion dissociates into an uncharged conjugate base and a solvated proton by a reaction that can be written in general terms as follows

$$BH^{+} + SH = SH_2^{+} + B \qquad (8)$$

where SH represents an amphiprotic solvent. From the electrostatic point of view, this reaction is a simple one, as there is no net change in the number of ions. The electrostatic contribution to the energy of dissociation should be rather small, and this type of process is therefore well suited to a study of the parameters necessary to account for the observed solvent effects on the dissociation. To do this, the electrostatic effect must be estimated in order to demonstrate whether it alone is sufficient to explain the changes in dissociation constant actually found.

For the past few years the solvent effect of methanol on the dissociation of cation acids has been a subject of interest in this laboratory. A detailed study of the dissociation of the protonated form of tris(hydroxymethyl)-aminomethane (tris, THAM) in 50 wt. percent methanol from 10 to 40 °C was recently published [13]. Further work on this acid in solvents containing 30, 70, and 90 wt. percent methanol at temperatures of 15, 25, and 35 °C has now been completed. In addition, the dissociation of ammonium ion in five methanol-water solvents at 25 °C has been studied.

The typical pattern for the solvent effect of methanol on the dissociation of a positively charged weak acid is represented by the curves at the bottom of figure 3. Methanol causes a decrease in the pK until a minimum is reached at a concentration of 60 to 80 percent methanol, after which the pK rises sharply and may exceed that in pure water. This behavior is in marked contrast to that shown by uncharged weak acids such as acetic acid and the phenols, represented by the curves at the top of the figure.

It has long been recognized that the contrasting behavior shown by the two types of curves of figure 3 can be explained qualitatively on electrostatic grounds. Thus the large increase in pK produced by adding methanol to an aqueous solution of an uncharged weak acid reflects the increased difficulty in separating the oppositely charged ions (hydrogen and the anion base) in the medium of lowered dielectric constant produced by addition of the organic constituent. The minimum in the pK curves for cationic acids cannot be explained, however, on simple electrostatic grounds alone. Recent efforts in this laboratory have been directed toward an identification of the other parameters which, together with the dielectric constant, can explain in a fairly satisfactory way the existence of a minimum and the course of the pK curve. Analyses of data for both uncharged and positively charged acids have led to the suggestion that the solvent effect on both types reflects a "basicity effect", namely, an increase in the total basicity of the solvent molecules represented by SH in eq. 8.

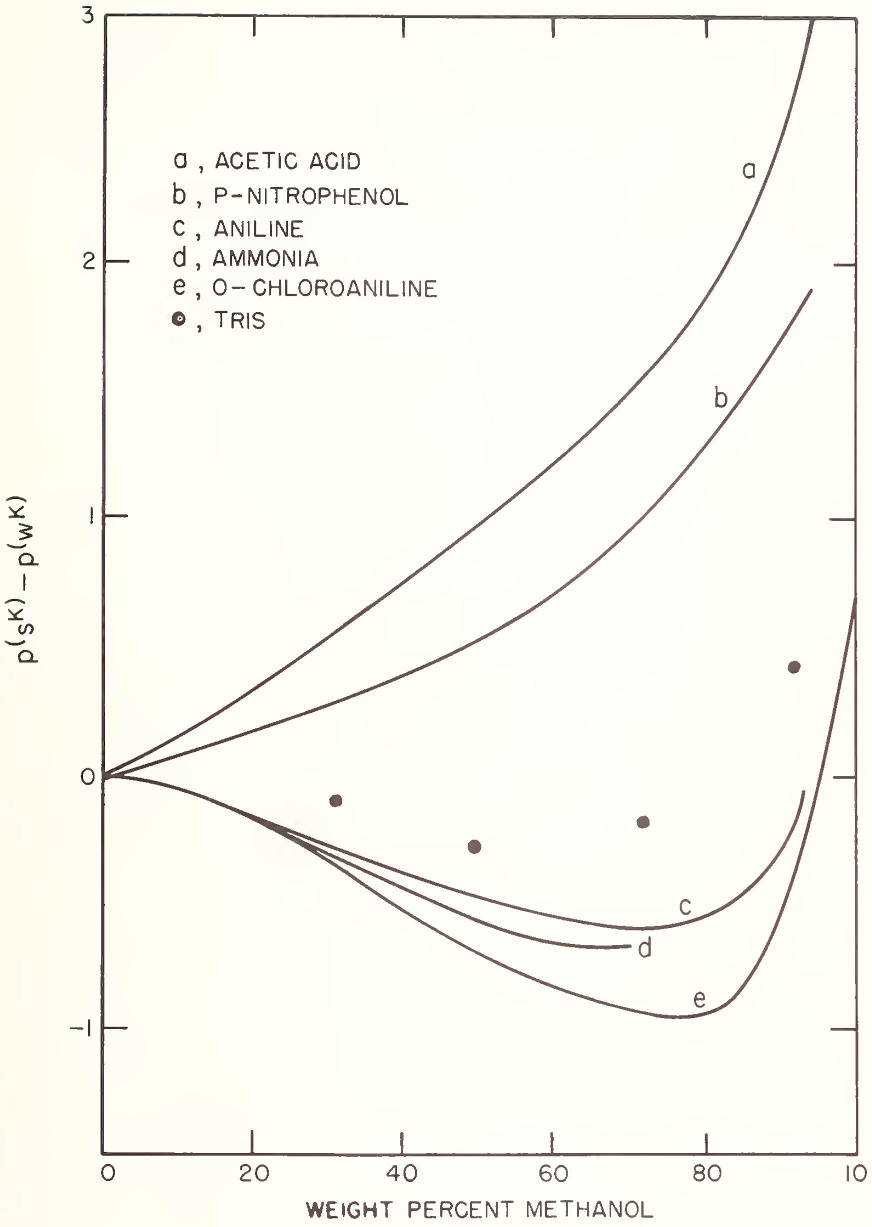


Figure 3. pK values for acids of two charge types in methanol-water solvents at 25 °C.

Reasonably concordant values for the magnitude of this basicity effect have been obtained from the analysis of data for the dissociation of weak acids of the two types. The nature of this basicity effect and the identification of the other parameters on which the solvent effect depends are still being investigated.

(R. G. Bates)

1. Ammonium Ion

Ammonium ion is the simplest and most important of the positively charged acids. Furthermore, the approximately spherical structure of the ammonium ion adds a certain amount of reliability to the calculations of the electrostatic work of charging the ion in a medium of known dielectric constant. It therefore seemed desirable to study the solvent effect of methanol on the dissociation of ammonium ion.

Inasmuch as the standard electromotive force of the hydrogen-silver chloride cell in methanol-water solvents covering a wide range of solvent compositions is now known with some accuracy, the conventional emf method was chosen. Contributing to the success of this experimental method is the fact that the solubility of silver chloride in ammonia solutions decreases as the solvent is enriched with methanol.

The cell is represented as follows:

$$\mathrm{Pt; H_2(g,\ 1\ atm),\ NH_3(m),\ NH_4Cl(m)\ in\ MeOH\text{-}H_2O,\ AgCl;\ Ag}$$

The measurements were made at 25 °C only, and the solvent compositions were 10, 20, 33.4, 50, and 70 wt. percent methanol. The results are given in table 5 as values of

Table 5. Acidic dissociation constant of ammonium ion in methanol-water solvents at 25 °C.

Wt. percent MeOH	$p({}_sK)$
0	9.245
10	9.146
20	9.044
33.4	8.893
50	8.687
60	8.591
70	8.571

Table 6. pa_H^* for buffer solutions of ammonia and ammonium chloride (each at molality m) in methanol-water solvents at 25 °C.

m	pa_H^* in --		
	20 percent MeOH	50 percent MeOH	70 percent MeOH
0.02	9.126	8.798	8.711
0.04	9.158	8.838	8.762
0.06	9.180	8.866	8.797
0.08	9.198	8.888	8.823
0.10	9.212	8.905	8.843

$p({}_{s}K)$; the subscript s signifies that the activity coefficients in the equilibrium expression are based on a standard state in the methanol-water medium, becoming unity at infinite dilution in that medium. The pa_H^* values given in table 6 were calculated as described in section 2.C. These acidity functions may be regarded as reference data useful in the study of the dissociation of other acid-base systems in methanol-water solvents. In view of the difficulty of preparing the buffer solutions, however, these values are not recommended as reference standards for pH* measurements. This work has already been published [14].

(R. G. Bates)

2. Tris(hydroxymethyl)methylammonium Ion

Tris(hydroxymethyl)aminomethane is a solid, crystalline base obtainable in a state of high purity. It is moderately soluble both in water and in methanol and is widely used as a standard reference material in acidimetry as well as for pH control. Like ammonium ion, protonated tris is presumably a roughly spherical ion whose electrostatic energy can be estimated by the Born calculation. All of these considerations have led us to choose this base for the study of the methanol solvent effect on acidic dissociation.

The conventional emf method, which has been used extensively in this laboratory, was inapplicable to a determination of the pK values at temperatures other than 25 °C, for the standard emf of the hydrogen-silver chloride cell is known only at 25 °C in several of the methanol-water solvents included in the study. It was, however, desired to include other temperatures in order to obtain information on the enthalpies and entropies of dissociation. A titration method was therefore devised, utilizing a cell without liquid junction consisting of a glass electrode and a silver-silver chloride electrode. As in earlier work [15], concentrations were adjusted so that the titration was performed in a medium of essentially unchanging ionic strength, constant chloride ion concentration, and, of course, fixed solvent composition. In essence, data for the following two cells were obtained:

1) Glass $\|$ $HClO_4(m)$, NaCl(m), AgCl; Ag

and

2) Glass $\|$ $HClO_4(m)$, Tris, NaCl(m), AgCl; Ag

where the composition of the methanol-water solvent was uniform throughout and the ionic strength was 2m.

The difference in the emf of these two cells may be expressed in terms of the pK of protonated tris (TH^+) as follows:

$$pK = \frac{E_2-E_1}{2.3026RT/F} + \log \frac{m_{TH^+}}{m \cdot m_T} + \log \frac{\gamma_{TH^+}(\gamma_{Cl})_2}{(\gamma_H)_1\gamma_T(\gamma_{Cl})_1} \qquad (9)$$

The last term of this expression is a combination of activity coefficients which, under the conditions of the experiments, should be small. Experience showed that this was indeed the case and that this term could be ignored for the low concentrations of electrolytes used. The values of pK found in 30, 70, and 90 wt. percent methanol at 25 °C are compared in table 7 with the pK in water [16,17] and in 50 percent methanol [13]. The last column gives the solvent effect, defined as $p({}_sK)-p({}_wK)$.

(P. W. Schindler and R. G. Bates)

Table 7. pK for the dissociation of protonated tris(hydroxymethyl)aminomethane in methanol-water solvents at 25 °C. The solvent effect.

Wt. percent MeOH	$p({}_sK)$	$p({}_sK)-p({}_wK)$
0	8.072	0
30	7.940	-0.132
50	7.819	-0.253
70	7.855	-0.217
90	8.462	+0.390

3. Solubility Studies of the Medium Effect

The pK values determined as described in the preceding section are in actuality $p({}_sK)$ values; ${}_sK$ is the dissociation constant expressed in activities, ${}_sa$, defined by ${}_sa = m({}_s\gamma)$, where m is molality and the activity coefficient ${}_s\gamma$ becomes unity at infinite dilution in the particular methanol-water solvent in question. Activities related to the conventional aqueous standard state are designated ${}_wa$ when it is necessary to distinguish the two types. The fundamental relationship between the two numerical scales for the activity coefficient is

$$ {}_w\gamma = {}_s\gamma \cdot {}_m\gamma \qquad (10)$$

which may be regarded as a definition of ${}_m\gamma$, the "medium effect activity coefficient" [4]. The magnitude of this medium effect is determined solely by the Gibbs energy of transfer of the species from one standard state to the other.

