Electrochemical Analysis Section:

Summary of Activities
July 1968 to June 1969
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3 Located at 5245 Port Royal Road, Springfield, Virginia 22151.
NBS TECHNICAL NOTE 503
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Electrochemical Analysis Section
Summary of Activities
July 1968 to June 1969

Edited by Roger G. Bates

Electrochemical Analysis Section
Analytical Chemistry Division
Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

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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 57 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 a highly important output of our laboratories. 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 about our programs. A word is perhaps in order about the philosophy of these yearly progress reports. In any research program a large amount of information is obtained and techniques developed which never find their way into the literature. This includes the "negative results" which are so disappointing and unspectacular but which can often save others considerable work. Of importance also are the numerous small items which are often explored in a few days and which are not important enough to warrant publication--yet can be of great interest and use to specialists in a given area. Finally there are the experimental techniques and procedures, the designs and modifications of equipment, etc., which often must be covered in only a line or two of a journal article.
Thus our progress reports endeavor to present this information which we have struggled to obtain and which we feel might be of some help to others. Certain areas which it appears will not be treated fully in regular publications are considered in some detail here. Other results which are being written up for publication in the journal literature are covered in a much more abbreviated form.

At the National Bureau of Standards publications such as these fit logically into the category of a Technical Note. In 1969 we plan to issue these summaries for all of our sections. The following is the fifth annual report on progress of the Electrochemical Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division
This is the fifth annual progress report of the Electrochemical Analysis Section of the Analytical Chemistry Division. It covers the fiscal year 1969, which began on July 1, 1968, and ended on June 30, 1969.

The Section concerns itself particularly with ionic processes occurring in solution, with areas of analytical measurement where ionic equilibria play a part, and with the explanation of solution behavior in terms of the interactions of ionic solutes with solvent molecules. The special interests of the members of the Section lie for the most part in solution electrochemistry, electrochemical thermodynamics, and ionic transport phenomena. In the context of modern analytical chemistry, their competences bear most directly on potentiometry, electrometric titrations, and conductometric analysis. 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 40 percent of the total effort of the Section was devoted to research and about 60 percent to the development of standard reference materials.

The permanent staff of the Section remained at four during the year. In addition, the Section enjoyed the valuable services of Dr. Marinus Alfenaar of the University of Utrecht from July until late September, when his temporary appointment was concluded. In October Dr. Harry P. Thun of the University of Ghent arrived to spend a year in the Section as a guest worker. Furthermore, the Section was augmented during the summer months of 1968 by the return of Edgar S. Etz and James T. Clark, Jr., and by the presence of Robert S. Carter, a student at Landon School.
Both Mr. Etz and Mr. Clark are graduate students at Clarkson College of Technology, where they are working under the direction of Professor Donald Rosenthal. Professor Rosenthal remains a consultant to the Section.

With a permanent staff of only four, it has obviously been impossible to conduct a broad program in the electrochemistry of solutions. For this reason, the activity of the past year has been limited to emf studies and conductance measurements. Unlike the formal publications that appear in the scientific journals, this report summarizes the total program of the Section, incomplete studies as well as finished work, and stresses its relationship to the missions of the Division and Institute.

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, Mrs. Marguerite Raudenbush, and Robert J. Boreni in the preparation of this report is gratefully acknowledged.

Roger G. Bates, Chief
Electrochemical Analysis Section

Washington, D.C.
June 30, 1969
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ELECTROCHEMICAL ANALYSIS SECTION: SUMMARY OF ACTIVITIES, JULY 1968 TO JUNE 1969

Edited by Roger G. Bates

ABSTRACT

This survey of the activities of the Electrochemical Analysis Section, Analytical Chemistry Division, covers the period July 1968 to June 1969. An attempt is made to summarize a year's progress on the technical projects of the Section, to indicate the composition and capabilities of the unit as a whole, and to stress the Section's role in the mission of the Institute. Brief summaries of several lines of work under way are given. The concept of a broad program on acidity measurements is outlined, and new efforts to provide assistance in clinical acid-base measurements are summarized. Progress toward reference standards for the calibration of ion-selective electrodes is reported. Equilibrium data for phosphoric acid in heavy water, for piperazinium ion in 50 wt % methanol-water, and for hydrochloric acid in a solvent composed of 2-methoxyethanol (80 wt %) and water (20 wt %) have been obtained. Considerable effort has been devoted to the development of new standard reference materials, including standards for conductivity measurements. Lists of publications, talks, and committee assignments of staff members are given.

Key Words
Acidity, Analysis, Conductivity, Electrochemical analysis, Electrochemistry of solutions, Ionic activity, Ion-selective electrodes, pD measurements, pH measurements, Medium effects, Solvent effects, Standard reference materials
1. FACILITIES AND EQUIPMENT

Excellent facilities for the Section's programs are provided on the second floor of the Chemistry Building at the Gaithersburg site of the National Bureau of Standards. The space devoted to research and development of standard reference materials consists at present of a conductance laboratory and four well-equipped emf laboratories. The instrumentation room has been outfitted to accommodate the instrument for measuring dielectric constants of solvents, an automatic titrator, and several pH meters. One of the emf laboratories, specially equipped for the study of ion-selective electrodes, is shown in figure 1.

Figure 1. Emf laboratory equipped for the study of ion-selective electrodes.
During the year, one of the four emf laboratories was devoted to studies of acid-base behavior in nonaqueous and mixed solvents. A second was devoted to work in deuterium oxide with deuterium gas electrodes and to the study of aqueous buffer systems of clinical interest. Investigations of ion-selective electrodes were conducted in a third, while a fourth, in use only during the summer months, was given over to studies of acid-base processes in sea water. The highly precise equipment for the measurement of conductivity was used throughout the year in establishing conductivity standards for oceanographic purposes.

This emf installation is sufficiently large to justify an automatic data read-out center capable of recording automatically and simultaneously the emf of all the cells under study in each of the laboratories. A multichannel digital voltmeter with an accuracy of 10 $\mu$V is needed. It would be coupled to a print-out unit from which a record of all the emf data could be obtained and, when desired, a tape could also be produced for computer analysis. Measurements of all cells at desired intervals could be programmed in advance.

Because of staff limitations, it has not yet been possible to initiate work on the accurate measurement of pH at high temperatures and pressures or to supplement our present capability with calorimetric studies of ionic processes in solution. When these types of work are begun, additional facilities and equipment will be needed.

(R. G. Bates)
2. ACIDITY MEASUREMENTS

A. Concepts and Program

The measurement of acidity continues to be one of the major concerns of the Section. The concepts and approaches of our efforts in this area were set forth in the annual progress reports for 1966 [1] and 1967 [2].

The NBS pH scale is fixed by a series of standard reference solutions chosen to cover uniformly that region of the scale in which the emf of the pH cell is a linear function of the pH of the solution in which the electrodes are immersed. Corrections are made, if necessary, for imperfections in the response of the glass electrode. Unlike the pH scale of the British Standards Institution [3], which recognizes only a single primary standard, the NBS approach permits a series of primary reference solutions. The search for new and better standards is going on continually. A new standard may be selected because it extends the useful range of the standard scale or because it shows a stability superior to those of existing standards in its pH range.

The pD scale in heavy water bears the same fundamental relationship to the deuterium gas electrode that the pH scale bears to the hydrogen gas electrode. Basically, the phenomena which are regarded as a manifestation of "acidity" in these two media can be attributed to two distinctly different entities, namely the deuterium ion and the hydrogen ion. For this reason, the pD scale is not related to the pH scale. The same methods can nonetheless be utilized for establishing acidity standards in deuterium oxide as have been used to set up pH standards in ordinary water.
During the past year, two new standards for the pH scale and three standards which fix a practical pD scale in deuterium oxide were described in published papers [4,5]. The new pH standard solutions contain potassium dihydrogen citrate (0.05 molal) and a mixture of sodium bicarbonate and sodium carbonate (each 0.025 molal). Solutions of the same salts in the same molalities, prepared in deuterium oxide, serve as pD standards, together with a mixture of potassium dideuterium phosphate and disodium deuterium phosphate (each 0.025 molal). Sodium bicarbonate and sodium carbonate were added to the list of Standard Reference Materials. The citrate, phosphate, and carbonate salts serve equally well for preparing pD and pH standard solutions; exchange of hydrogen for deuterium when the protium salts are dissolved in heavy water alters the acidity so slightly that it causes no concern. A source of pure potassium dihydrogen citrate in quantity is still being sought.

The extension of the pH concept to media other than pure water has received considerable attention in the Section during the past few years. Solvent effects on acidity are not only of great theoretical interest but have an important bearing on the behavior of equilibrium systems of analytical interest. Practical acidity scales in non-aqueous and partly aqueous solvents would, for example, greatly facilitate the study of metal complexation with a variety of ligands that are themselves proton donors or acceptors. As a guest worker in the Section, Dr. Harry P. Thun is turning his attention to the establishment of a useful acidity scale for a mixed solvent system with which a range of dielectric constants can be achieved. For this study, mixtures of 2-methoxyethanol (methylcellosolve) and water were chosen. This work is aimed at setting up standard scales for the measurement of acidity at low ionic
strengths in these mixed solvents and also in media of ionic strength 1.0 (1 molal with respect to sodium perchlorate). Complexation studies are often conducted in media of a constant, rather high, ionic strength in order to minimize changes in activity coefficients. It is therefore useful to have available secondary acidity standards in special solvent media of this sort.

With the increased attention being given to clinical measurements, secondary standards for other media of special significance to biomedicine are assuming importance in the Section's future plans. Of most immediate concern is isotonic saline, or 0.16M sodium chloride. Preliminary work in this medium has already begun. These studies parallel closely the work in sea water which has been conducted at a relatively low level during the past two years.