For the process

$$\text{Species (in } H_2O) = \text{Species (in solvent s)}$$

the Gibbs energy of transfer ΔG° is given by

$$\Delta G° = RT \ln {}_m\gamma \qquad (11)$$

A consequence of this relationship is that the solvent effect on pK is a combination of the medium effects for the ions and molecular species involved in the dissociation process:

$$p({}_sK)-p({}_wK) = \log {}_m\left(\frac{\gamma_H \ \gamma_B}{\gamma_{BH^+}}\right) \qquad (12)$$

This expression can be written in another form which involves only mean activity coefficients:

$$p({}_sK)-p({}_wK) = \log {}_m\gamma_B + 2[\log {}_m\gamma_\pm (HCl)-\log {}_m\gamma_\pm (BHCl)] \qquad (13)$$

In order to elucidate as thoroughly as possible the factors on which the solvent effect depends, we have undertaken to evaluate the separate medium effects occurring in eq. 13. For this purpose, we have studied the Gibbs energy and corresponding medium effect for the transfer of tris from water to methanol-water solvents. This was done by means of solubility measurements in the media at 15, 25, and 35 °C. Inasmuch as saturated solutions of tris in water and in a methanol-water solvent are both in equilibrium with solid crystalline base, we may write

$$m_w({}_w\gamma)_1 = m_s({}_w\gamma)_2 = m_s({}_s\gamma \cdot {}_m\gamma)_2 \qquad (14)$$

where 1 represents the saturated aqueous solution and 2 represents the saturated solution in the methanol-water solvent. From this relationship,

$$ {}_m\gamma_T = \frac{m_w}{m_s} \cdot \frac{({}_w\gamma)_1}{({}_s\gamma)_2} \approx \frac{m_w}{m_s} \qquad (15) $$

Thus the ratio of solubilities yields an approximate value for the medium effect of tris base (T); a more accurate value could be obtained by correcting for the difference in the "salt effect activity coefficients" $({}_w\gamma)_1$ and $({}_s\gamma)_2$ derived from independent measurements. The approximate values of ${}_m\gamma_T$ for tris are adequate for the present studies of the solvent effect. They are summarized in table 8.

(P. W. Schindler and R. G. Bates)

Table 8. Medium effects for tris(hydroxymethyl)aminomethane in methanol-water solvents, obtained from solubility measurements.

Wt. percent MeOH	log ${}_m\gamma_T$ (15 °C)	log ${}_m\gamma_T$ (25 °C)	log ${}_m\gamma_T$ (35 °C)
10	0.067	0.055	0.045
20	0.135	0.114	0.095
30	0.208	0.180	0.154
40	0.285	0.254	0.221
50	0.379	0.343	0.303
60	0.499	0.459	0.412
70	0.653	0.604	0.549
80	0.834	0.791	0.729
90	1.094	1.032	0.935
100	1.322	1.297	1.231

4. Parameters for the Solvent Effect

With a knowledge of the medium effect for tris base, it is possible to make some interesting comparisons between the predicted solvent effect and that actually observed. The medium effect for the transfer of hydrochloric acid can be derived readily from the standard electromotive force for the hydrogen-silver chloride cell [18,19] containing hydrochloric acid in methanol-water solvents. The medium effect for tris hydrochloride has unfortunately not been determined. Data for sodium chloride and lithium chloride are, however, available from the work of Akerlof [20]. The values for these three electrolytes are compared with those for undissociated tris and ammonia in figure 4. It is evident that the medium effects for the two alkali halides do not differ greatly and show a continuous, nearly linear, rise with the weight percentage of methanol. On the other hand, the medium effect for hydrochloric acid remains low at all water-rich solvent compositions and does not rise rapidly until the solvent composition has reached 60 percent methanol.

Figure 5 shows that data such as these can account for the minimum in the plot of pK for a cation acid as a function of the composition of the methanol-water solvent. The broken lines of the figure were calculated by eq. 13 using the data for lithium chloride as an approximation to the unknown medium effects for ammonium chloride and tris hydrochloride. The pK values actually observed are shown as solid lines. The minimum in the pK curve can thus be attributed to the fact that the free energy of transfer of alkali metal salts and ammonium salts increases much more rapidly when methanol is added to their aqueous solutions than does the free energy of hydrochloric acid at the same

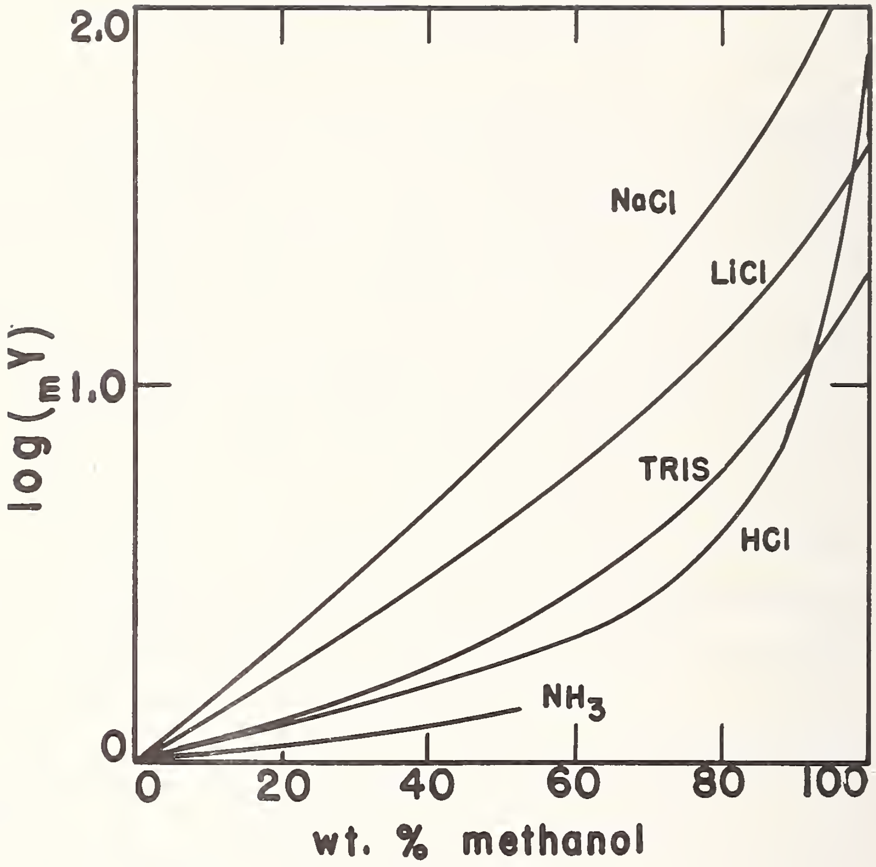


Figure 4. Medium effects (${}_m\gamma$) for ammonia, tris, hydrochloric acid, and alkali halides in methanol-water solvents at 25 °C.

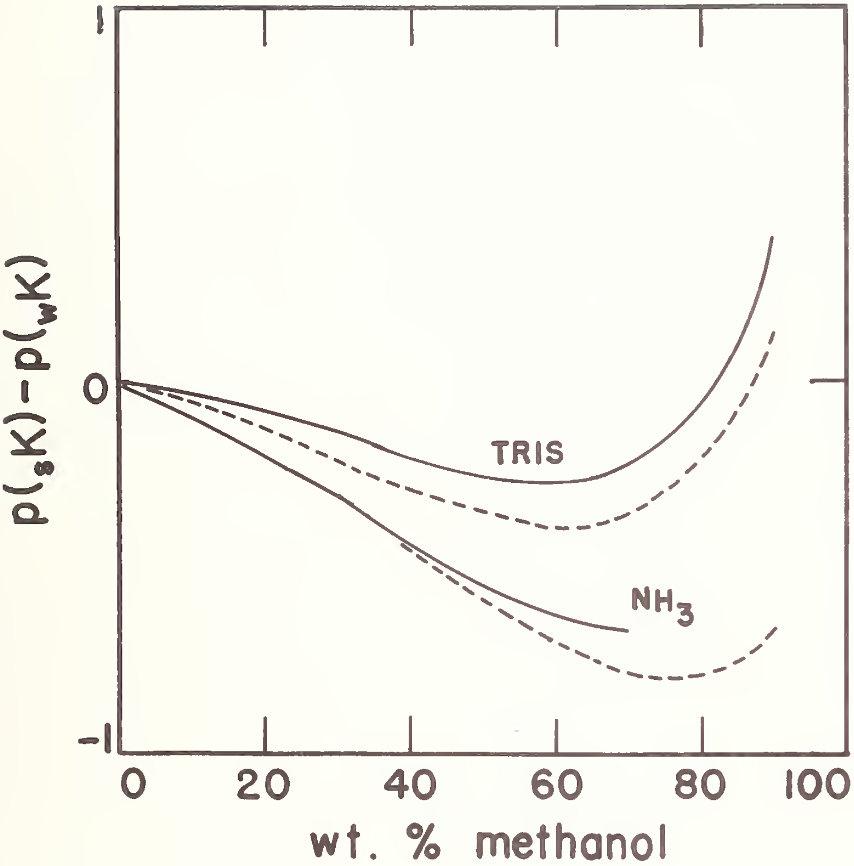


Figure 5. Observed solvent effects on the pK of protonated tris and ammonia (solid lines) compared with the solvent effect calculated by eq. 13 (broken lines).

solvent compositions. One can only speculate as to the cause of this behavior. If normal behavior is represented by the course of the curves for the alkali metal salts shown in figure 4, it must be concluded that at low methanol concentrations the escaping tendency for hydrochloric acid from the methanol-water media is unexpectedly low. This is just another way of expressing the "basicity effect" earlier postulated [21]. An increase in basicity as methanol is added could indeed be attributed to a breakdown in the structure of the water. It would appear that the proton is solvated primarily by water molecules in solvents containing less than 60 wt. percent methanol and that the rapid rise in methanol-rich solvents reflects the increased escaping tendency of protons solvated by the relatively weakly basic methanol molecules.

(R. G. Bates)

B. Isotope Effects on the Dissociation of Acetic Acid in Water and Deuterium Oxide

The dissociation of "ordinary" acetic acid, CH_3COOH, in "ordinary" water, H_2O:

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^- \tag{16}$$

is a process about which much quantitative information has been available for many years. Thus, in 1932 MacInnes and Shedlovsky [22] measured the dissociation constant,

$$K_1 = \frac{m_{H^+}\, m_{CH_3COO^-}}{m_{CH_3COOH}} \; \frac{\gamma_{H^+}\, \gamma_{CH_3COOH}}{\gamma_{CH_3COOH}} \tag{17}$$

at 25 °C by a conductance method. At the same time, Harned and Ehlers [23], using an emf method, determined the dissociation constant from 0 to 60 °C. The concordance between the two results at 25 °C is excellent, and for this temperature we can write $pK_1 = 4.756$ with confidence.

Acetic acid, however, can be dissolved in heavy water (deuterium oxide, D_2O), and there is good reason to believe that there is exchange between deuterium and the hydrogen of the carboxyl group in acetic acid but no exchange with the hydrogen atoms in the methyl radical. Thus "ordinary" acetic acid in deuterium oxide forms the molecule CH_3COOD, and this in turn dissociates according to the process

$$CH_3COOD \rightleftharpoons D^+ + CH_3COO^- \tag{18}$$

with a dissociation constant

$$K_2 = \frac{m_{D^+} \, m_{CH_3COO^-}}{m_{CH_3COOD}} \; \frac{\gamma_{D^+} \, \gamma_{CH_3COO^-}}{\gamma_{CH_3COOD}} \qquad (19)$$

The thermodynamics of this dissociation process has been studied recently in the Section and a report has been published [11]. In addition to measurements of the pK_2 value between 5 and 50 °C, pD ($\equiv -\log a_{D^+}$) values were evaluated for buffer solutions containing 0.05 m CH_3COOD and 0.05 m CH_3COONa in deuterium oxide, thus continuing the work towards establishment of a pD scale in deuterium oxide which had commenced with measurements of the pD values of solutions of 0.025 m KD_2PO_4 and 0.025 m Na_2DPO_4 in deuterium oxide (see section 2.D).

Besides the "ordinary" form of acetic acid, CH_3COOH, a deuterated form is available. This acid, which has the formula CD_3COOD, is sometimes called acetic acid-d_4. When dissolved in ordinary water, the following exchange would be expected:

$$CD_3COOD + H_2O \rightleftharpoons CD_3COOH + HDO \qquad (20)$$

with the production of acetic acid-d_3 which in turn dissociates,

$$CD_3COOH \rightleftharpoons H^+ + CD_3COO^- \qquad (21)$$

Corresponding to this equilibrium, there is a dissociation constant K_3:

$$K_3 = \frac{m_{H^+} \, m_{CD_3COO^-}}{m_{CD_3COOH}} \; \frac{\gamma_{H^+} \, \gamma_{CD_3COO^-}}{\gamma_{CD_3COOH}} \qquad (22)$$

The thermodynamics of this dissociation process has been studied during the current year [24], and details of the results are given below.

In addition, there is a fourth dissociation process which completes the series. If acetic acid-d_4 is dissolved in deuterium oxide, the dissociation process is

$$CD_3COOD \rightleftharpoons D^+ + CD_3COO^- \qquad (23)$$

with

$$K_4 = \frac{m_{D^+} \, m_{CD_3COO^-}}{m_{CD_3COOD}} \; \frac{\gamma_{D^+} \, \gamma_{CD_3COO^-}}{\gamma_{CD_3COOD}} \qquad (24)$$

This dissociation reaction has also been the subject of study during the current year. The results are now in the process of publication.

Measurements were made of the emf of the cell

$$Pt;H_2(g,\ 1\ atm),\ CD_3COOH(m_1),\ CD_3COONa(m_2),\ NaCl(m_3),\ AgCl;Ag$$

The pK_3 value of acetic acid-d_3 in ordinary water is given in terms of the emf (E) of this cell by the expression

$$pK'_3 \equiv pK_3 - \log (\gamma_{Cl}-\gamma_{HAc})/\gamma_{Ac^-}$$

$$= (E-E°)/k + \log m_3 + \log (m_1-m_{H^+})/(m_2+m_{H^+}) \qquad (25)$$

where $Ac^- = CD_3COO^-$, $HAc = CD_3COOD$, and E°, the standard emf of the cell in ordinary water as solvent, has already been measured [25]. As usual, k represents (RT ln 10)/F.

It would be anticipated that the term log $(\gamma_{Cl^-}\gamma_{HAc})/\gamma_{Ac^-}$ would be small, and this proved to be true. Almost horizontal, straight-line plots of pK_3' against the ionic strength gave extrapolated values of pK_3 at 10 temperatures from 5 to 50 °C.

In order to obtain the pK_4 value of acetic acid-d_4 in deuterium oxide, the cell

$$Pt; D_2(g, 1 \text{ atm}), CD_3COOD(m_1), CD_3COONa(m_2), NaCl(m_3), AgCl; Ag$$

was employed, using deuterium oxide as solvent. The standard emf, E°, of this cell in deuterium oxide has already been measured [9]. The pK_4 value of acetic acid-d_4 is given by the expression:

$$pK_4' \equiv pK_4 - \log (\gamma_{Cl^-}\gamma_{DAc})/\gamma_{Ac^-}$$

$$= (E-E°)/k + \log m_3 + \log (m_1-m_{D^+})/(m_2+m_{D^+}) \quad (26)$$

where $Ac^- = CD_3COO^-$ and $DAc = CD_3COOD$. The intercept pK_4 is obtained by extrapolation of a plot of pK_4' against ionic strength.

A knowledge of the variation of the dissociation constant of an acid with temperature leads to values of the changes in enthalpy, $\Delta H°$, entropy, $\Delta S°$, and heat capacity, $\Delta C_p°$, for the dissociation process. These values at 25 °C for the four dissociation processes now under consideration are collected in table 9. It will be observed that the entropy changes for CH_3COOH and CD_3COOH in ordinary water are almost the same.

This means that the exchange reaction:

$$CD_3COOH + CH_3COO^- \rightleftharpoons CH_3COOH + CD_3COO^- \quad (27)$$

proceeds with virtually no change in entropy. This is also true for the exchange reaction

$$CD_3COOD + CH_3COO^- \rightleftharpoons CH_3COOD + CD_3COO^- \qquad (28)$$

in deuterium oxide. However, this simple relationship does not hold for the enthalpy changes. Here small, but perhaps significant, differences are found.

Table 9. Thermodynamic quantities for the dissociation of acetic acid and deuterioacetic acid in water and deuterium oxide at 25 °C.

(1 cal = 4.1840 J)

pK	$\Delta H°$ cal mol^{-1}	$\Delta S°$ cal mol^{-1} deg^{-1}	$\Delta C_p°$ cal mol^{-1} deg^{-1}
		CH_3COOH in H_2O	
4.756	-98	-22.1	-37
		CD_3COOH in H_2O	
4.772	-69	-22.1	-34
		CH_3COOD in D_2O	
5.313	+275	-23.4	-39
		CD_3COOD in D_2O	
5.325	+279	-23.4	-37

Calculations can also be made of the temperature at which the dissociation constant will have its maximum value and what this maximum value will be. In all four instances, this temperature is found to lie close to room temperature, being about 8 °C higher for deuterium oxide than for ordinary water as solvent.

It is a common practice to list dissociation constants on the molality scale of concentration, moles per kg of solvent. For ordinary water, this is equivalent to moles per 55.51 moles of solvent, but in heavy water it corresponds to moles per 49.94 moles of solvent. A more valid comparison of dissociation constants is obtained by expressing them in terms of the mole fraction scale. When this is done, it is seen that the pK values of CH_3COOH in ordinary water and CH_3COOD in deuterium oxide differ by about 0.5 unit. This is about the difference found between CD_3COOH in ordinary water and CD_3COOD in deuterium oxide. This relationship can be expressed in another way: the pK values of CH_3COOH and CD_3COOH in ordinary water differ by only about 0.01, and this is true also for the pK values of CH_3COOD and CD_3COOD in deuterium oxide. Thus, the main isotope effect can be attributed to the change of solvent. Deuteration of the methyl radical of acetic acid itself produces a very small isotope effect.

(R. A. Robinson)

C. Acid-Base Behavior in Organic Solvents with Low Dielectric Constants

A definitive monograph with the above title is being prepared for publication by the Analytical Chemistry Division; it is also to be published by Academic Press (possibly in a condensed version) as a chapter in one of a series of volumes on "The Chemistry of Non-Aqueous Solvents", edited by Dr. J. J. Lagowski of the University of Texas. The main topics to be covered (in the sequence indicated) are as follows: I. Introduction. II. Acid-Base Concepts. III. Classification of Organic Solvents. IV. The Role of Hydrogen Bonding in Aprotic Media. V. Quantitative Aspects of Acid-Base Behavior in Aprotic Solvents.

The longest section will be Section IV, which will deal with the following sub-topics: A. Self-association of nitrogen-containing bases. B. Self-association of acids (for example, phenols, carboxylic acids, nitric acid, phosphorus-containing organic acids). C. Hydrogen-bonded ion pairs. D. Conjugate ions. E. Solute-solvent interactions. F. Theoretical aspects of hydrogen bonding. The discussion in the various sub-sections is based on varied kinds of experimental evidence, principally from measurements of conductance, dielectric polarization, colligative properties, and absorption spectroscopy (electronic, infrared, NMR).

As of May 1966, the literature research for the monograph was at least 95 percent complete. The writing of Section IV was about two-thirds completed. There were about 140 typed pages of manuscript, 18 figures, and 41 tables.

(M. M. Davis)

D. Spectrophotometric Studies of the Dissociation of Phenols

The Section has devoted considerable attention to acid-base effects in 50 wt. percent water-methanol as solvent. The acids studied have been mainly of the A^+B° charge type such as ammonium ion, the protonated form of tris(hydroxymethyl)aminomethane, and 4-aminopyridinium ion. The pK values of acids of this type are lower in 50 percent methanol than they are in water, and this difference is a measure of the "solvent effect," which is, in turn, a combination of the medium effects for the individual species involved in the dissociation process (see section 3.A.3).

It is known that the solvent effect is of the opposite sign for acids of the charge type $A^\circ B^-$. This is true for aliphatic acids such as acetic acid and for aromatic acids like benzoic acid. Here the pK value is higher in 50 percent methanol than it is in water.

Measurements have now been made with a number of acids of the $A^\circ B^-$ type derived from phenol. A spectrophotometric method was used, together with buffer solutions whose pa_H^* values in 50 percent methanol have been determined in earlier emf studies. In all cases, the pK value in 50 percent methanol was found to be greater than in water. The differences observed between the pK value in 50 percent methanol and in water at 25 °C are listed in table 10. The solvent effect is seen to amount to about 0.6 in pK, but it is clear that there is a considerable dependence on the nature of the substituent groups in the phenol. The work is now being prepared for publication.

(B. J. Steel and R. A. Robinson)

Table 10. Increase in pK for six substituted phenols resulting from a change of solvent composition from pure water (w) to 50 wt. percent methanol at 25 °C.

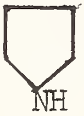
Acid	$\Delta pK \equiv p({}_sK) - p({}_wK)$
o-Nitrophenol	0.687
m-Nitrophenol	0.615
p-Nitrophenol	0.536
4-Methyl-2-nitrophenol	0.687
2,6-Dichlorophenol	0.889
Pentachlorophenol	0.458

4. EQUILIBRIUM STUDIES OF SYSTEMS OF ANALYTICAL INTEREST

A. Thermodynamics of the Dissociation of Morpholinium Ion in Water

The aqueous dissociation constants of a number of nitrogenous bases over a temperature range have been measured previously in this laboratory by the emf method. Earlier studies of the three ethanolamines [see reference 26] and of the series of aminoalcohols derived from t-butylamine [27] made possible comparisons of the basicities and other thermodynamic properties of these structurally related compounds. It was therefore of interest to compare the heterocyclic amine, morpholine, with the cyclic aliphatic amines piperidine [28] and pyrrolidine [29] studied earlier. The three compounds have the following structures:

Piperidine



Pyrrolidine

Morpholine

Morpholine is of industrial importance in organic chemical reactions, as a solvent, and as a corrosion inhibitor in steam boilers.

The dissociation constant was determined from 0 to 50 °C by the measurement of the emf of hydrogen-silver, silver chloride cells without liquid junction containing buffer solutions composed of morpholine and its hydrochloride. Details of the work are contained in a report now in the process of publication.