(R. G. Bates)
B. Standards for Clinical pH Measurements

1. Tris(hydroxymethyl)aminomethane in Isotonic Saline

Acidity measurements in biological media with glass electrodes, standardized in the usual aqueous reference buffer solutions, often involve a considerable error due to the change in liquid-junction potential when the glass electrode is transferred from the relatively dilute standard buffer to a medium of higher ionic strength. This source of error can be minimized or eliminated by developing a new set of reference buffers in a medium of a composition close to that of the biologic fluid. Furthermore, buffer solutions of this sort are very useful for pH control in biomedical research.

A sodium chloride solution with a constant total ionic strength of 0.16 (isotonic saline) approximates closely the colligative properties of blood plasma. Tris(hydroxymethyl)aminomethane (tris, THAM) has been selected tentatively as the first pH standard in this new medium. Emf measurements of the cell

\[
\text{Pt;H}_2(g), \text{Tris·HCl(m), Tris(m), NaCl (0.16-m), AgCl;Ag}
\]

were made from 0 to 50 °C. The concentration of free base was kept equal to that of the hydrochloride, and enough sodium chloride was added to make the total ionic strength equal to 0.16. The molality of the base was varied from 0.005 to 0.05 mol kg\(^{-1}\). The acidity function \(p(aH\gamma Cl)\) was derived from the measured emf \(E\) of the cell, and its variation with buffer composition was studied. The following equation was used:
\[ p(a_\text{HCl}) = \frac{E-E^\circ}{k} + \log m_{\text{Cl}} \]  

(1)

where \( E^\circ \) is the standard emf of the cell and \( k \) is \((RT \ln 10)/F\). The results at 25 °C are given in table 1. Cell vessels and constant-temperature bath can be seen in figure 2.

Figure 2. Equipment for standardization of clinical pH measurements.
Table 1. Emf of the cell: Pt;H₂, Tris·HCl(m), Tris(m), NaCl(0.16-m), AgCl;Ag at 25 °C. Values of $p(a_H\gamma_{Cl})$.

<table>
<thead>
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<th>m</th>
<th>E</th>
<th>$p(a_H\gamma_{Cl})$</th>
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<tr>
<td>0.005004</td>
<td>0.76292</td>
<td>8.342</td>
</tr>
<tr>
<td>0.01001</td>
<td>.76322</td>
<td>8.347</td>
</tr>
<tr>
<td>0.01999</td>
<td>.76340</td>
<td>8.350</td>
</tr>
<tr>
<td>0.03001</td>
<td>.76346</td>
<td>8.351</td>
</tr>
<tr>
<td>0.05001</td>
<td>.76354</td>
<td>8.353</td>
</tr>
</tbody>
</table>

To date, only one series of measurements has been made. When the work is resumed, sufficient data to permit the assignment of primary standard pH values to a tris buffer in isotonic saline will be obtained.

2. Dissociation of Protonated "Bis-Tris" in Water

A new buffer material suitable for biochemical work in the pH range from 5.5 to 7.5 has recently been made available commercially. This compound, 2,2-bis(hydroxy-methyl)-2,2'2"-nitrilotriethanol [(HOCH₂CH₂)₂N(CH₂OH)₃], or "bis-tris", is a solid, easily purified, water-soluble compound with $pK_a$ value of 6.46 at 25 °C [6].

The structure of bis-tris is closely related to that of tris. Since it does not contain primary amine groups which can react with carboxyl groups, bis-tris is preferred over tris for pH control in studies of enzyme-catalyzed reactions. An accurate knowledge of the acidic dissociation constant of bis-tris over a range of temperature will be useful in applying the new buffer system to pH measurement and regulation in biological work.
Bis-tris was purified by recrystallization from absolute ethanol (assay 99.98 percent as determined by potentiometric titration). An attempt to prepare the bis-tris hydrochloride by passing anhydrous hydrogen chloride gas into a solution of bis-tris dissolved in methanol yielded a product whose chloride content was only 99.80 percent of the theoretical. For this reason, the solutions used for the emf measurements of the cell

\[ \text{Pt;H}_2(\text{g}), \text{Bis-Tris-HCl(m), Bis-Tris(m), AgCl;Ag} \]

was prepared from bis-tris and a standard solution of hydrochloric acid. The molality (m) of the free base was kept equal to that of the hydrochloride salt; m was varied from 0.01 to 0.1 mol kg\(^{-1}\). The temperatures at which the measurements were made ranged from 0 to 50 °C.

The emf of the cell is related to the dissociation constant of protonated bis-tris by the equation

\[ \text{pK}_a = \frac{(E-E^°)F}{2.3026 \text{RT}} + \log m_{\text{Cl}^-} + \log \frac{m_{\text{BT}^+}}{m_{\text{BT}}} + \log \frac{\gamma_{\text{BT}^+} \gamma_{\text{Cl}^-}}{\gamma_{\text{BT}}} \]  

(2)

where \(E^°\) is the standard emf of the cell. The "apparent" dissociation constant \(\text{pK}_a'\) is defined as follows:

\[ \text{pK}_a' = p(a_{\text{H}^+} \gamma_{\text{Cl}^-}) - \frac{2AI^{1/2}}{1+BAI^{1/2}} \]  

(3)

where A and B are the Debye-Hückel constants, I is the total ionic strength, and \(a\) is the ion-size parameter. For these measurements, the buffer ratio was unity, and hydrolysis of the buffer substances was negligible.
The true value of $pK_a$ is equal to $pK'_a$ at $I=0$; it was obtained by extrapolating values of $pK'_a$ to zero ionic strength, using the method of least squares. Table 2 lists the experimental $pK_a$ values together with the $\sigma$ values which gave the smallest standard deviation ($\sigma$) for $pK_a$.

The method of least squares was also used to express the $pK_a$ as a function of absolute temperature according to the equation

$$pK_a = \frac{A}{T} + B + CT \quad (4)$$

Between 0 and 50 °C, $pK_a$ is given by

$$pK_a = 1287.855/T + 2.7905 - 0.00210396T \quad (5)$$

Standard changes of enthalpy, entropy, and heat capacity in the dissociation of protonated bis-tris were derived from the constants of equation 5, and the values at 25 °C are summarized in table 3.
Table 2. $pK_a$ of protonated "bis-tris" from 0 to 50 °C.

<table>
<thead>
<tr>
<th>t, °C</th>
<th>$pK_a$</th>
<th>Ion-size parameter (Å)</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.9314</td>
<td>1.9</td>
<td>0.0002</td>
</tr>
<tr>
<td>5</td>
<td>6.8344</td>
<td>2.0</td>
<td>0.0002</td>
</tr>
<tr>
<td>10</td>
<td>6.7428</td>
<td>2.2</td>
<td>0.0001</td>
</tr>
<tr>
<td>15</td>
<td>6.6535</td>
<td>2.4</td>
<td>0.0001</td>
</tr>
<tr>
<td>20</td>
<td>6.5665</td>
<td>2.6</td>
<td>0.0001</td>
</tr>
<tr>
<td>25</td>
<td>6.4835</td>
<td>2.8</td>
<td>0.0001</td>
</tr>
<tr>
<td>30</td>
<td>6.4012</td>
<td>2.7</td>
<td>0.0001</td>
</tr>
<tr>
<td>35</td>
<td>6.3212</td>
<td>2.9</td>
<td>0.0002</td>
</tr>
<tr>
<td>40</td>
<td>6.2441</td>
<td>3.2</td>
<td>0.0002</td>
</tr>
<tr>
<td>45</td>
<td>6.1689</td>
<td>3.2</td>
<td>0.0002</td>
</tr>
<tr>
<td>50</td>
<td>6.0977</td>
<td>4.4</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

Table 3. Thermodynamic quantities for the dissociation of protonated "bis-tris" at 25 °C.

$\Delta H^\circ$: 28,238 J mol$^{-1}$

$\Delta S^\circ$: -29.4 J K$^{-1}$ mol$^{-1}$

$\Delta C_p^\circ$: 24 J K$^{-1}$ mol$^{-1}$
From the emf data one can also derive acidity functions which may be regarded as reference data useful in the study of biological systems at these particular total ionic strengths. The \( p_{a_H} \) values for bis-tris buffer solutions in water were evaluated with the aid of two relations. The first was used to interpolate \( p(a_H\gamma_{Cl}) \) at even values of \( m \):

\[
p(a_H\gamma_{Cl}) = pK_a - \beta I + \frac{2AI^{1/2}}{1+BdI^{1/2}}
\]

where \(-\beta\) is the slope of the plot of \( pK_a' \) as a function of the ionic strength. The second equation was

\[
p_{a_H} = -\log a_H = p(a_H\gamma_{Cl}) + \log \gamma_{Cl^-}
\]

The single-ionic activity coefficient \( \gamma_{Cl^-} \) was defined by the Bates-Guggenheim convention [7]

\[
-\log \gamma_{Cl^-} = \frac{AI^{1/2}}{1+1.5 I^{1/2}}
\]

The \( p_{a_H} \) values for equimolal buffer solutions are given in table 4.
Table 4. $p_{aH}$ values for buffer solutions composed of bis-tris(m) and bis-tris\cdot HCl(m) at 25 °C.

<table>
<thead>
<tr>
<th>m</th>
<th>$p_{aH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>6.532</td>
</tr>
<tr>
<td>0.02</td>
<td>6.551</td>
</tr>
<tr>
<td>0.03</td>
<td>6.565</td>
</tr>
<tr>
<td>0.04</td>
<td>6.576</td>
</tr>
<tr>
<td>0.05</td>
<td>6.586</td>
</tr>
<tr>
<td>0.06</td>
<td>6.595</td>
</tr>
<tr>
<td>0.07</td>
<td>6.603</td>
</tr>
<tr>
<td>0.08</td>
<td>6.610</td>
</tr>
<tr>
<td>0.09</td>
<td>6.617</td>
</tr>
<tr>
<td>0.1</td>
<td>6.623</td>
</tr>
</tbody>
</table>

Table 5. Residual liquid-junction errors for bis-tris buffer solutions at 25 °C.