Electromotive force measurements of cells of the type

$$Pt;H_2(g,\ 1\ atm),\ \underbrace{(CH_2)_2O(CH_2)_2}NH_2Cl(m_1),\ \underbrace{(CH_2)_2O(CH_2)_2}NH\ (m_2),\ AgCl;\ Ag$$

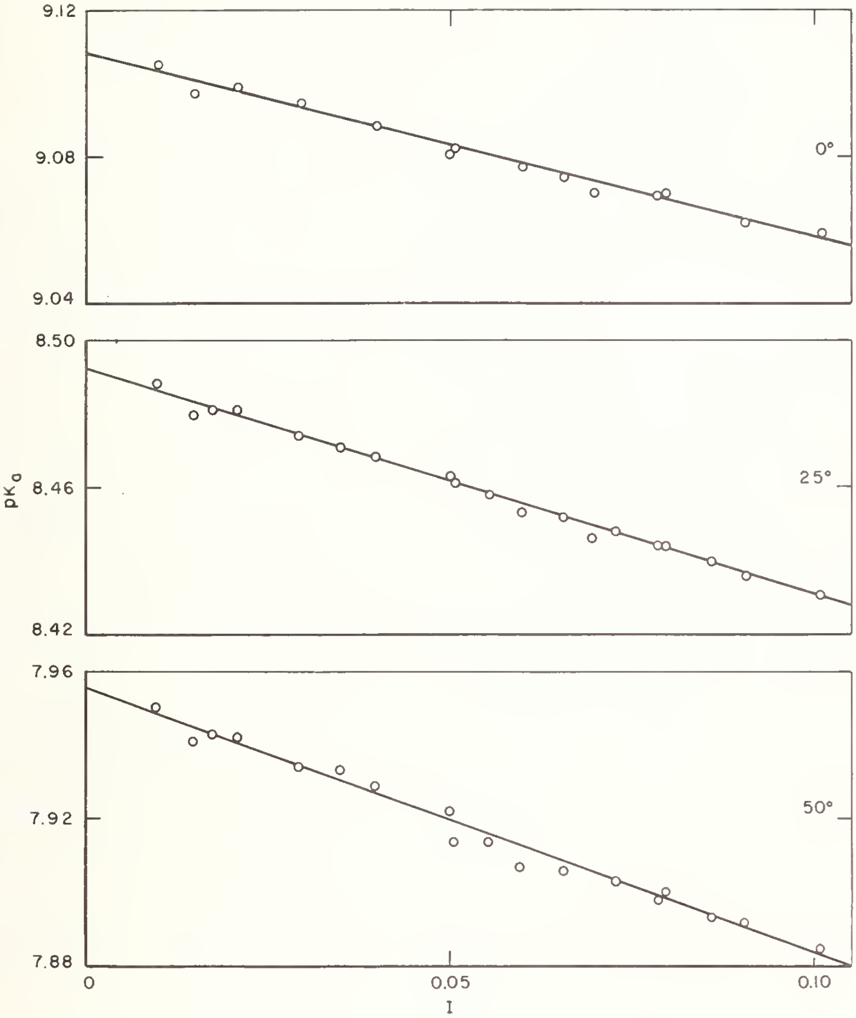


Figure 6. pK$'_a$ in morpholine-morpholinium chloride buffer solutions as a function of ionic strength (m_1) at 0, 25, and 50 °C.

where m_1 and m_2 represent the molalities of the salt and of the free amine, respectively, were made at 11 temperatures from 0 to 50 °C. An expression for calculating the "apparent" dissociation constant (K'_a) from the emf data was obtained by substitution of the acidity function $p(a_H\gamma_{Cl})$ into the expression for the dissociation constant of the protonated base. These values of the apparent dissociation constant were calculated from the measured emf E (corrected to 1 atm of dry hydrogen) by the equation

$$pK'_a \equiv (E-E°)/k + \log(m_1^2/m_2) - 2Am_1^{1/2} \qquad (29)$$

in which E° is the standard emf, k is (RT ln 10)/F, and A is the Debye-Hückel constant on the molal scale. Straight-line plots of pK'_a against m_1, positioned by least squares, gave limiting values of pK_a at $m_1 = 0$ with a standard deviation of 0.001 pK unit. Representative extrapolation lines are shown in figure 6. The pK_a values were expressed as a function of temperature (T) in °K by an equation of the Harned-Robinson form

$$pK_a = \frac{1663.29}{T} + 4.1724 - 0.0042239T \qquad (30)$$

Values of the enthalpy, entropy, and heat capacity changes for the dissociation process were calculated by the application of the standard thermodynamic formulas to eq. 30. The thermodynamic data for the dissociation of morpholinium ion and the two related substances at 25 °C are summarized in table 11. It may be noted that the introduction of an oxygen atom into the pyrrolidine ring decreases the basicity more than 2.8 pK units at 25 °C.

(H. B. Hetzer)

Table 11. Thermodynamic quantities for the dissociation of morpholinium, piperidinium, and pyrrolidinium ions in water at 25 °C.

(1 cal = 4.1840 J)

Acid	pK_a	$\Delta H°$	$\Delta S°$	$\Delta C_p°$
		cal mol^{-1}	cal deg^{-1} mol^{-1}	cal deg^{-1} mol^{-1}
Morpholinium ion	8.492	9,330	-7.6	11.5
Piperidinium ion	11.123	12,760	-8.1	21.0
Pyrrolidinium ion	11.305	13,020	-8.1	16.2

B. Ionization Constant of Deuterium Oxide from 5 to 50 °C

In earlier sections of this report, a number of thermodynamic measurements using deuterium oxide as a solvent have been described. For acid-base studies in heavy water, a knowledge of the ionization constant of deuterium oxide is indispensable. In view of the considerable uncertainty in the literature values, this constant has now been redetermined.

The cell chosen was that of Abel, Bratu, and Redlich [30],

$$Pt;D_2(g, 1\ atm), NaOD, NaCl\ (in\ D_2O), AgCl; Ag$$

and the emf was measured over the temperature range 5 to 50 °C. A constant ratio of the molalities of NaOD and NaCl was maintained, but the total ionic strength was varied over a range sufficient to permit an accurate extrapolation to zero concentration of the ionized solutes.

A solution of sodium hydroxide (NaOD) in heavy water was prepared by an adaptation of the method of Marsh and Stokes [31], using the apparatus shown in figure 7. The separatory funnel of 1000 ml capacity contained 500 ml of triply-distilled mercury and 400 ml of a 30 wt. percent solution of sodium hydroxide in deuterium oxide. Electrolysis was carried out for 3 hr at a current of 4 A using a platinum anode 2 cm^2 in area. Stirring of the mercury was necessary to prevent solidification of the amalgam at the mercury-solution interface. At the conclusion of the electrolysis the amalgam was allowed to run into the flask containing 600 ml of deuterium oxide through which CO_2-free, dry nitrogen had been bubbled for some hours. The reaction between sodium amalgam and water is very slow at room temperature. However, when the flask was maintained at a temperature of 80 to 90 °C on a hot plate for eight hr, sufficient reaction took place to yield a solution about 0.5M in NaOD.

The ionization constant of deuterium oxide on the molal (m) scale is defined by the equation

$$K_m = m_{D^+} \cdot m_{OD^-} \cdot \gamma_{D^+} \cdot \gamma_{OD^-} / a_{D_2O} \tag{31}$$

Values of pK_m' were calculated from the equation:

$$pK_m' \equiv pK_m - \log \gamma_{Cl^-}/\gamma_{OD^-} - \log a_{D_2O}$$

$$= (E-E°)/k + \log m_{Cl^-}{}^{-}/m_{OD^-} \, , \tag{32}$$

where k is written for (RT ln 10)/F. Values of E° have been determined earlier [9]. The pK_m' varies little with ionic strength (I), even with changes in m_{Cl^-}/m_{OD^-} ratio; this is to be expected since both the activity coefficient term $\gamma_{Cl^-}/\gamma_{OD^-}$ and a_{D_2O} are close to unity.

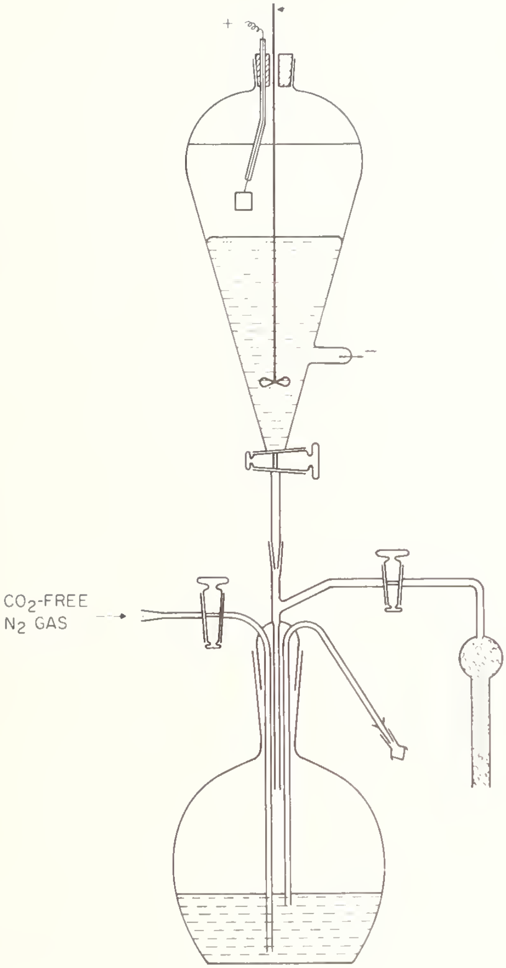


Figure 7. Apparatus for the electrolytic production of the sodium amalgam used to prepare the standard solution of NaOD.

The values of pK'_m were fitted to equations linear in I by the method of least squares, and the intercepts (pK_m) at zero ionic strength were determined in this way. The values of pK on the molal scale (pK_m), the molarity scale (pK_c), and the mole fraction scale (pK_N) are summarized in table 12 and compared with the corresponding quantities for the self-dissociation of ordinary water [32]. Values of the ratio $K(H_2O)/K(D_2O)$ on the molal scale are also given. The pK_m from 5 to 50 °C is given as a function of T, the temperature in °K, by the equation

$$pK_m = \frac{4913.14}{T} - 7.5117 + 0.0200854T \qquad (33)$$

The difference between the experimental value and that calculated by eq. 33 did not exceed 0.001 in pK_m at any temperature. The thermodynamic quantities $\Delta H°$, $\Delta S°$, and $\Delta C_p°$ for the ionization of deuterium oxide have been calculated with the use of eq. 33. They are compared with similar data at 25 °C for ordinary water in table 13. The results for H_2O have been recomputed to the basis 0 °C = 273.15 °K.

The value of $pK_c = 14.869$ at 25 °C is in good agreement with 14.86 found by Gold and Lowe [33]. The work of Wynne-Jones [34] is not inconsistent with these two values if one of his points is discarded. Other discordant results recorded in the literature are based on extrapolations to pure D_2O of data for D_2O-H_2O mixtures and involve considerable uncertainty.

(A. K. Covington)

Table 12. Comparison of the ionization constants of deuterium oxide and water from 10 to 50 °C.

t, °C	D_2O			H_2O			$\frac{K_m(H_2O)}{K_m(D_2O)}$
	pK_m	pK_c	pK_N	pK_m	pK_c	pK_N	
10	15.526	15.439	17.224	14.535	14.535	16.279	9.79
20	15.136	15.049	16.384	14.167	14.169	15.911	9.31
25	14.955	14.869	16.653	13.997	14.000	15.741	9.08
30	14.784	14.699	16.482	13.833	13.837	15.577	8.93
40	14.468	14.385	16.166	13.535	13.542	15.279	8.57
50	14.182	14.103	15.880	13.262	13.272	15.006	8.32

Table 13. Comparison of the changes in enthalpy, entropy, and heat capacity for the ionization of deuterium oxide and water at 25 °C (molal scale).

	t, °C	D_2O	H_2O
$\Delta H°$, cal mol^{-1}	5 25 50	15,371 14,311 12,884	14,427 13,526 12,312
$\Delta S°$, cal mol^{-1} deg^{-1}	5 25 50	-16.76 -20.43 -25.03	-15.55 -18.68 -22.59
$\Delta C_p°$, cal mol^{-1} deg^{-1}	25	-54.8	-46.6
t_{max} (°C)		221	239
$-\log K_{max}$		12.356	11.382

C. Response of the Glass Electrode in Heavy Water

Although there are indications that the glass electrode functions as well in heavy water as it does in ordinary water, no confirmation of the response appears to have been made by direct comparison with the deuterium gas electrode. An empirical correction of 0.40 unit in order to obtain pD from the operational pH (based on aqueous standards) has, however, been recommended [35,36]:

$$pD = pH + 0.40 \qquad (34)$$

This correction, determined with the use of solutions of strong acid and strong alkali, converts the operationally defined pH into values on a scale of pD.

The establishment of a pa_D scale based on the emf of cells without liquid junction and the deuterium gas electrode now makes it possible to confirm the deuterium ion response of the glass electrode in buffer solutions as well as in strong acid and strong alkali. Collateral measurements now under way will also furnish a check of the validity of the correction factor in eq. 34. It is hoped they will shed some light also on the origin of this correction factor, that is, on whether the difference of 0.40 unit results in large part from a difference in the standard potentials of the glass $\|D^+$ and the glass $\|H^+$ couples or whether differences in the potentials at the liquid junctions $D_2O\,|\,KCl$ (aq.) and $H_2O\,|\,KCl$ (aq.) are of significance also.

The following solutions were prepared:

1. 0.05417 m DCl
2. Potassium tetroxalate, about 0.05 m
3. Deuterioacetic acid, NaAc, and NaCl, each at a molality of 0.1043
4. KD_2PO_4 and Na_2DPO_4, each at a molality of 0.02502
5. Borax and NaCl, each at a molality near 0.1
6. NaOD and NaCl, each at a molality near 0.01

The glass electrodes, four in number, were of four different commercial types. Three were new, and the fourth had been used for several months in aqueous solutions. The new electrodes were conditioned in heavy water for five days before use. The emf measurements were made on a commercial pH electrometer of the chopper type. The voltage scale was

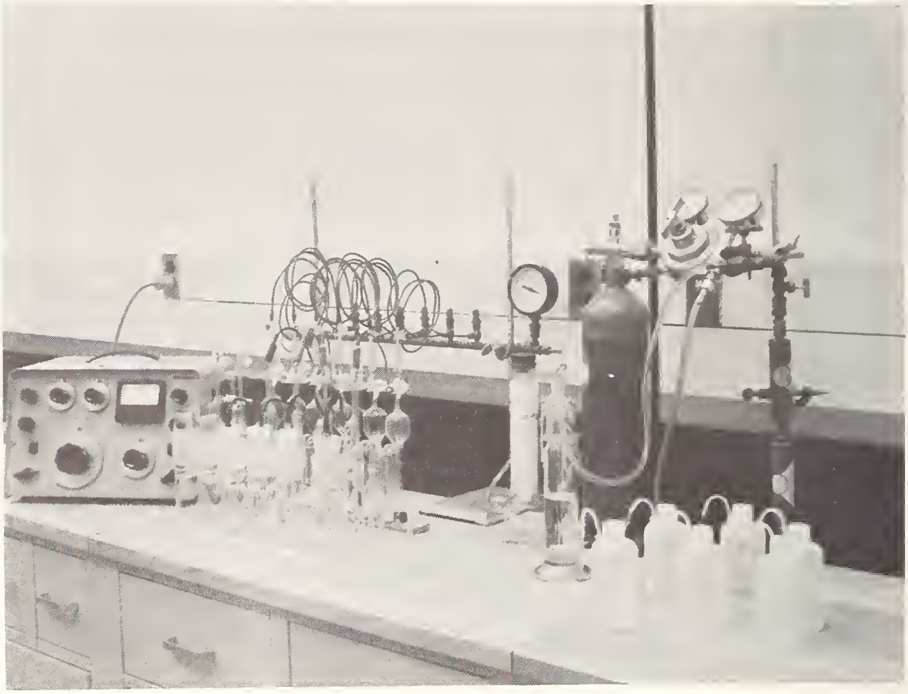


Figure 8. Equipment for a direct comparison of the deuterium gas electrode and the glass electrode in deuterium oxide.

calibrated against a precise potentiometer and was considered reliable to 0.2 mV.

Measurements of the cell

$$\text{Pt}; \text{D}_2\ (\text{g}),\ \text{Soln in D}_2\text{O} \,\|\, \text{glass}$$

were made at 25 °C. The deuterium gas electrodes were allowed two hours to reach equilibrium. Each glass electrode was placed successively in each of the six cells containing the six test solutions, with intermediate rinsing by the next solution before transfer. As a check, each electrode was returned to the first solution at the end of the series. The arrangement of cells and electrodes is shown in figure 8.

All of the glass electrodes followed the potential of the deuterium gas electrode within 0.5 mV in the first four solutions. In solutions 5 and 6 (pH 9.2 and 12.4, respectively), there was evidence that the alkaline error is larger than would be expected for electrodes at the same pH in ordinary water. Drifts of the electrodes on transfer from one solution to the next were slight, but those electrodes which had been conditioned in heavy water and used only in this medium performed best.

(A. K. Covington and R. G. Bates)

5. THERMODYNAMIC STUDIES OF AQUEOUS SOLUTIONS OF MIXED SALTS

The program for investigating the thermodynamic properties of solutions containing two dissolved salts is being carried out in cooperation with the Office of Saline Water of the U. S. Department of the Interior.

The research utilizes the isopiestic method of measuring the aqueous vapor pressure of a solution. The immediate result of an isopiestic experiment is, therefore, a knowledge of the vapor pressure of the solutions, which can also be expressed in terms of the water activity, a_w, of the solution or the osmotic coefficient, ϕ . Further calculations lead to a knowledge of the activity coefficients and chemical potentials of each of the salts in the solution.

Work on the system water-sodium chloride-barium chloride was described in last year's report [1] and has been published [37]. In the current year, work on the three systems:

water-potassium chloride-barium chloride
water-calcium chloride-magnesium chloride
and water-sodium chloride-calcium chloride

has been completed. A paper on the first of these systems has been published [38], and manuscripts describing work on the other two are in press.

Data are also available for the system water-potassium chloride-calcium chloride, and the analysis of these results is under way. A paper has also been published on the thermodynamics of the system water-potassium chloride-glycine [39]. Another paper, already published, describes the extent to which the vapor pressure lowering of a solution of two salts can be calculated from the vapor pressure lowerings of the separate, single salt solutions [40].

It has been found that the activity coefficients of two salts B and C in a mixed solution of constant total ionic strength can be represented by the equations

$$\log \gamma_B = \log \gamma_B^\circ - \alpha_B m_C \qquad (35)$$

and

$$\log \gamma_C = \log \gamma_C^\circ - \alpha_C m_B \qquad (36)$$

Here γ° is the activity coefficient of a salt in its own solution in the absence of the other salt. For example, in the system water-calcium chloride (B)-magnesium chloride (C) at $(m_B+m_C) = 4$, $\alpha_B = -0.0373$ and $\alpha_C = 0.0371$. The activity coefficient of calcium chloride in its own solution at 4m is 2.93 and, hence, its activity coefficient in a solution containing 2m calcium chloride and 2m magnesium chloride is 3.48. Thus the activity coefficient of calcium chloride is considerably higher in the mixed salt than in a solution of the same total molality consisting only of calcium chloride and water.

Similarly, the activity coefficient of magnesium chloride in its own solution at 4m is 5.53, and it is 4.67 in a solution containing 2m calcium chloride and 2m magnesium chloride. Thus the activity coefficient of magnesium chloride is considerably lower in the mixed salt solution.

Trace activity coefficients, γ_B^{tr} and γ_C^{tr}, can also be calculated. These are the activity coefficients of one salt when its concentration is reduced to trace amounts, $m_B \rightarrow 0$ or $m_C \rightarrow 0$. Thus the trace activity coefficient of calcium chloride as $m_B \rightarrow 0$, $m_C \rightarrow 4$ is 4.13, and that of magnesium chloride as $m_B \rightarrow 4$, $m_C \rightarrow 0$ is 3.93.

These relations are illustrated in figure 9. It will be observed that the admixture of one salt with another tends to equalize the activity coefficients, so that, in the limit, the trace activity coefficients are almost, but not completely, identical.

(R. A. Robinson)

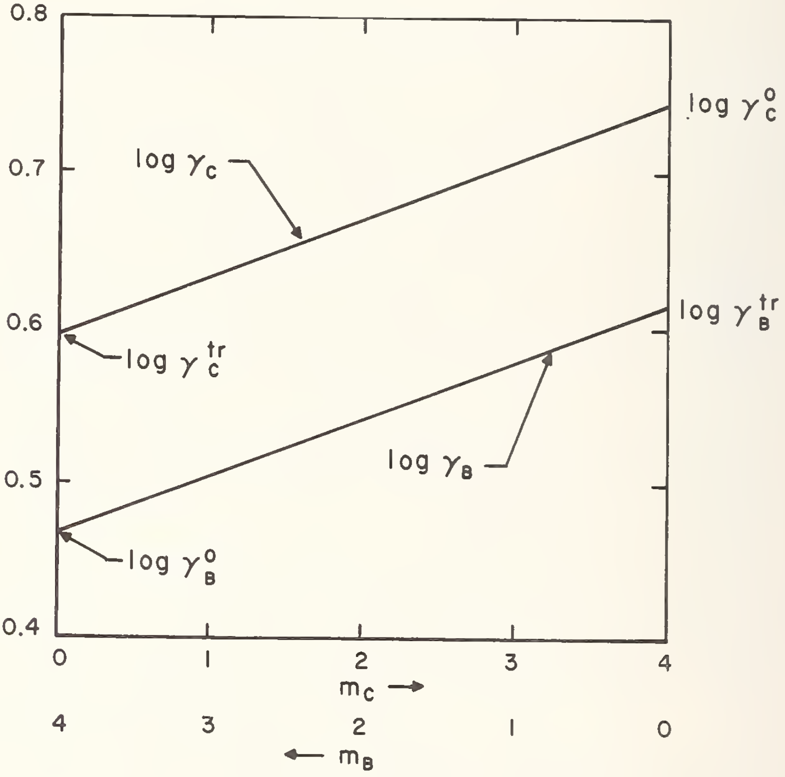


Figure 9. Variation of activity coefficients (γ) with composition in an aqueous mixture of calcium chloride (B) and magnesium chloride (C) of total molality 4.

6. CONDUCTOMETRIC DETERMINATION OF TRACES OF WATER

A. Objectives and Principle of Method

Work has continued on the development of an instrument for the determination of water in amounts of 0.5 to 5 mg. The water is to be determined in a few hundred cc of a gas stream, such as the combustion product obtained in the microanalysis of organic compounds for hydrogen. The principle of the instrument is based on the large effect of water upon the conductance of 0.2M solution of sulfuric acid in a propionic acid solvent. The specific conductance, κ, of this system at 25 °C is well represented by the empirical equation:

$$10^5\kappa = (0.012705 + 9.785W)/(1.12860 - 130.85W) \qquad (37)$$

where W is the weight fraction of water in the solution. Thus, the addition of 0.1 percent of water nearly doubles the conductance.

B. Modification of Apparatus

New conductance cells, circulation system, and Wheatstone bridge were constructed to reduce the working volume of solution, to eliminate several sources of leakage and contamination, and to improve the electrical measurements.

Electrodes were made of platinum foil silver-soldered to nickel plates for rigidity and were separated by an annular gasket, 1/32 in. thick, of poly-(tetrafluoroethylene), designated PTFE. The electrolyte cavity of the cell was 38 mm in diameter and 0.8 mm wide. This provided about the same cell constant as the previous cell but only one-fourth the volume. External tubing was replaced by 1/16 in. PTFE tubing with Luer fittings, and the 4-way stopcock of the previous apparatus was replaced by a PTFE plug valve.

A serious problem has been the design of a suitable circulating pump which would be chemically inert, have a small volume, and be able to circulate the entire electrolyte through the conductance cell in about one minute or less. The previous report [1] described a proposed glass-enclosed magnetic plunger operated by external solenoids. This model, with its associated check valves and tubing, required a liquid volume of about 20 cc. The major disadvantage, however, was serious overheating of the solution by the solenoids. The centrifugal design shown in figure 10 was adapted from Petriconi et al. [41]. These authors did not furnish dimensions, but the present model appears to be close to the smallest practicable size.

The rotor is made from quarter-inch round PTFE rod 2.5 cm. long and contains embedded permanent magnets. This length barely provides a useful pumping action in light of the unavoidable clearances required by the glassblowing. Under the conditions of use, the rotor can be run at about 1,000 rpm before it gets out of phase with the driving magnet. At this rate it circulates 6 to 8 cc of electrolyte per minute through the cell. It was found necessary to install a spindle on the shaft in order to keep the rotor centered in the housing. A particular advantage of the design is the provision for gas scrubbing. The sample stream of gas is introduced near the periphery of the housing and is thoroughly dispersed and mixed with the electrolyte before it leaves through the vertical axial tube. An inner axial tube, 1 mm in inside diameter, provides both an upper bearing for the spindle and a channel for the downward flow of returning electrolyte while the spent gas bubbles are rising through the outer channel.