<table>
<thead>
<tr>
<th>m=I</th>
<th>$p_{aH}$</th>
<th>pH</th>
<th>$\Delta^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>6.532</td>
<td>6.517</td>
<td>-0.015</td>
</tr>
<tr>
<td>0.02</td>
<td>6.551</td>
<td>6.529</td>
<td>-0.022</td>
</tr>
<tr>
<td>0.05</td>
<td>6.586</td>
<td>6.547</td>
<td>-0.039</td>
</tr>
<tr>
<td>0.1</td>
<td>6.623</td>
<td>6.566</td>
<td>-0.057</td>
</tr>
</tbody>
</table>

$^a$ pH - $p_{aH}$
The internal agreement of these $p_{a_H}$ values with the pH scale fixed by the NBS primary standards was examined by the intercomparison of bis-tris buffer solutions with the 0.025 m phosphate buffer [$pH(S) = 6.865$ at $25^\circ C$] in the following cell

\[
\begin{array}{c|c|c|c}
\text{Standard} & \text{KCl} & \text{Hg, KCl} & \text{Bis-Tris} \\
\text{Pt;H}_2, \text{ solution (S)} & \text{satd. calomel satd.} & \text{solution, H}_2;\text{Pt (X)} \\
\end{array}
\]

where each vertical line represents a liquid junction. The operational pH of bis-tris solutions is given by the equation

\[
pH = 6.865 + \frac{E_X - E_S}{(RT \ln 10)/F}
\]

where $E_X$ and $E_S$ are the potentials of the hydrogen electrodes in the compartments containing bis-tris and standard solution, respectively, measured with respect to the calomel reference electrode. If there is no residual liquid-junction potential, the operational pH values should be in close agreement with the corresponding assigned $p_{a_H}$ values. The degree of internal consistency can be judged by the results given in table 5.

The deviations ($\Delta$) noted for bis-tris may be compared with deviations for the following nitrogen-base buffer systems at $I = 0.02$: ammonia $\Delta = -0.014$, 4-aminopyridine $\Delta = -0.008$, and tris $\Delta = -0.020$ [8]. The results suggest that the more dilute bis-tris buffer solutions should be used for pH standardization purposes.

(M. Paabo)
C. Measurement of Acidity in Sea Water

This work has as its objective the development of standards for pH measurements in media approximating sea water in composition. These reference standards would be used to adjust pH equipment for the accurate determination of hydrogen ion concentration or activity in oceanographic studies. Materials for the preparation of the standards would be made available through the Standard Reference Materials program.

During the reporting year, this project was active in the Section only during the summer months which James T. Clark, Jr., spent at NBS as a guest worker. During the academic year, Mr. Clark continued the work as part of his graduate program at Clarkson College of Technology.

Electromotive force data for the cell

\[ \text{Pt}; \text{H}_2, \text{HCl in SSW}, \text{AgCl}; \text{Ag} \]

at several concentrations of synthetic sea water (SSW) have now been obtained at 5, 15, 25, and 35 °C. The molality of hydrochloric acid was varied over a sufficiently wide range to allow the standard potentials for the cell to be obtained by the usual extrapolation procedure. The data are now being analyzed with the aid of a computer.

Amine buffer systems have been chosen as secondary standards for sea water, in order to avoid undesirable interactions occurring with phosphates, borates, and other organic buffer materials. The emf measurements which will lead to a certification of the pH of a buffer solution composed of tris(hydroxymethyl)aminomethane and its hydrochloride in SSW have been started.

(R. G. Bates)
D. Acidity Standards for Mixtures of 2-Methoxyethanol (80 Weight Percent) and Water (20 Weight Percent)

Nonaqueous solvents and mixtures of organic solvents with water are becoming of increasing interest to complexation chemists. Indeed, many promising organic ligands cannot be investigated in aqueous solutions as they are too insoluble in water. Of the many organic solvents available, few meet the chief requirements of stability with time and acidity, ability to dissolve many organic and inorganic compounds, sufficiently high dielectric constant, and a high boiling point. In addition, ease of purification is of the utmost importance. As the overwhelming majority of stability data for complexes have been obtained through emf measurements, mainly pH measurements, it becomes urgent to establish reliable standard buffer solutions in suitable solvents.

After unsuccessful experiments with dimethylformamide were concluded (see Section 6.A), attention was given to 2-methoxyethanol, known commercially as methylcellosolve. This liquid is an extremely good solvent with a high boiling point (123.4 °C). It has low hygroscopicity and is readily miscible with water. As it has a rather low dielectric constant (16.0 at 25 °C), it seemed preferable to start the investigation with mixtures of the solvent with water. The mixture containing 80 wt percent of the organic solvent seemed particularly attractive as the dissociation constants of a number of organic compounds had already been determined in this mixture by Simon, Heilbronner, and their co-workers [9,10].
1. Media of Low Ionic Strength

Insofar as the ligands are acids or salts of organic acids, most measurements intended for the determination of stability constants are carried out in the region pH 2 to 6. Moreover, most complexation chemists work in media of constant ionic strength, most frequently using sodium perchlorate or lithium perchlorate as inert electrolytes. Even in media of low ionic strength, therefore, the usual NBS standard buffers cannot be used, as most of them contain potassium ions which cause the precipitation of insoluble potassium perchlorate. Hence, two new buffer solutions will be examined, namely 0.033M oxalic acid + 0.016M sodium oxalate, and 0.025M sodium dihydrogen phosphate + 0.025M disodium hydrogen phosphate, both in an 80 wt percent 2-methoxyethanol - 20 wt percent water solvent. For both buffers, the pH(S) will be determined in the same way as for other NBS buffers, namely through emf measurements in cells without liquid junction, together with the Bates-Guggenheim convention (equation 8) for the activity coefficient of the chloride ion.

2. Media of I = 1.0

Inasmuch as most stability constants are determined in media of high ionic strength, very often I = 1.0, it will be of importance to assign pH(S) values to buffers of ionic strength I = 1.0. The same two buffer solutions selected for low ionic strengths will be used, and the ionic strengths will be adjusted to 1.0 by the addition of suitable quantities of sodium perchlorate. The pH(S) values can be obtained in three different ways:

a. through comparison with the primary NBS buffers in cells with a liquid junction,
b. through comparison with the buffers described in the previous section, also in cells with a liquid junction, and

c. through measurements in cells without liquid junction after choice of a reasonable convention for the activity of the chloride ion in 1M solutions of sodium perchlorate. In essence, procedures a and b will lead to secondary pH standards, while c will yield primary standards. In work under way, these three approaches will be examined in detail.

(H. P. Thun)
3. STANDARDIZATION OF ION-SELECTIVE ELECTRODES

Recent progress in the development of a variety of commercial ion-selective electrodes has given the chemist access to the reasonably selective determination, by electrochemical methods, of an ever-expanding number of individual ionic species. The application, seemingly unlimited, that these electrodes may have in the fields of chemistry and biology, in industry and in the clinical laboratory emphasizes the pressing need for standardization methods and standard reference materials for use with ion-selective electrodes.

A proposed method of standardization, based on the same concepts used in the standardization of pH (hydrogen ion activity), was outlined in the last progress report [11] and in a lecture presented at the Symposium on Ion-Selective Electrodes held at NBS Gaithersburg, January 30 and 31, 1969, and soon to be published [12]. This procedure is being recommended because of the wide acceptance of the convention used to arrive at the practical activity of the hydrogen ion in fixing NBS standard pH scale. The convention entailed in the definition of the NBS standard pH scale is reasonable as well as consistent with the response of the glass electrode and other practical electrochemical sensors.

It is the purpose of the present line of investigation to demonstrate how the pH convention can be extended to a variety of activity standards for ion-selective electrodes. There are, however, several sources of error which influence this measurement of ionic activity. These errors, which include imperfect response of the electrodes, variation of potential with time or other influences (stirring, etc.), and errors due to liquid-junction potentials, are the subject of study in the Section.

(B. R. Staples)
A. The pH Convention

The convention on which a practical pH scale has been based is discussed in detail in a host of previous publications. The proposed method of adapting the convention to provide activity scales for ion-selective electrodes will be described in the sections to follow.

For pH assignment, the emf of a cell without liquid junction is measured and an acidity function $p(a_H^+\gamma_{Cl^-})$ is evaluated from it (see equation 1):

$$p(a_H^+\gamma_{Cl^-}) = -\log(m_{H^+}+\gamma_{H^+}+\gamma_{Cl^-})$$

(10)

The activity of the hydrogen ion in a chloride-free buffer solution is formally related to the acidity function in the limit of $m_{Cl^-}=0$ by

$$p_{a_H^+} = p(a_H^+\gamma_{Cl^-})^o + \log \gamma_{Cl^-}$$

(11)

The $p_{a_H^+}$ is then calculated by introducing a convention [7] for $\gamma_{Cl^-}$:

$$\log \gamma_{Cl^-} = \frac{-AI^{1/2}}{1+1.5 I^{1/2}}$$

(12)

The operational pH value for an "unknown" solution X is defined in terms of a reference standard pH(S), and the values of the emf of a pH cell containing the standard ($E_S$) and the unknown ($E_X$) by

$$pH(X) = pH(S) + \frac{E_X-E_S}{(RT \ln 10)/F}$$

(13)

In the NBS standardization procedure, the conventional $p_{a_H^+}$ values obtained as described above for selected buffer solutions are identified with pH(S) in the operational definition (equation 13).

(B. R. Staples)
B. Proposed Conventional Activities for Calibrating Ion-Selective Electrodes

The experimental arrangement by which "pA" measurements with an electrode selective for the ion A are made is entirely analogous to that for pH measurements. The electrode is usually combined with a suitable reference electrode such as a calomel electrode in a cell with liquid junction:

Electrode (sel. for A), Soln. X|Bridge, Reference Electrode

where the liquid junction is indicated by a vertical line. It is reasonable, therefore, to define operational pA values in the same manner that operational pH values are defined. If the ion A is a cation with n unit charges

\[
pA(X) = pA(S) + \frac{(E_X - E_S)nF}{RT \ln 10} \tag{14}
\]

and if A is an anion with n unit charges

\[
pA(X) = pA(S) - \frac{(E_X - E_S)nF}{RT \ln 10} \tag{15}
\]

The only difference between equations 14 and 15 is the sign of the last term.
The convention proposed for the assignment of single ionic activities to standard solutions of the ions A is the same one used in the calculation of hydrogen ion activities, namely equation 12. This convention yields values of the activity coefficient of chloride ions and therefore permits the sodium ion activity in a sodium chloride solution to be obtained from the known mean activity coefficients of NaCl:

\[ \gamma_{Na^+} = \frac{\gamma_{\pm}^2 (NaCl)}{\gamma_{Cl^-}} \]  \hspace{1cm} (16)

If the activity coefficients of sodium and chloride ions are taken to be a function only of temperature and ionic strength, it becomes possible to use these values as pathways to other single ion activity coefficients.