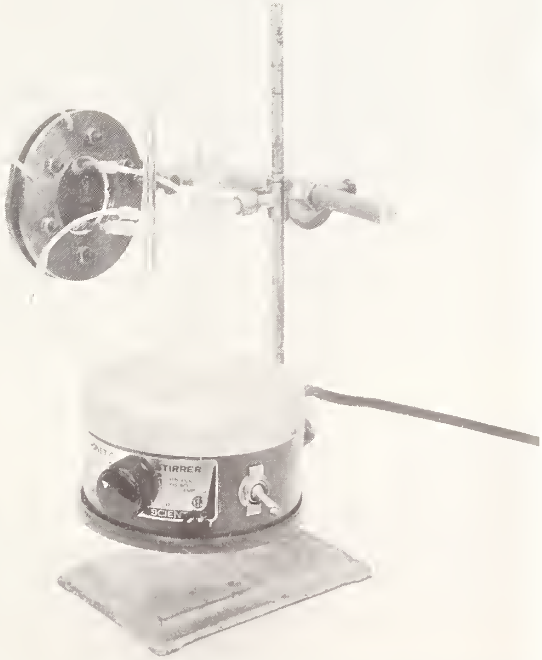


Figure 10. Conductance cell and circulation system for the determination of traces of water.

For test purposes, a "breadboard" bridge was wired according to the schematic diagram shown in figure 11. The major changes were the introduction of a Wagner earth branch and selector switches to permit more versatility in range, precision, and linearizing circuits. The balancing section of the ratio arms was replaced by four 100-ohm steps in series, across each of which the 10-turn precision potentiometer could be shunted successively by a selector switch, thus increasing the range of dial settings four-fold.

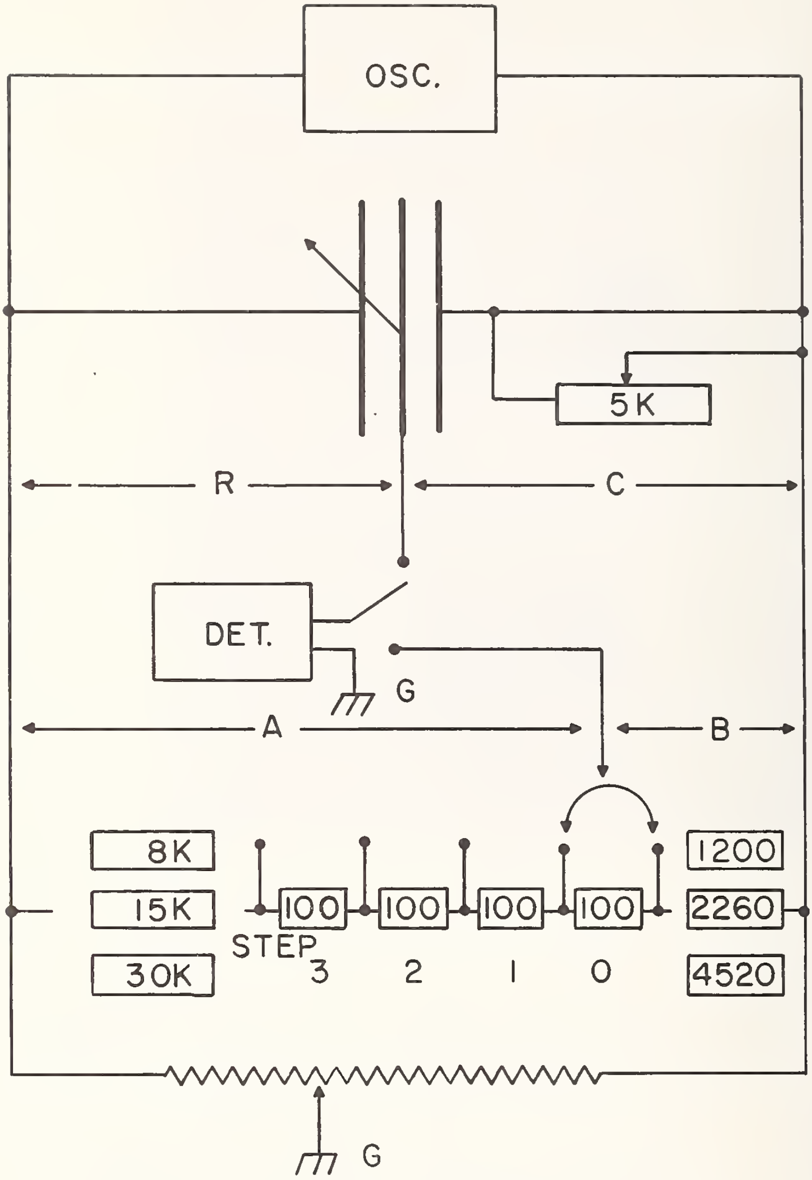


Figure 11. Schematic wiring diagram for conductance bridge.

It was originally planned that the fixed reference arm, in parallel with the variable shunt C, would be a closely similar conductance cell, as indicated in figure 11. This cell, filled with the starting electrolyte solution, would provide automatic compensation for the initial conductance of the solution, polarization, and any temperature changes. Because of various erratic effects and drifting of the initial balance, described further below, this reference cell was replaced by a fixed 5000-ohm resistor during most of the tests. Provision was made for plug-in capacitors in parallel with either ratio arm or with the Wagner earth, as required for balance.

The previous report [1] described a bridge circuit which approximately compensated for the non-linear conductance function (eq. 37). Further analysis has shown that a bridge with unequal arms can be designed which will provide either an unbalance signal, or a dial reading at null balance, which is directly proportional to the water concentration of the electrolyte.

Equation 37 can be rearranged to the equivalent form

$$W = a(1 - r)/(c + br) \qquad (38)$$

where $a = 0.1434$, $b = 110.43$, $c = 16.624$, and r is the specific resistance of the solution relative to that of the anhydrous solvent. For a simple Wheatstone bridge, it can be shown that the ratio (e) of the output signal to the input signal is given by

$$e = (SC-R)/[(1 + B)(C + R)] \qquad (39)$$

where S is the ratio of ratio arms, A/B; C is the equivalent resistance of the reference arm, and R is the resistance of the unknown arm. If it is required that $e = kW$, where k is a proportionality constant, then a comparison of the equations reveals the conditions:

$$SC = 1 \qquad (40a)$$

$$(1 - S)C = kc/a \qquad (40b)$$

and $$(1 + S) = kb/a \qquad (40c)$$

with the result that $S = b/c$, $C = c/b$, and $k = bc/[a(b+c)]$, in terms of the parameters of the conductance formula set forth in eq. 38; S is 6.64 and k has about half the maximum value of de/dW for an equal-arm bridge. This loss of sensitivity is the price of a linear response.

A corresponding treatment in terms of the change in resistance ratio required to bring the bridge to null balance gave a corresponding value of k and, further, defined absolute values for the fixed resistors in A and B such that the 400 ohms available for dial settings should correspond to any desired concentration range of water. Three such ranges were provided in the bridge.

C. Calibration with Water

Calibration of the system by means of weighed additions of water from a micropipet have, in general, confirmed the response of the electrolyte system and the circuitry as derived from the conductance equation. The precision of these measurements, however, was very disappointing. When fresh electrolyte was put in the clean, dry instrument, the initial balance condition fluctuated erratically, but somewhat cyclically, for an hour or two, eventually settling down to a steady drift toward increasing conductance. When the apparatus stood idle for several days at a time, there was little change, but as soon as circulation of the solution was resumed the same drift was observed; hence the calibrations had to be made against the background of changing reference and conductance. It seemed improbable that contamination was responsible for the effect, because leakage or corrosion would be expected to produce a localized concentration of contaminant during static conditions. Resumption of circulation would then produce a sharp peak as the concentration gradient entered the cell, but such a peak was never observed. After five or six hours of circulation, the solution became noticeably cloudy, and eventually a fine precipitate settled in the pump chamber. Recently it has been established that the precipitate is a nickel compound. Thus, corrosion of the short nickel connecting tubes between the cell and external PTFE tubing must be a factor in the poor reproducibility.

In an automatic analytical instrument it is desirable that the output be displayed directly on a chart or dial. This requires that, after an initial adjustment of the bridge, the unbalance signal be related to the water content of the electrolyte. In order to obtain a direct graphical indication of performance, the output from the bridge was fed through a full-wave rectifier to a chart recorder with a full-scale range of 1 mV. In order to calibrate the chart divisions against the bridge dial, the successive step positions were first recorded. The bridge was then rebalanced on the first position and three additions of water were made. The resulting trace is shown in figure 12. It is immediately apparent that the successive steps did not produce equal pen displacements. This result is still unexplained, but it may be related to the fact that a true null balance could not be obtained on the chart, perhaps because of a lack of shielding on the bridge or a faulty rectifier. For this measurement, the bridge and recorder were connected to the same ground.

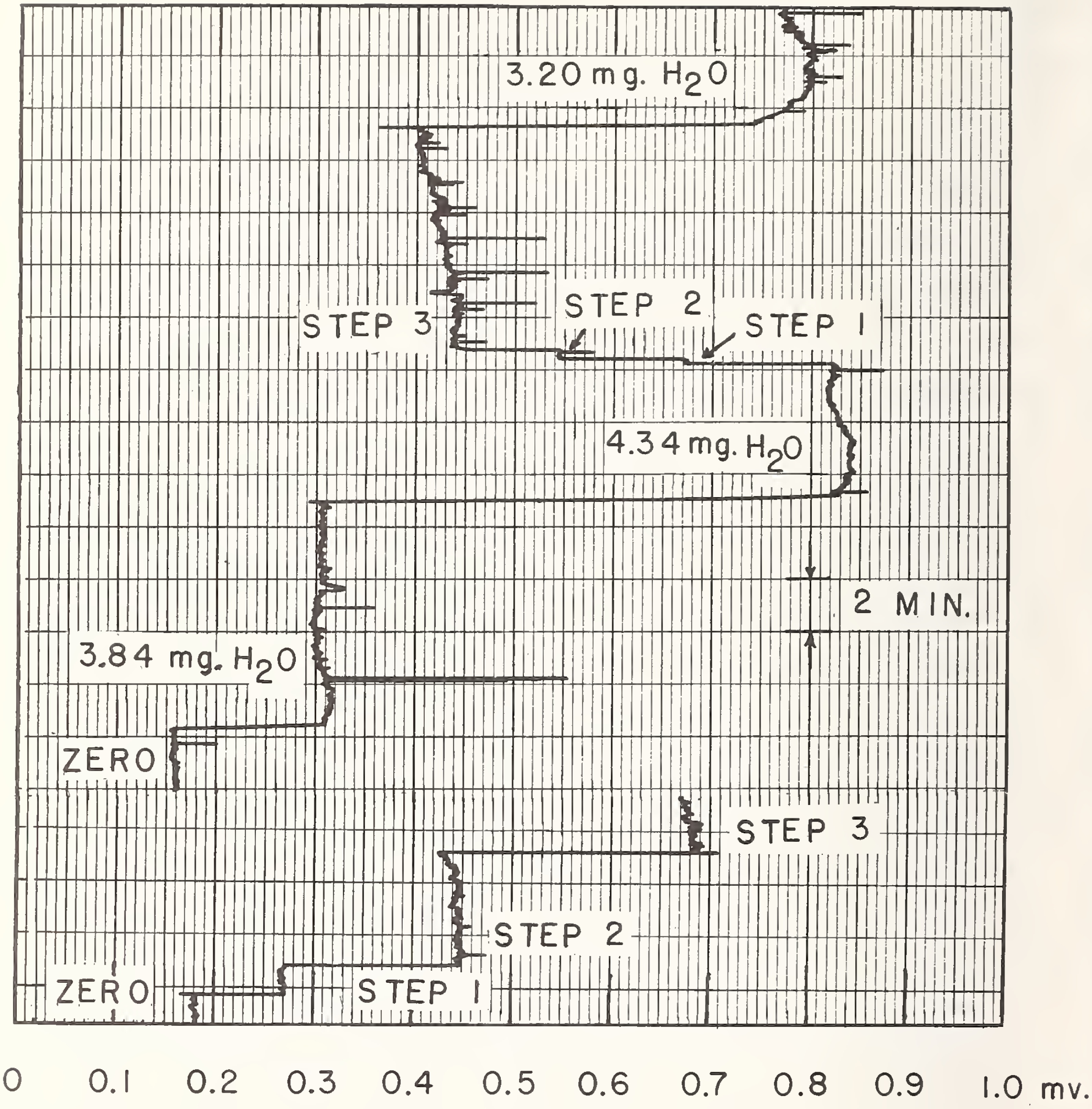


Figure 12. Recorder trace of calibrations by resistance steps and by addition of water.

Although it is less obvious, the chart record for water additions is also nonlinear. In curve I of figure 13, "equivalent" step positions, as derived by an admittedly crude interpolation of the chart calibration, are plotted against the water additions. The system contained 13.224 g of electrolyte, so the final point represents nearly 0.1 percent water. The chart shows a very rapid response after the addition of water, but there seems to be a small cyclic change with a period of 5 min as complete mixing takes place. Despite the rather noisy record, it is evident that 0.2 mg of water is detectable in the more sensitive region of the chart.

For a more careful calibration, the output of the bridge was connected to a tuned amplifier-null detector combination, and the bridge was rebalanced after each addition of water. The result of one such calibration is shown in curve II of figure 13. The difference in slopes of curves I and II is due to different positions of the range switch. The expected slope of curve II is 0.0573 while the observed value is 0.0545.

D. Analysis of Errors

Consideration has been given to the ultimate precision which might be obtainable. For observation of the bridge unbalance signal, the relation between W and signal, as outlined in section 6.B, is $dW/de = 1 \times 10^{-2}$. It is doubtful that a digital a.c. voltmeter costing under $3,000 could measure the signal with an error much less than 0.1 percent. Thus, the probable error in W would be 1×10^{-5}, corresponding to 0.1 mg of water in 10 g of electrolyte. As related to the microanalysis of organic compounds, this uncertainty corresponds to about 0.01 mg of hydrogen, or 1 percent absolute on a sample weighing 1 mg. The method

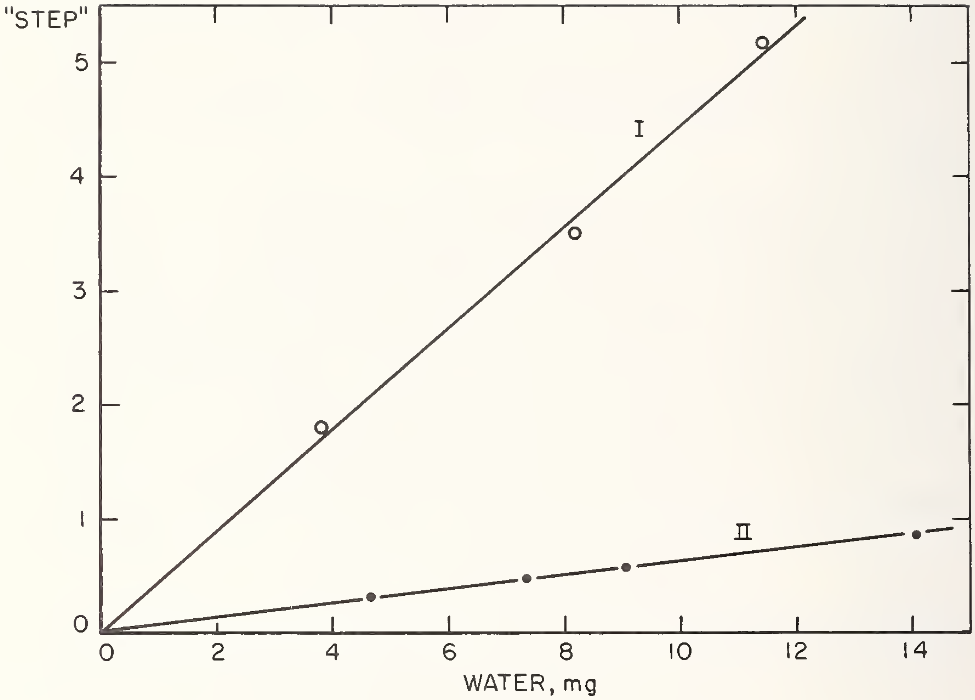


Figure 13. Comparison of calibration methods.
Curve I, derived from figure 12
as a function of time
Curve II, obtained by the
null-balance method

would thus be suitable only for routine or uncritical applications. The null-detector balance method of operation places less stringent requirements on the detector but is limited by the accuracy of the potentiometer (0.1 percent). The corresponding analysis indicates that the probable error in W would be an order of magnitude less, permitting the determination of hydrogen in a 1 mg sample with an absolute error of 0.1 percent. To extend the accuracy further would require precision conductance techniques and several decades of precision resistors in the bridge. This entire analysis is based on the application of eq. 37 for the conductance of the electrolyte system. It is unlikely that this empirical relationship is accurate to better than 0.5 percent over the working range, and therefore a careful calibration will be required.

E. Status of the Project

Steps which are called for immediately are the replacement of nickel in the cell and the provision of better shielding and placement of the bridge components. There is room for further improvement in the absorption-circulation system in the direction of reducing the volume and the time required to reach a steady value of the conductance.

(T. B. Hoover)

7. KINETIC TECHNIQUES IN TRACE ANALYSIS

The principal investigator was on assignment to the Coast and Geodetic Survey as a Science and Technology Fellow during most of the year. For this reason, there is very little progress on this project to report.

During the early months of the reporting year, however, a summary describing the use of reaction rate methods in analytical chemistry was written. This summary was prepared for internal use as an aid to the Division and Section in formulating future plans for work in this area. Reaction rate methods were subdivided into three general classes, namely catalytic methods, enzyme-catalyzed reactions, and differential rate methods.

Catalytic methods take advantage of the susceptibility of certain reactions to catalysis by substances present in trace amounts, and are, therefore, directly applicable to problems in trace analysis. Nearly 90 different reactions which have been successfully employed for this purpose were identified in the literature. The summary contains a table which lists 32 elements that have been determined by the catalytic method, summarizes the concentration range or sensitivity, and notes any serious interferences that have been studied. The transition metals constitute most of the group of 32 elements.

The current status of enzyme-catalyzed reaction methods was discussed, although the literature search was not as exhaustive as it was for the catalytic methods.

Quantitative methods based on the use of differential reaction rates depend on the fact that two or more related compounds in a mixture may undergo the same type of reaction at different rates. These methods are generally applicable to binary and often to ternary mixtures of organic compounds such as homologs or isomers containing the same functional group. The summary lists all of the binary and ternary mixtures for which special procedures have been established and reported in the literature.

(R. K. Wolford)

8. STANDARD REFERENCE MATERIALS FOR ACIDIMETRY

A. Homogeneity Tests of Potassium Hydrogen Phthalate 84h

The purpose of this work was to determine if the commercial "candidate" lot of potassium hydrogen phthalate was of sufficient uniformity and purity to warrant analysis and certification as an NBS acidimetric standard.

The material was analyzed by weight titration with aqueous carbonate-free alkali standardized against NBS potassium hydrogen phthalate 84d. The value of 99.98_8 percent purity, obtained by Bates and Wichers [92] by differential titration with the hydrogen electrode, was used for sample 84d. The procedure was essentially that suggested on the NBS certificate for the use of this material as an acidimetric standard, except that larger samples (approximately 2 g) were titrated. The base was added from an enlarged weight buret delivering approximately 120 g of solution.

The end point at pH 8.7, the inflection point obtained experimentally by Bates and Wichers, was detected by means of a glass electrode. The change in pH per drop of base was recorded for several drops below and the one immediately above pH 8.7. The buret was then weighed. From the known weight of one drop of base, the weight which would have changed the pH to 8.7 was interpolated. Results of analyses of samples taken from the top, middle, and bottom of each of the seven containers are given in table 14. The assay values are given in percent.

With the three sets of duplicates averaged, the standard deviation for the variability of the results is 0.0073. The conclusion from the analysis of variance was that, since the differences from container to container and from top to bottom in a particular container were not sufficiently larger than the residual error, one may regard the entire lot as being homogeneous.

Thanks are due to Mr. J. M. Cameron for the statistical analysis of these data and to Dr. W. J. Youden for assistance in the design of the experiments.

(H. B. Hetzer)

Table 14. Assay of potassium hydrogen phthalate 84h for homogeneity.

Location	Container						
	I	II	III	IV	V	VI	VII
Top	99.972 99.982	99.984	99.989	99.986	99.991	99.992	99.970 99.978
Middle	99.985	99.975	99.980	99.970	99.971 99.990	99.973	99.973
Bottom	99.985	99.972	99.973	99.986	99.990	99.975	99.990

B. Certification of Potassium Hydrogen Phthalate 84h as an Acidimetric Standard

The constant-current coulometric method was chosen for the determination of the assay of a new lot of potassium hydrogen phthalate, to be issued as a Standard Reference Material for acidimetry. This method has the advantage over other conventional methods of analysis that it involves the titration of the sample with a measured quantity of electricity. The results are therefore referred to fundamental physical constants such as the volt, ohm, and second, all of which can be easily and accurately measured.

By combining Faraday's law of electrolysis with Ohm's law, one can calculate the amount of electrochemical reaction during electrolysis by means of the equation

$$\text{(no. of equivalents)} = \frac{i\Delta t}{F} \qquad (41)$$

where i is the current in amperes, Δt is the elapsed time in seconds, and F is the faraday. The latest value for the faraday is 96,487.0 C equiv^{-1}. Thus in a hydrogen coulometer the quantity of hydroxyl ions produced as the titrating reagent can be determined with a high degree of accuracy and precision from the known magnitude of the current passed and the time elapsed.

The technique for precise coulometric titration of acids and bases has been worked out previously by Taylor and Smith [43]. The facilities used in this work were part of the equipment of the Microchemical Analysis Section and have been described and illustrated in the annual report of that section for the year 1965 [44]. Acknowledgment is made to George Marinenko for instruction in the use of the equipment.

In general, the experimental procedures developed by Taylor and Smith were followed. From the seven containers of potassium hydrogen phthalate, the homogeneity of which had been studied by H. B. Hetzer (see section 8.A), six samples were taken at random for coulometric study. Two-gram samples were ground gently, dried at 120 °C for two hr, and titrated by passing a known amount of current through a cell consisting of a platinum cathode and a silver anode, with a 1 M solution of potassium chloride as the supporting electrolyte. The titration was performed under a nitrogen atmosphere, and the end point of the titration was determined by noting the pH changes, indicated by a glass-calomel combination electrode, as the last 0.05 percent of the total current was passed in small increments through the solution. A typical end point determination is shown in figure 14. Curve a represents the pH indicated by the glass electrode as a function of time. Curve b is the differential plot from which the inflection point of the titration curve was determined. An error of 0.005 percent in the total assay is represented by 25 seconds on the plot.

The results obtained for 17 titrations of the new lot are given in table 15. The values in curly brackets indicate duplicate titrations of the same grind. The data were analyzed by Mr. J. M. Cameron, and the purity of the sample was found to be 99.9921 percent, with a standard deviation of 0.0065 for a single determination. The analysis of variance supports the statement, with approximately 95 percent confidence, that 99 percent of all samples have assay values lying in the interval 99.9921 ± 0.0288.