Using the values of \( \gamma_{Cl^-} \), for example, one can obtain, through solutions of chlorides, the activity coefficients of cations other than sodium as shown schematically in figure 3. Similarly, one can use \( \gamma_{Na^+} \) and proceed through sodium salt solutions to other single anion activity coefficients. As in the standardization of pH, these conventional values of \( pa_A \) for selected standard reference solutions are identified with \( pA(S) \) in the operational definitions set forth in equations 14 and 15. In order to demonstrate the utility of the activity scales set up in this way, however, it remains to be shown that the responses of the electrodes are consistent with the defined activities of the respective ions in solutions of a standard electrolyte.
Figure 3. Pathways leading to the activity coefficients of single ionic species.

Table 6 lists the standard pA values for solutions which have thus far been proposed. Other ions will pose more difficult problems, especially when no completely ionized reference salt can be found. Cadmium, for example, forms highly complexed species with chloride ion in solution, yet a cadmium-selective electrode senses only the free ion and must be standardized in a solution in which the activity of that ion is known. One possibility in cases of this sort is to proceed through the perchlorate
salts, most of which are highly dissociated. Further study is being devoted to elaborating procedures for ions which present special difficulties.

Table 6. Standards for pA measurements.

<table>
<thead>
<tr>
<th>Material</th>
<th>Molality</th>
<th>pCl</th>
<th>pNa</th>
<th>pCa</th>
<th>pF</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.001</td>
<td>3.015</td>
<td>3.015</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>2.044</td>
<td>2.044</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1.110</td>
<td>1.108</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.204</td>
<td>0.162</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>0.000333</td>
<td></td>
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<td>3.537</td>
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</tr>
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<td></td>
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<td></td>
<td>0.0333</td>
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<td>0.333</td>
<td></td>
<td></td>
<td>1.104</td>
<td></td>
</tr>
<tr>
<td>NaF</td>
<td>0.001</td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>2.048</td>
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<td></td>
<td>0.1</td>
<td></td>
<td></td>
<td>1.126</td>
<td></td>
</tr>
</tbody>
</table>

(B. R. Staples)
C. Measurement of Electrode Response

1. Equipment

The apparatus for measuring the emf of cells containing ion-selective electrodes was shown in figure 1 (Section 1). It consists of a vibrating-reed electrometer and a precision potentiometer which opposes the emf from the electrometer. The small difference in emf, usually 1 mV or less, is then amplified and displayed on a strip-chart recorder. It is hoped that a digital voltmeter with a degree of computer control may be obtained in the future.

2. Experimental Results

To date, all of the ion-selective electrodes have shown a nearly ideal response, i.e., a Nernstian slope when the emf of the cell is plotted as a function of the single ion activity.

a. Sodium Electrode

Measurements with the sodium glass electrode, Corning NAS 11-18, were described previously [11]. The electrode was found to respond ideally in sodium chloride solutions of concentrations from $10^{-4}$ M to 1 M. Its response was measured in a cell without liquid junction Na(gl); NaCl(m), AgCl;Ag, where m is molality. The measurements in sodium fluoride solutions, described below, depend for their interpretation on the demonstrated Nernstian behavior of the sodium glass electrode.

b. Fluoride Electrode

The potential of the fluoride electrode, Orion Model 94-09 (lanthanum fluoride type), was measured against each of the sodium glass electrodes and a saturated calomel electrode of the fiber type at temperatures of 10, 25, and 40 °C and in a concentration range from $10^{-4}$ M to 1.0 M.
The cell without liquid junction is represented by

\[ \text{Na(gl)}; \text{NaF(m), F(sel)} \]

It was standardized in a solution of sodium fluoride with a molality of 0.01 mol kg\(^{-1}\).

Mean activity coefficients of sodium fluoride were calculated from the emf data. The results at 25 °C are shown in figure 4, where the curve is drawn through the known activity coefficients of solutions of NaF. The experimental values are shown as circles.

![Figure 4](image-url)

Figure 4. Mean activity coefficients of sodium fluoride from a cell without liquid junction.
c. Calcium Electrode

The response of a calcium-selective electrode of the liquid ion-exchanger type (Orion Model 92-20) was studied in a cell without liquid junction represented by

\[ \text{Ca}(\text{sel}); \text{CaCl}_2 (I), \text{AgCl}; \text{Ag} \]

where \( I \) is ionic strength (three times the molality of calcium chloride). The cell was standardized at \( I = 0.01 \), using the known activity coefficient of calcium chloride [13]. The mean activity coefficients of calcium chloride at 25 °C obtained experimentally are plotted in figure 5 as a function of ionic strength. The curve is again drawn through the mean activity coefficients obtained by other thermodynamic methods and recorded in the literature [13,14]. The agreement is quite satisfactory, confirming the accuracy of the response of the calcium electrode in solutions of calcium chloride.

![Figure 5. Mean activity coefficients of calcium chloride from a cell without liquid junction.](image-url)
In order to examine the response of the calcium-selective electrode in mixtures of sodium chloride and calcium chloride, emf measurements of this same cell with aqueous salt mixtures of a total molality of 1.0 mol kg\(^{-1}\) were made. Poor reproducibility was observed, especially in solutions of high sodium content. In calcium chloride solutions at 25 °C, however, the calcium-selective electrode was found to be reproducible to 0.2 to 0.3 mV (0.01 pCa unit) and to reach equilibrium in about 1 min after immersion in the solution.

The response of the Beckman calcium electrode, No. 39608, was found to be Nernstian at 25 °C. Further determinations are under way.

The response of the calcium-selective electrode in calcium chloride solutions was also explored by measurements of a pCa cell with a saturated calomel reference electrode and a liquid junction [12]. The cell was standardized at I = 0.01. The results are shown in figure 6, where \(-\log \gamma_{\text{Ca}^{2+}}\), that is \(\text{pCa} + \log m_{\text{Ca}^{2+}}\), is plotted as a function of the logarithm of the ionic strength. Curve 1 was calculated by the convention proposed here, curve 2 by the MacInnes convention, and curve 3 by assuming the \(z^2\) relationship embodied in the Debye-Hückel formula, which leads to \(\gamma_{\text{Ca}^{2+}} = \gamma_+^2(\text{CaCl}_2)\). Curve 4 resulted from setting \(\gamma_{\text{Ca}^{2+}}\) equal to the mean activity coefficient of calcium chloride, as suggested by Shatkay [15].
Figure 6. Comparison of "experimental" values of the activity coefficient of calcium ion with values furnished by four conventions.

d. **Bromide Electrode**

The Beckman bromide electrode, no. 39602, (solid membrane type) has been found to respond nearly ideally at 25 °C. Further studies at temperatures of 10 and 40 °C are now going on.

(B. R. Staples)

29
D. **Liquid-Junction Errors**

The influence of the composition and concentration of the solution on the liquid-junction potential error ($\Delta E_j$) is shown in figure 7 [12]. A value of $\Delta E_j$ of 3 mV corresponds to 0.05 pCl unit. The cell consisted of a silver-silver chloride electrode used in conjunction with the saturated calomel electrode. It was standardized in a sodium chloride solution of molality 0.01 mol kg$^{-1}$, and all of the measurements were made at 25 °C. The "true" activity coefficients of chloride ion in each of the four salt solutions or aqueous salt mixtures were calculated by equation 12.

![Graph showing influence of $\Delta E_j$ on pCl measurements](image)

**Figure 7.** Liquid-junction errors in the determination of pCl.
It is seen that the variation of the liquid-junction potential error with ionic strength is about the same for all four types of solutions, but for the solutions of calcium chloride and the two mixtures it is 1 to 2 mV different from that for pure solutions of sodium chloride. The corresponding error of 0.02 to 0.04 pCl unit could be eliminated only by standardizing the cell in a solution containing the same salt or salt mixture as is present in the "unknown" solutions.

On the other hand, an error of about 4 mV (0.07 pCl unit) is incurred when the cell is standardized in 0.01 m sodium chloride and used for measurements in solutions of the same salt at a molality of 1.0 mol kg$^{-1}$. These estimates are consistent with calculated liquid-junction potentials [16]. To eliminate this concentration effect on the liquid-junction potential, it would be necessary to have a series of standard solutions of concentrations spaced over the entire range in which the electrode gives useful results. For example, if the electrode were standardized in 0.5 M sodium chloride, the error in 1.0 M sodium chloride would be reduced to about 1 mV (0.017 pCl unit).

(M. Alfenaar)
A. Dissociation of Phosphoric Acid in Deuterium Oxide

1. Measurement of the First Dissociation Constant

As a continuation of the study of acid-base equilibria in heavy water, it was of interest to determine the dissociation constant of a moderately strong acid in order to obtain more information on the relationship between the d-isotope effect and acidic strength. The first dissociation constant of phosphoric acid \( \text{pK}_1 = 2.148 \) in \( \text{H}_2\text{O} \) at 25 °C has been determined previously in heavy water only at 25 °C [17,18].