(M. Paabo)

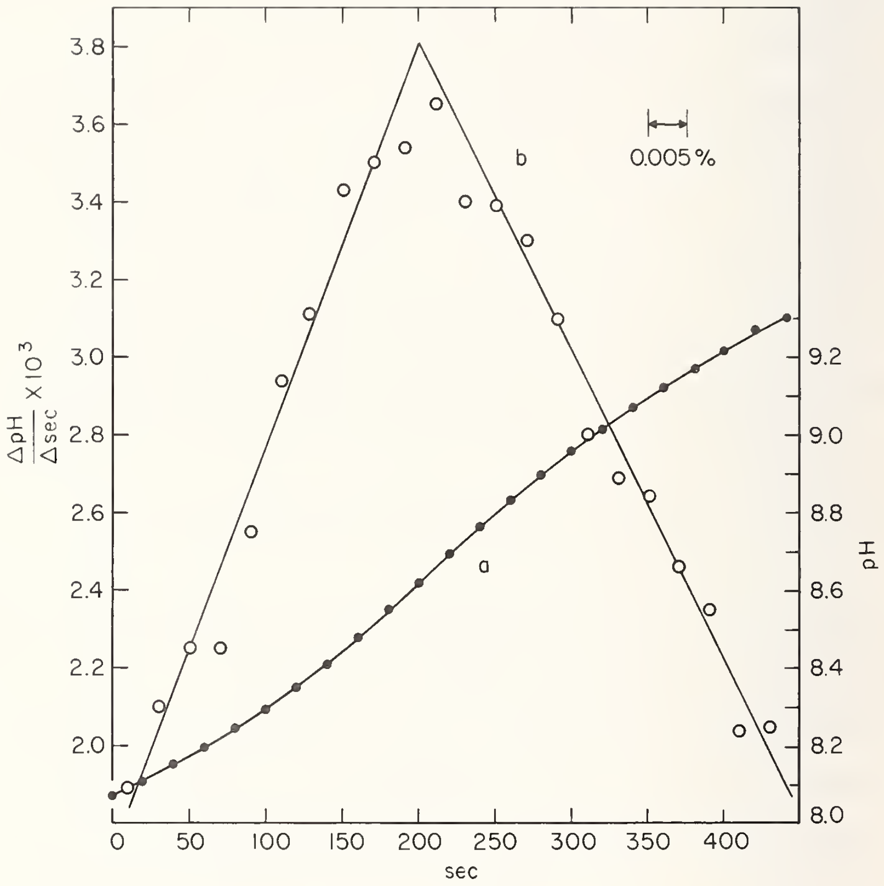


Figure 14. End point determination in a typical coulometric titration.

Curve a, pH change as a function of time

Curve b, differential plot used to locate the end point.

Table 15. Assay of potassium hydrogen phthalate 84h for certification as a standard for acidimetry.

(values in percent)

Location	Container				
	I	II	IV	V	VI
Top		99.9975 99.9952 100.0024			99.9822 99.9869 100.0018
Middle			99.9907 99.9967	99.9863 99.9856 99.9964	
Bottom	99.9926 99.9930		99.9856 99.9825 99.9959 99.9944		

C. Status of Certification Procedures for Standard Reference Materials

Precise acidimetry has always presented an unrelenting challenge. Coulometric titrations and differential potentiometric titrations with the hydrogen electrode have shown themselves capable of sensitivities of a few thousandths of one percent in the assay of standard materials for acidimetry. As conducted here, these methods are providing accuracy which we believe is not exceeded elsewhere. The statistical examination of the data for potassium hydrogen phthalate 84h suggests strongly that the accuracy of the analysis surpasses the degree of homogeneity now attainable on a large lot of material. The sensitivities of these refined methods are likewise so great that distinctions between the inflection point of the titration curve and the true equivalence point may have to be made. These differences are not clearly understood, and studies of end points may have to be undertaken.

Somewhat different problems are encountered in the certification of reference standards for pH measurements. The experimental emf measurements which lead unambiguously to values of the acidity function $p(a_H\gamma_{Cl})$ have been developed to a high level of precision in our laboratory. An accuracy of 0.002 pH unit is attainable in water and in the other media we have studied, over most of the experimental temperature range. However, the assigned pH(S) is derived from this well-defined acidity function by introduction of an arbitrary convention whose "accuracy" cannot be assessed. Furthermore, the instruments used almost universally in the measurement of pH utilize a cell with liquid junction. The vagaries of the liquid-junction potential are such that the experimental pH values can rarely be considered reproducible to better than 0.01 unit regardless of the refinements in the standard values for the reference materials with which the assembly is standardized. There remains always the challenge to reduce the variance in the assigned pH(S); an even greater challenge is presented by the prospect of designing an improved instrument for practical pH measurements.

(R. G. Bates)

9. FOREIGN-CURRENCY PROGRAMS

Two projects being conducted at universities in India and financed through the provisions of Public Law 480 are sponsored by the Electrochemical Analysis Section. A brief description of these programs follows.

A project entitled "Properties of Electrolytes in Nonaqueous Media" is being conducted at Jadavpur University in Calcutta under the supervision of Dr. M. N. Das and Dr. K. K. Kundu. At the present time Dr. Das and Dr. Kundu are studying the properties of weak electrolytes in glycol-water solvents over a range of temperatures. Work has been done on the standard emf of the hydrogen-silver chloride cell in glycol-water media, and similar studies of the hydrogen-silver bromide cell have been initiated. Data for the pK_a values of monoethanolammonium ion and diethanolammonium ion have also been obtained in these solvents.

A project entitled "Physicochemical Studies in Nonaqueous Solvents" is being pursued at Panjab University, Chandigarh, under the supervision of Professor Ram Chand Paul. Professor Paul's current interests include the behavior of Lewis acids in molten acetamide solvents. Conductometric methods have been used, and several solvates have been isolated and identified. The work is being extended to studies of the solvation of electrolytes in general, including protonic acids, in amide solvents. Dissociation constants of weak electrolytes will be determined, and an investigation of ion-pair formation in these media is planned.

(R. G. Bates)

10. PERSONNEL

Roger G. Bates, Section Chief

R. A. Robinson, Assistant Section Chief

Marguerite Raudenbush, Section Secretary

Electromotive Force and Optical Measurements of Acidity

V. E. Bower

A. K. Covington, On leave from the University of Newcastle upon Tyne, England.

R. Gary

Hannah B. Hetzer

Maya Paabo

R. A. Robinson

Barry J. Steel, On leave from the University of Adelaide, South Australia.

Conductance Measurements

T. B. Hoover

Dielectric Measurements

C. G. Malmberg

Acid-Base Studies in Inert Solvents

Marion M. Davis

Isopiestic Vapor Pressure Measurements

V. E. Bower

R. A. Robinson

Kinetic Studies

R. K. Wolford

Solubility Studies

P. W. Schindler, Guest worker of the Swiss National Foundation, on leave from the University of Bern.

11. COMMITTEE MEMBERSHIPS

Roger G. Bates

Member, Subcommittee on Hydrogen Ion Determinations, ASTM Committee E-1, Sub. 22.

Councilor, American Chemical Society, Washington Section.

Member, NRC Committee on Symbols, Units, and Terminology for the Physical Sciences (U.S. National Committee for ISO/TC-12).

Member, U.S. National Committee for IUPAC.

Member, Commission on Electrochemistry, IUPAC.

Member, Commission on Symbols, Terminology, and Units, IUPAC.

Associate Member, Commission on Electroanalytical Chemistry, IUPAC.

Member, Subcommittee on Physiocochemical Symbols and Terminology, Committee on Physical Chemistry, NRC.

Member, Advisory Board, *Analytical Chemistry*.

Member, Board of Editorial Advisors, *Analytica Chimica Acta*.

Member, Board of U.S. Civil Service Examiners (Chemistry Panel).

Member, Washington Editorial Review Board (NBS).

Member, Committee on Units and Usage (NBS).

Member, Museum Committee (NBS).

Marion M. Davis

Member, American Association of University Women Educational Foundation, Committee on Fellowships to American Women.

Member, Committee on Long-range Planning, Chemical Society of Washington.

Member, Board of U.S. Civil Service Examiners (Chemistry Panel).

Robert Gary

Treasurer, Society of The Sigma Xi, D.C. Chapter.

R. A. Robinson

Secretary, Commission on Electroanalytical Chemistry, IUPAC.

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2. Bates, R.G., "Solvent Effects on Acidity in Nonaqueous Media", The Electrochemical Society, Buffalo, N.Y. October 11, 1965.

3. Bates, R.G., "Solvent Role in Acidity", American Chemical Society, Susquehanna Valley Section, King's College, Wilkes-Barre, Pennsylvania. October 20, 1965.

4. Bates, R.G., "Acid-Base Processes in Alcohol-Water Solvents", Chemistry Seminar, Michigan State University, East Lansing, Michigan. November 16, 1965.

5. Bates, R.G., "Acid-Base Behavior in Water-Like Solvents", Wabash Valley Section, American Chemical Society, Terre Haute, Indiana. January 11, 1966.

6. Bates, R.G., "pH Numbers -- their Measurement and Meaning", Combined Student Group, Rose Polytechnic Institute and Indiana State University, Terre Haute, Indiana. January 12, 1966.

7. Bates, R.G., "Acid-Base Behavior in Alcohol-Water Solvents", Chemistry Seminar, Indiana University, Bloomington, Indiana. January 12, 1966.

8. Bates, R.G., "Dissociation of Ammonium Ion in Methanol-Water Solvents", American Chemical Society, National Meeting, Phoenix, Arizona. January 20, 1966.

9. Covington, A.K., "Dissociation of Moderately Strong Acids", Department of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pennsylvania. February 21, 1966.

10. Covington, A.K., "Dissociation of Moderately Strong Acids", Reactor Chemistry and Chemistry Division, Oak Ridge National Laboratory, Oak Ridge. Tennessee. March 3, 1966.

11. Covington, A.K., "Dissociation of Moderately Strong Acids", Brookhaven National Laboratory, Upton, Long Island, New York. March 14, 1966.

12. Covington, A.K., "The Hydrogen-ion Response of the Glass Electrode", Department of Chemistry, Brown University, Providence, Rhode Island. March 16, 1966.

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14. Bates, R.G., "Solvent Effects on Acid-Base Behavior in Amphiprotic Media", Chemistry Colloquium, Pennsylvania State University, University Park, Pennsylvania. March 17, 1966.

15. Covington, A.K., "The Hydrogen-ion Response of the Glass Electrode", Exploratory Chemistry Research Department, Corning Glass Works, Corning, New York. March 18, 1966.

16. Schindler, P.W., "Heterogenous Equilibria Involving Oxides, Hydroxides, Carbonates and Hydroxide Carbonates", American Chemical Society, National Meeting, Pittsburgh, Pennsylvania. March 24, 1966.

17. Bates, R.G., "Potentiometric Measurements and pH Standards", Course in Advanced Laboratory Instrumentation, Walter Reed Army Institute of Research, Washington, D.C. March 25, 1966.

18. Covington, A.K., "The Hydrogen-ion Response of the Glass Electrode", The Electrochemical Society, National Capital Section, Reiss Science Center, Georgetown University, Washington, D.C. April 7, 1966.

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21. Bates, R.G., "pH: Its Meaning and Measurement", Physical Chemistry Class, Bucknell University, Lewisburg, Pennsylvania. April 12, 1966.

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23. Bates, R.G., "Solvent Effects on Acid-Base Behavior", Chemistry Seminar, University of the State of New York at Buffalo, Buffalo, New York. April 20, 1966.

24. Bates, R.G., "Acid-Base Chemistry of Partially Aqueous Media", Chemistry Seminar, George Washington University, Washington, D.C. April 29, 1966.

25. Covington, A.K., "Dissociation of Moderately Strong Acids", Rockefeller University, New York, New York. May 5, 1966.

26. Bates, R.G., "Behavior of the Glass Electrode and Other pH-Responsive Electrodes in Biological Media", Conference on Bioelectrodes, New York Academy of Sciences, Woldorf-Astoria Hotel, New York, New York. June 6, 1966.

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