In view of the difficulties in measuring pK for an acid as strong as phosphoric, it seemed worthwhile to re-determine the dissociation constant from 5 to 50 °C by accurate emf measurements of the cell

\[
\text{Pt;D}_2\text{(g)}, \text{DCl(m)}, \text{KD}_2\text{PO}_4 \text{ (4m)}, \text{AgCl;Ag}
\]

The buffer mixture had a composition ratio of 3 moles \( \text{KD}_2\text{PO}_4 \) to 1 mole \( \text{D}_3\text{PO}_4 \) to 1 mole KCl. The molality of \( \text{D}_3\text{PO}_4 \) was varied from 0.003 to 0.05.

An expression relating the dissociation constant \( K_1 \) to the emf \( E \) of the cell was obtained by combining the Nernst equation for the emf with the mass law:

\[
\frac{(E-E^\circ)F}{2.3026 \text{ RT}} = \log m_{\text{Cl}^-} + \log m_{\text{D}_3\text{PO}_4} + \log \frac{m_{\text{D}_2\text{PO}_4}}{m_{\text{D}_2\text{PO}_4}}
\]

Since the last term of equation 17 is negligible in dilute solutions (and varies linearly with ionic strength at higher concentrations), the approximate pK value \( (\text{pK}_1) \) is given by

\[
\text{pK}_1' = \text{p}(a_D \gamma_{\text{Cl}^-}) + \log \frac{m - m_{\text{D}^+}}{3m + m_{\text{D}^+}}
\]
The acidity function $p(a_{\text{D}^\text{Cl}})$ is equivalent to the first two terms on the right of equation 17. A small correction for the ionization of phosphoric acid had to be made. This was done by estimating the deuterium ion concentration from the acidity function $p(a_{\text{D}^\text{Cl}})$:

$$-\log m_{\text{D}^+} = p(a_{\text{D}^\text{Cl}}) - \frac{2AI^{1/2} d_o^{1/2}}{1 + BaI^{1/2} d_o^{1/2}}$$

where $A$ and $B$ are the Debye-Hückel constants for heavy water, $I$ is the ionic strength, $\hat{a}$ is the ion-size parameter, and $d_o$ is the density of heavy water.

The value of $pK_\perp$, that is, the limit of $pK_\perp^I$ at $I=0$, was obtained by fitting the data to an equation linear in $I$ by the method of least squares. The ion-size parameter was varied between 3.5 and 7.0 Å, and the average value which gave the best fit at all temperatures was 5.0 Å. A plot of the data at 25 °C is shown in figure 8. The $pK_\perp$ values found at each temperature were also fitted by the method least squares to the following equation

$$pK_\perp = \frac{A}{T} + B + CT$$

where $T$ is in kelvins. The values of the constants are given in table 7, together with the calculated $pK_\perp$ values (molal scale) in heavy water and the corresponding $pK_\perp$ values obtained in ordinary water by Bates [19].
The values in water were checked by repeating the experimental procedures described above with ordinary water as solvent.

Figure 8. Removal of activity coefficient effects by extrapolation in the determination of the dissociation constant of phosphoric acid in deuterium oxide.
Table 7. Dissociation constant of phosphoric acid in deuterium oxide from 5 to 50 °C.

<table>
<thead>
<tr>
<th>t°C</th>
<th>pK₁ in D₂O&lt;sup&gt;a&lt;/sup&gt;</th>
<th>pK₁ in H₂O&lt;sup&gt;b&lt;/sup&gt;</th>
<th>pK₁ in H₂O&lt;sup&gt;c&lt;/sup&gt;</th>
<th>ΔpK&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.345</td>
<td>2.071</td>
<td>2.065</td>
<td>0.274</td>
</tr>
<tr>
<td>10</td>
<td>2.361</td>
<td>2.088</td>
<td>2.084</td>
<td>0.273</td>
</tr>
<tr>
<td>15</td>
<td>2.379</td>
<td>2.106</td>
<td>2.104</td>
<td>0.273</td>
</tr>
<tr>
<td>20</td>
<td>2.399</td>
<td>2.127</td>
<td>2.125</td>
<td>0.272</td>
</tr>
<tr>
<td>25</td>
<td>2.420</td>
<td>2.148</td>
<td>2.148</td>
<td>0.272</td>
</tr>
<tr>
<td>30</td>
<td>2.443</td>
<td>2.171</td>
<td>2.171</td>
<td>0.272</td>
</tr>
<tr>
<td>35</td>
<td>2.468</td>
<td>2.196</td>
<td>2.196</td>
<td>0.272</td>
</tr>
<tr>
<td>40</td>
<td>2.494</td>
<td>2.222</td>
<td>2.222</td>
<td>0.272</td>
</tr>
<tr>
<td>45</td>
<td>2.521</td>
<td>2.249</td>
<td>2.248</td>
<td>0.272</td>
</tr>
<tr>
<td>50</td>
<td>2.550</td>
<td>2.278</td>
<td>2.276</td>
<td>0.272</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated from the equation pK₁ = 843.979/T - 4.5714 + 0.0139555T

<sup>b</sup> Reference [19]

<sup>c</sup> This work

<sup>d</sup> (Column 2) - (Column 3)

(M. Paabo)
2. Thermodynamic Quantities for the Dissociation

The thermodynamic constants for the dissociation of phosphoric acid in heavy water at 25 °C have been determined from the temperature coefficient of $pK_1$ and are given in table 8. They can be compared with those for the dissociation of phosphoric acid in ordinary water. From these values, one can calculate the standard thermodynamic constants for the transfer process from ordinary water to heavy water, with results discussed in the next section of this report.

Table 8. Thermodynamic constants for the dissociation of phosphoric acid in deuterium oxide and water at 25 °C.

<table>
<thead>
<tr>
<th></th>
<th>in $D_2O^a$</th>
<th>in $H_2O^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^o$, J mol$^{-1}$</td>
<td>-7593 (12)</td>
<td>-7650</td>
</tr>
<tr>
<td>$\Delta S^o$, J K$^{-1}$ mol$^{-1}$</td>
<td>-71.8 (0.1)</td>
<td>-66.8</td>
</tr>
<tr>
<td>$\Delta C_p^o$, J K$^{-1}$ mol$^{-1}$</td>
<td>-159 (2)</td>
<td>-154</td>
</tr>
</tbody>
</table>

$^a$ Values in parentheses refer to the uncertainties in thermodynamic constants as estimated by the method of variance analysis.

$^b$ Reference [19] (M. Paabo)
3. **Deuterium Isotope Effects**

Soon after the discovery of heavy water it was found that weak acids are weaker in this solvent than in ordinary water. It was soon apparent that the increase in pK over that in ordinary water, known as the "deuterium isotope effect", is not the same for all acids but varies in some manner with the strength of the acid. The exact relationship between ΔpK, that is, pK (in D₂O) - pK (in H₂O), and the pK of the acid in water is not yet completely clear. It has long been agreed that the isotope effect for moderately strong acids is smaller than that for very weak acids, and it has been suggested that the isotope effect varies linearly with pK (in H₂O) [20].

Exact tests of the linear relationship are rendered difficult by the scarcity of precise data for ionization constants in deuterium oxide. This situation is slowly being remedied by the appearance of new data, in large part furnished by careful measurements made in this laboratory. For this reason, Dr. R. A. Robinson, formerly a member of the Section, was led to re-examine the data on isotope effects during the past year. The results have recently been published, together with data for the isotope effect on two protonated amines, a substituted phenol, and the mean of pK₁ and pK₂ for a polybasic carboxylic acid (citric acid) [21]. The cation acids for which pK values were reported are o-nitroanilinium and m-nitroanilinium ions; very few acids of this charge type have been studied in deuterium oxide.
A summary of the results for the deuterium isotope effect (ΔpK) on the dissociation of 15 acids is shown in graphical form in figure 9. It is clearly evident that the data do not fall on a single straight line.

Figure 9. Deuterium isotope effects (ΔpK) for weak acids at 25 °C.

1 o-Nitroanilinium ion 9 Deuterioacetic acid
2 Bisulfate ion 10 Hydrogen succinate ion
3 Phosphoric acid 11 3,5-Dinitrophenol
4 m-Nitroanilinium ion 12 Dihydrogen phosphate ion
5 4-Chloro-2,6-dinitrophenol 13 Boric acid
6 Citric acid \( (pK_1 + pK_2)/2 \) 14 Bicarbonate ion
7 Succinic acid 15 Self-dissociation of solvent
8 Acetic acid
It is more difficult, however, to classify the deviations from linearity in terms of structure and charge type. One notes that the smallest values of $\Delta pK$ are found for two mineral acids, sulfuric (2nd stage) and phosphoric acid (1st stage). It should be noted that the value of $\Delta pK$ for the latter (point 3) has been redetermined very recently with the deuterium gas electrode in cells without liquid junction [22] and found to lie very close to the straight line drawn in the figure (see Section 4.A.1). Likewise, those acids, numbered 12 through 15, which are the weakest studied, lie on or close to the straight line; they may also be classified as inorganic.

Of the acids remaining, 1 and 4 are positively-charged substituted anilinium ions; 5 and 11 are neutral phenols; 7, 8, and 9 are neutral carboxylic acids; and 6 and 10 involve carboxylic acids with a negative charge. All of these acids are organic, but both aliphatic and aromatic types are represented. Quite evidently the new data just reported (points 1, 4, 5, and 6) alter quite profoundly the concept of an isotope effect that decreases in a regular manner as the strength of the acid increases. Taken as a whole, the data tend to minimize the importance of charge type as a parameter determining the magnitude of $\Delta pK$. They do suggest, however, that organic acids may behave differently from inorganic acids. Further work may be necessary in order to demonstrate whether aromaticity plays a part in the solvent effect.

The $pK$ values of a sufficient number of weak acids have now been determined over a range of temperature in both water and deuterium oxide to make worthwhile a comparison of the enthalpy, entropy, and heat capacity effects. Such a comparison is made in table 9; the acids are arranged in order of increasing $pK$ (decreasing strength).
The figures given in each column represent the excess of the indicated thermodynamic quantity (ΔH°, ΔS°, or ΔC°p) in deuterium oxide over the value in water. The differences in enthalpy and heat capacity are seen to increase as the acid becomes weaker, but the isotope effect on the entropy change appears to be nearly independent of the acidic strength.

Table 9. Deuterium isotope effect on the thermodynamic constants for the dissociation of weak acids at 25 °C.\(^a\)

<table>
<thead>
<tr>
<th>Acid</th>
<th>ΔH°(d)-ΔH°(h)</th>
<th>ΔS°(d)-ΔS°(h)</th>
<th>ΔC°p(d)-ΔC°p(h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric</td>
<td>57(^b)</td>
<td>-5.0(^c)</td>
<td>-4(^c)</td>
</tr>
<tr>
<td>Acetic</td>
<td>1561</td>
<td>-5.4</td>
<td>-8</td>
</tr>
<tr>
<td>Acetic-d(_3)</td>
<td>1456</td>
<td>-5.4</td>
<td>-17</td>
</tr>
<tr>
<td>Primary phosphate ion</td>
<td>1628</td>
<td>-5.9</td>
<td>-18</td>
</tr>
<tr>
<td>Bicarbonate ion</td>
<td>2564</td>
<td>-5.9</td>
<td>+15</td>
</tr>
<tr>
<td>Solvent</td>
<td>3284</td>
<td>-7.3</td>
<td>-34</td>
</tr>
</tbody>
</table>

\(^a\) d = in D\(_2\)O; h = in H\(_2\)O

\(^b\) J mol\(^-1\)

\(^c\) J K\(^-1\) mol\(^-1\)

(R. G. Bates)
B. First Dissociation Constant of Piperazinium Ion in 50 Weight Percent Methanol-Water Solvent

As part of a study of the process by which cationic weak acids dissociate, the acidic ionization constants of tris(hydroxymethyl)aminomethane [23], ammonia [24], and 4-aminopyridine [25] have been determined in the 50 weight percent methanol-water solvent.

Work is now in progress on diprotonated piperazine. This acid has a double positive charge, and a positively charged conjugate base is formed in the first dissociation step.

\[ \text{PzH}_2^{++} + \text{SH} \iff \text{PzH}^+ + \text{SH}_2^+ \]

where Pz is written for the neutral base piperazine and SH represents the amphiprotic solvent. The two dissociation constants of piperazinium ion in water were determined recently in this laboratory [26] thus making it possible to estimate the medium effect \( p(K_s) - p(K_w) \). The subscripts \( s \) and \( w \) indicate the standard state to which the thermodynamic quantity is referred: 50 percent methanol (s) or water (w).

Emf measurements were made at seven temperatures from 10 to 40 °C for the cell

\[ \text{Pt}, \text{H}_2(g), \text{Pz} \cdot 2\text{HCl}(m), \text{Pz} \cdot \text{HCl}(m) \text{ in 50 wt } \% \text{ MeOH-H}_2\text{O, AgCl;Ag} \]

The concentrations of the two hydrochlorides were kept equal and the molality of each varied from 0.0025 to 0.05 mol kg\(^{-1}\). A slight correction was made for the ionization of \( \text{PzH}_2^{++} \). The molality of hydrogen ion was estimated with the aid of the acidity function \( p_s(a_{H\gamma Cl}) \).

The method of calculating \( p(K_1) \) followed closely that outlined above in Section 4.A.1. In this instance, however, the activity coefficient term was, as expected, far from
negligible. For the calculation of $p(sK_1)'$ it was estimated by a Debye-Hückel equation having the same form as the last term in equation 19 (the coefficient 2 in the numerator being replaced by 4, as required by the charges of the species participating in the dissociation process).

The value of $p(sK_1)$, that is, the limit of $p(sK_1)'$ at zero ionic strength, was calculated by the method of least squares for several values of the ion-size parameter (Å) at 25 °C. The smallest standard deviation for $p(sK_1)$ was obtained with $\text{Å}=2$ Å. The resulting medium effects for piperazinium ion and other weak bases studied are given in table 10.

It is evident that the initial decrease in $pK_a$ for positively charged weak acids now generally recognized to occur when methanol is added to the aqueous solvent, is accentuated by doubling the charge on the cation acid. Further work on this base in other solvent compositions at 25 °C is planned.

Table 10. Values of $p(sK)$ for the dissociation of protonated weak bases in 50 wt % methanol-water at 25 °C and related solvent effects.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$p(sK_a)$</th>
<th>$p(wK_a)$</th>
<th>$\Delta^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piperazinium (first step)</td>
<td>4.583</td>
<td>5.333</td>
<td>-0.750</td>
</tr>
<tr>
<td>Protonated tris</td>
<td>7.818</td>
<td>8.075</td>
<td>-0.254</td>
</tr>
<tr>
<td>4-Aminopyridinium</td>
<td>8.518</td>
<td>9.114</td>
<td>-0.596</td>
</tr>
<tr>
<td>Ammonium</td>
<td>8.687</td>
<td>9.245</td>
<td>-0.558</td>
</tr>
</tbody>
</table>

$\Delta = p(sK_a) - p(wK_a)$

(M. Paabo)
C. Dissociation of Protonated Tris(hydroxymethyl)aminomethane in Aqueous Alcohol Solvents

Acid-base behavior in mixed solvents of which water is one component has been a subject of interest in the Section for a number of years. These studies have the aim of shedding light on ion-solvent interactions and other medium effects. Investigations of this sort, it is hoped, may eventually point the way to a single acidity scale for different mixed solvent systems. The nature of solvent effects on the equilibrium behavior of electrolytes in mixed solvents was discussed in earlier progress reports [2,11] and in a lengthy review published during the past year [27].

Schindler, Robinson, and Bates [28] determined the dissociation constant of the protonated form of tris(hydroxymethyl)aminomethane in methanol-water solvents containing 30, 50, 70, and 90 wt percent methanol by a potentiometric titration method. This procedure is relatively simple, utilizing glass electrodes in a cell without liquid junction, yet capable of yielding results accurate to better than 0.01 in pK.

We have now extended these measurements to demonstrate the influence of the nature of the alcohol, studying the pK of protonated tris in aqueous solvent mixtures containing 50 wt percent ethanol, n-propanol, or tert-butanol. All of the measurements were made at 25 °C.
The cell

Glass electrode; HCl (0.01m) + tris in 50 wt % alcohol-water, AgCl;Ag

was used. The cell vessel is shown in figure 10. The initial emf \(E_1\) was measured at equilibrium before any tris had been added.

Figure 10. Cell vessel for determining pK by potentiometric titration without a liquid junction.
Successive additions of a solution 0.01 m in HCl and 0.1 m in tris (m=molal) in the alcohol-water solvent under study led to emf values designated E₂. In this way, both E₁ and E₂ were determined at a constant chloride molality and a constant total ionic strength, while the buffer ratio (tris/tris.HCl) was changed. A similar procedure, using the hydrogen gas electrode instead of the glass electrode, was developed in the Section many years ago [29].

The activity coefficient term in the expression for pK is of such form as to be negligible in dilute solutions [28]; hence, a close approximation to the pK is obtained from the equation

$$pK = \frac{(E_2 - E_1)}{(RT \ln 10)/F} + \log \frac{m_{BH^+}}{0.01m_B}$$ (21)

where $m_{BH^+}$ and $m_B$ are respectively the molalities of protonated tris and the free tris base in the solution for which $E_2$ was measured.

Preliminary results for the pK of protonated tris in 50 wt percent aqueous methanol, ethanol, n-propanol, and tert-butanol at 25 °C are given in table 11. On the basis of these results, the pK seems to be lower in ethanol than in the other alcohols of the series.

Table 11. pK values for tris.H⁺ in 50 wt % aqueous alcohols.

<table>
<thead>
<tr>
<th>Alcohol (50 wt %)</th>
<th>pK</th>
<th>Solvent density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>7.799</td>
<td>0.9125</td>
</tr>
<tr>
<td>Ethanol</td>
<td>7.654</td>
<td>0.9138</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>7.780</td>
<td>0.9095</td>
</tr>
<tr>
<td>tert-Butanol</td>
<td>7.758</td>
<td>0.8985</td>
</tr>
</tbody>
</table>
Further work is under way. In a qualitative manner, the trend in pK suggests a possible influence of solvent structure. The differences in pK are not large, and it is possible that the comparison may have to be made at equal mole fractions of alcohol, where the numbers of solvent molecules are the same. The pK of tris\(\cdot\)H\(^+\) in water at 25 °C is 8.075 [30].

(B. R. Staples, R. S. Carter, Jr.)

D. Thermodynamics of Hydrochloric Acid in N-Methylpropionamide Solvents

Electromotive force studies in N-methylpropionamide (NMP) and in mixtures of NMP with cyclohexane or decalin have been conducted in the Section by Edgar S. Etz as part of his graduate program at Clarkson College of Technology. The experimental work was described in the two preceding annual reports [2,11]. Measurements have been made from 5 to 55 °C.

Mr. Etz returned to the Section for the summer months of 1968, devoting his time to a detailed computer analysis of the data. His efforts resulted in 1) values of the standard emf of the hydrogen-silver chloride cell when the solvent is NMP or a mixture of NMP with one of the two hydrocarbons studied, 2) the activity coefficient, partial molal heat content, and partial molal heat capacity of hydrochloric acid in these nonaqueous solvents, and 3) the changes in Gibbs energy, enthalpy, and entropy on the transfer of one mole of HCl from the standard state in water to the standard state in these three nonaqueous solvent systems.
Accurate thermodynamic data for electrolytes in anhydrous systems have rarely been obtained, and consequently these results are of considerable scientific interest. Pure NMP has a very high dielectric constant (175.6 at 25 °C). Interionic attractive forces might therefore be expected to be small, and indeed the activity coefficient of hydrochloric acid in this solvent exceeds 0.96 for all concentrations (C) less than 0.1 mole per liter, as shown in figure 11.

Figure 11. Comparison of the activity coefficient of hydrochloric acid in NMP with that in water.
Through the study of NMP-hydrocarbon mixtures "isodielectric" with water it was hoped to compare solvent basicities. When electrostatic contributions are approximately equalized by this device, it is reasonable to expect that the energy change in the transfer of hydrochloric acid from water to a nonaqueous solvent will reflect primarily the relative magnitudes of the solvation interactions in the two solvents. The interaction between the proton and solvent proton acceptors (bases) is likely to be important here. Because of the large difference between the dielectric constants of the pure solvents water and NMP, such a comparison of transfer energies is not likely to be very useful as a measure of relative basicities.

Thus far, it has not been possible to interpret the results in terms of a difference in intrinsic basicity of the two solvents water and NMP. This conclusion is consistent with the growing recognition [31] that "intrinsic basicity" is not a meaningful concept in hydrogen-bonded mixed solvent systems.

A portion of this work was presented by Professor Donald Rosenthal in the Fisher Award Symposium held on April 17, 1969, as part of the National Meeting of the American Chemical Society at Minneapolis, Minnesota.

(R. G. Bates)
E. Thermodynamics of Hydrochloric Acid in Mixtures of 2-Methoxyethanol (80 Weight Percent) and Water (20 Weight Percent)

In order to base standards for pH in 80 wt percent 2-methoxyethanol on emf measurements, it is first necessary to determine the standard emf of the hydrogen-silver chloride cell for this solvent system. The requisite measurements, made over a range of temperatures, will yield not only the standard emf but also information on the thermodynamic behavior of hydrochloric acid in this mixed solvent.

1. Vapor Pressures of the Solvent

In order to make the hydrogen pressure corrections to the measured emf values, the vapor pressures of the solvent at different temperatures have to be known. The apparatus for the vapor pressure determination is shown in figure 12. A flask containing the solvent is submerged in a water bath with temperature control to ±0.01 °C. The flask is connected with a U-tube mercury manometer and the pumping system. To obtain a good vacuum, three pumps were used in series; these were a mercury diffusion pump, an oil diffusion pump, and a mechanical pump. Because 2-methoxyethanol attacks the high vacuum grease, Teflon stopcocks had to be used.

Before connecting the flask to the vacuum line, the temperature of the solvent was lowered to -72 °C, so that the evacuation of the system could not cause any change in the composition of the liquid. To avoid condensation of vapors in the manometer, the latter was placed in a controlled air bath with a transparent plastic panel, so that the manometer could be kept at 54 °C throughout the measurements.
The rest of the apparatus, except for the flask, was wrapped with heating tape and kept at a temperature well above 50 °C. Before starting the measurements, the pressure in the apparatus was reduced below 1 μm Hg. The manometer was read with a cathetometer giving a precision of 0.05 mm Hg.

Figure 12. Apparatus for measuring the vapor pressure of solvents.
The measured values of the vapor pressures of the binary solvent mixture 2-methoxyethanol (80 wt percent) - water (20 wt percent) in the temperature range 10 to 50 °C are given in table 12. Least-squares treatment of the results yielded the following equation:

\[ \log p = 11.502 - \frac{2,419.46}{T} \]  \hspace{1cm} (22)

where \( p \) is the vapor pressure in \( \text{Nm}^{-2} \) and \( T \) is the temperature in kelvins (1 normal atmosphere = 1.01325x10^5 \( \text{Nm}^{-2} \)).

Table 12. Vapor pressures of a mixture of 2-methoxyethanol (80 wt %) and water (20 wt %) from 10 to 50 °C.

<table>
<thead>
<tr>
<th>( t, , ^\circ\text{C} )</th>
<th>( p, , \text{Nm}^{-2} )</th>
<th>( p, , \text{mm Hg} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>907</td>
<td>6.8</td>
</tr>
<tr>
<td>15</td>
<td>1266</td>
<td>9.5</td>
</tr>
<tr>
<td>20</td>
<td>1733</td>
<td>13.0</td>
</tr>
<tr>
<td>25</td>
<td>2480</td>
<td>18.6</td>
</tr>
<tr>
<td>30</td>
<td>3333</td>
<td>25.0</td>
</tr>
<tr>
<td>35</td>
<td>4486</td>
<td>33.6</td>
</tr>
<tr>
<td>40</td>
<td>5993</td>
<td>44.9</td>
</tr>
<tr>
<td>45</td>
<td>7846</td>
<td>58.9</td>
</tr>
<tr>
<td>50</td>
<td>10159</td>
<td>76.2</td>
</tr>
</tbody>
</table>
2. Dielectric Constants of the Solvent

The dielectric constants of the mixed solvent were measured at 10, 25, and 50 °C, using freshly distilled water and spectro-grade acetone as reference materials. The measurements were carried out with the Multidekameter instrument. The temperature of the cell was adjusted to within 0.1 °C of the desired temperature by circulating water from a constant-temperature bath. The following values of the dielectric constant have been obtained: 34.7 at 10 °C, 31.5 at 25 °C, and 27.8 at 50 °C.

3. Determination of Acidity Functions

Electromotive force measurements of cells without liquid junction of the type

\[ \text{Pt;H}_2(g), \text{HCl(m)} \text{ in 2-methoxyethanol-H}_2\text{O, AgCl;Ag} \]

were made with 12 different molalities (m) of hydrochloric acid in the solvent 2-methoxyethanol (80 wt percent) - water (20 wt percent) over the temperature range 10 to 50 °C. The temperature was controlled to 0.01 °C, and the emf was measured with a precision potentiometer. The observed potentials were very stable, and the reproducibility of duplicate cells was nearly always better than 0.1 mV. These data will serve for a calculation of the standard emf of the cell for this mixed solvent system.

Values of the acidity function \( p_w(a_{H\gamma Cl}) \), referred to the aqueous standard state, have been derived from the emf, with the use of the standard emf obtained from measurements in water solvent [32]. Acidity functions at 25 °C are given in table 13. The mean activity coefficient of hydrochloric acid \( (w\gamma_\pm) \), referred to the standard state in pure water, is also of interest. It was calculated from the acidity functions by the equation
\[-\log w \gamma_\pm = \left[ p_w(a_H \gamma_{Cl}) + \log m \right]/2 \quad (23)\]

and is listed in the last column of the table.

**Table 13.** Values of \( p_w(a_H \gamma_{Cl}) \) and \( w \gamma_\pm \) for hydrochloric acid in a mixture of 2-methoxyethanol (80 wt %) and water (20 wt %) at 25 °C.

<table>
<thead>
<tr>
<th>( m \times 10^3 )</th>
<th>emf, mV</th>
<th>( p_w(a_H \gamma_{Cl}) )</th>
<th>( w \gamma_\pm )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.05</td>
<td>401.38</td>
<td>0.634</td>
<td>7.59</td>
</tr>
<tr>
<td>6.01</td>
<td>382.32</td>
<td>0.483</td>
<td>7.40</td>
</tr>
<tr>
<td>9.31</td>
<td>364.28</td>
<td>0.368</td>
<td>6.78</td>
</tr>
<tr>
<td>10.90</td>
<td>356.14</td>
<td>0.299</td>
<td>6.79</td>
</tr>
<tr>
<td>17.07</td>
<td>338.17</td>
<td>0.190</td>
<td>6.15</td>
</tr>
<tr>
<td>21.83</td>
<td>326.50</td>
<td>0.100</td>
<td>6.04</td>
</tr>
<tr>
<td>32.38</td>
<td>311.58</td>
<td>0.019</td>
<td>5.45</td>
</tr>
<tr>
<td>42.13</td>
<td>299.18</td>
<td>-0.077</td>
<td>5.32</td>
</tr>
<tr>
<td>58.58</td>
<td>287.19</td>
<td>-0.136</td>
<td>4.83</td>
</tr>
<tr>
<td>78.55</td>
<td>273.70</td>
<td>-0.237</td>
<td>4.69</td>
</tr>
<tr>
<td>94.24</td>
<td>267.77</td>
<td>-0.258</td>
<td>4.39</td>
</tr>
<tr>
<td>106.20</td>
<td>261.16</td>
<td>-0.318</td>
<td>4.43</td>
</tr>
</tbody>
</table>

The magnitude of the activity coefficient (4 to 8) demonstrates that hydrochloric acid has a higher free energy or "escaping tendency" in the mixed solvent than in water. This result is consistent with data for
other mixed solvents such as dioxane-water [33]. It may be attributed largely to the lowered dielectric constant produced by the addition of 2-methoxyethanol to water, with the consequent increase in the energy of charged species in the medium. It is likely that a contrary influence, obscured by this larger electrostatic effect, is exerted by ion pairing, some of which is to be expected in a solvent of dielectric constant near 30.

(H. P. Thun)
5. OCEANOGRAPHIC CONDUCTANCE STANDARDS

A. Apparatus

The program of conductivity research has been directed toward the attainment of the highest accuracy in the measurement of the conductance of aqueous salt solutions. The direct objective is the certification of sodium chloride solutions suitable for the calibration of oceanographic salinometers. The needs for that project were outlined in the annual progress report for 1968 [11].

Since last year the major modification of equipment was the incorporation of the Janz-McIntyre bridge in a single cabinet, shown in figure 13. At the same time, the following changes were made to the bridge:

(1) The output from the impedance unbalance meter was brought to an external d-c amplifier, permitting interpolation of the lowest decade of the resistance arm to 0.01 ohm.

(2) Shields of the cell leads were connected to the reversing switch so that the shields of the low-potential leads are in the guard circuit of the comparator, while the shields of the high-potential leads are grounded.

(3) Provision was made for connecting a fixed 10,000-ohm coil in parallel with the unknown in order to extend the range of measurements to higher impedances. In this configuration, the four-terminal method of measurement does not strictly eliminate the effect of lead impedance, but the small correction can be calculated readily.
Figure 13. Janz-McIntyre bridge for conductivity measurements.

Five cells, having constants of approximately 10, 40, 80, 120, and 160, were constructed. Three of these are shown in figure 14. The others are similar, differing only in the length and diameter of the capillary section. All have 2.5 cm diameter bright platinum electrodes and four leads terminating in shielded connectors.

(T. B. Hoover)
B. Calibration of Cells

Three of the cells were calibrated at 18 and 25 °C with 0.1 demal potassium chloride solutions prepared with salt from two different sources. Statistical analysis of the results showed a standard deviation of the cell constants of 100 ppm. About half of this is accounted for by a significant trend of the deviations in the direction of higher constants at the end of the week of measurements.
Another series of calibrations of all five cells with 0.01, 0.1, and 1 demal solutions from a single supply of potassium chloride has been completed experimentally, also at 18 and 25 °C, but the results have not been fully analyzed.

In addition to the calibration corrections for the resistances of the bridge coils, two other significant corrections need to be applied to the raw data. These are for variations of temperature and for frequency effects.

Temperatures of the oil thermostat, which is shown in figure 15, were measured with two platinum resistance thermometers. In 28 measurements, the maximum difference between the readings of the two thermometers was $3.6 \times 10^{-3}$ K, while the mean difference and standard deviation were $2 \times 10^{-4}$ K and $16 \times 10^{-4}$ K, respectively. A continuous record of the temperature for several hours indicated cyclic fluctuations of ± 0.001 K with a period of 2-3 minutes. The heat capacity of the cell probably smooths out some of this variation, but the absolute temperature must be considered uncertain to at least 0.002 K. This uncertainty is equivalent to about 40 ppm in the conductance of the solution.

Frequency effects resulting from polarization of the electrodes are an inherent source of error in electrode-type conductivity cells. It was considered desirable to avoid platinization of the electrodes because of the uncertainty associated with adsorption effects on platinum black. Consequently, other experimental means of reducing the effects of polarization were investigated. These included: (1) differential measurement between cells with different cell constants in the reference and unknown arms of the bridge [34], (2) constant impedance, in which the reference arm was a fixed resistor and the variable resist-
Figure 15. Oil thermostat for conductivity measurements.

... ance was in series with the cell, and (3) four-electrode cells, such as that shown in figure 16. In the latter method the electrodes are part of the lead impedances, and polarization effects were expected to cancel by the four-terminal method of measurement. The cylindrical potential electrodes shown in the photograph were placed in a region of minimum potential gradient.

In each of these procedures very large frequency effects were observed, which probably were a consequence of introducing an impedance in series with the cell. One current lead then was neither at the detector potential nor at the output potential of the bridge.
Figure 16. Four-electrode conductivity cell.

Admittance from this lead to its shield would act as a frequency-dependent shunt across other portions of the circuit. When the impedance between current and potential electrodes of the four-electrode cells was made small, as shown, the effect was reduced, but not to the level found for the conventional two-electrode cells.

The mathematical correction for polarization effects by extrapolation is strictly empirical, although Feates, Ives, and Pryor [35] solved the balance conditions for a simple model of electrode polarization. The Janz-McIntyre bridge is not very suitable for investigating frequency effects because it provides only four output frequencies.
Nevertheless, a computer program to fit the observations to the Feates-Ives-Pryor model showed that the high-frequency limit of extrapolation was always very close to the value measured at 10 kHz. On the other hand, measurement of some of the same cells with the unshielded Jones-Dike bridge at nine or ten frequencies showed a precisely linear relation between resistance and reciprocal frequency between 1 and 20 kHz, provided the resistance was less than 1500 ohms.

As a further check of results obtained with the Janz-McIntyre bridge, the same solution was measured in a cell before and after the electrodes had been coated with palladium black, and again after stripping off the palladium electrolytically. As expected, the calculated double-layer capacity and leakage resistance varied considerably with electrode treatment. The high-frequency resistance of the electrolyte also varied significantly according to the Feates-Ives-Pryor calculation but was quite consistent according to the simpler inverse frequency extrapolation. It was concluded that the theoretical model [35] is not applicable to the systems under investigation.

(T. B. Hoover)
C. Conductance of Natural and Synthetic Sea Water

Specific conductances of samples of synthetic sea water used for acidity measurements (Section 2.C) were measured at 15 and 25 °C. In general, the conductances were about 7 percent lower than the values corresponding to natural sea water of the same chlorinity [36]. Two ampoules of Standard Sea Water, Lot P50, were also measured at 15 and 25 °C in each of two cells. These results lay within a range of 50 ppm at each temperature and were in close agreement with the published values of Reeburgh [36]. Twenty-two samples of natural sea water varying in salinity from 0.5 to 40% have been measured at 20 °C for use by the Naval Oceanographic Instrumentation Center in calibrating salinometers.

(T. B. Hoover)
6. PREPARATION AND PROPERTIES OF SOLVENTS

A. Dimethylformamide

Dimethylformamide and water appeared to form a suitable solvent system for the study of the stability of complexes dependent on acidity and dielectric constant. Dimethylformamide boils at 153 °C, has a dielectric constant of 36.7 at 25 °C, and dissolves readily most organic as well as many inorganic compounds. It can be easily purified, but it has the disadvantage of high hygroscopicity and is subject to hydrolysis catalyzed by acids and bases. Dimethylformamide of the highest grade commercially obtainable was stated to contain less than 0.01 percent of water. The solvent was distilled to remove possible organic impurities. After the bottles had been opened several times during normal use, the water content was found to be 0.015 percent by Karl Fischer titration.

Unfortunately, dimethylformamide had to be abandoned after preliminary emf measurements were made. The emf was unstable, the marked drift presumably being caused by hydrolysis and the formation of complexes with silver chloride [37,38].

(H. P. Thun)

B. 2-Methoxyethanol

Reagent-grade 2-methoxyethanol (methylcellosolve) was acquired from commercial sources. It was stated to contain less than 0.03 percent water. Gas chromatographic analysis, performed by D. Enagonio of the Separation and Purification Section, confirmed this statement; no other impurities could be detected.

(H. P. Thun)
C. Sulfolane

A new dipolar aprotic solvent, tetramethylene sulfone (sulfolane), with a moderately high dielectric constant (43 at 30 °C), has attracted recent attention. It has been used as a solvent for potentiometric titrations, for kinetic and spectrophotometric measurements, and for polarography. As a continuation of our program of development and application of acidity scales in nonaqueous media, it was of interest to use this new solvent in emf studies.

Commercial sulfolane was purified by vacuum distillation from sodium hydroxide pellets [39] through a 1-meter column packed with fine glass rings. This particular still has been used previously in the Section for the purification of various organic solvents. It is shown in figure 17. The original sample had a conductivity of 1.7x10^{-6} \ \Omega^{-1} \ \text{cm}^{-1}. A gas chromatographic analysis performed by Dr. R. T. Leslie of the Separation and Purification Section indicated that the sample contained about 0.5 percent water and about 1.8 percent of an unidentified compound.

The first distillation at 4 mm Hg reduced the conductivity to 3.7-7.8x10^{-8} \ \Omega^{-1} \ \text{cm}^{-1}. The product of a second distillation at 4 mm Hg and 126 °C had a conductivity of 6.1x10^{-8} \ \Omega^{-1} \ \text{cm}^{-1}, and its appearance was clear and colorless as compared to the original amber sample.

Emf measurements at 25 °C were made of the cell

\[
\text{Pt;H}_2(g), \text{HCl in sulfolane, AgCl;Ag}
\]

The cell solution was prepared by passing anhydrous hydrogen chloride through sulfolane. The color of the solution soon changed to pale yellow, and in a few days it resembled the amber shade of the original sample.
The molality of hydrogen chloride was about 0.0175 as determined by titration with aqueous sodium hydroxide solution using bromothymol blue indicator to detect the end point. The emf of the cell never became constant; it increased from -0.02 to +0.28V in the course of 2-1/2 days. The concentration of hydrochloric acid was the same at the end of the run as at the beginning.
A second cell containing 0.026 molal HCl in a mixture of 50 moles percent sulfolane and water was studied. No coloration of the aqueous solution of sulfolane was observed. The emf of the cell came to an equilibrium value of about 0.255 V, but the emf readings were very sensitive to the rate of hydrogen bubbling. An increase in the rate reduced the emf by several millivolts, and a decrease of the rate increased the emf. At a constant rate of flow the emf was stable to about 0.5 mV for a period of 12 hours. The cause of the instability was not determined. Coetzee and Bertozzi [40] found the hydrogen electrode to function normally in sulfolane. It is likely that the source of instability is the silver-silver chloride electrode.

(M. Paabo)
### 7. STANDARD REFERENCE MATERIALS ACTIVITY

#### A. Summary

<table>
<thead>
<tr>
<th>Material</th>
<th>SRM No.</th>
<th>Determined</th>
<th>Analyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Bicarbonate</td>
<td>(191)</td>
<td>pH</td>
<td>BRS</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>(192)</td>
<td>pH</td>
<td>BRS</td>
</tr>
<tr>
<td>Potassium Dihydrogen Phosphate (2186I)</td>
<td></td>
<td>pD</td>
<td>MP</td>
</tr>
<tr>
<td>Disodium Hydrogen Phosphate (2186II)</td>
<td></td>
<td>pD</td>
<td>MP</td>
</tr>
<tr>
<td>Sodium Bicarbonate</td>
<td>(2191)</td>
<td>pD</td>
<td>MP</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>(2192)</td>
<td>pD</td>
<td>MP</td>
</tr>
<tr>
<td>Ion-selective electrodes (In process)</td>
<td>(3024767)</td>
<td>pA</td>
<td>BRS, MA</td>
</tr>
<tr>
<td>Sea Water Conductivity (In process)</td>
<td>(3024759)</td>
<td>Conductivity</td>
<td>TBH</td>
</tr>
<tr>
<td>Bilirubin (In process)</td>
<td>(3024761)</td>
<td>Assay</td>
<td>TBH</td>
</tr>
<tr>
<td>pH in Sea Water (In process)</td>
<td>(3022753)</td>
<td>pH</td>
<td>ESE</td>
</tr>
</tbody>
</table>

**Analyst**

- BRS - B. R. Staples
- MP - M. Paabo
- MA - M. Alfenaar
- TBH - T. B. Hoover
- ESE - E. S. Etz
B. **Standard Materials for Acidity Measurements**

With the completion of the analysis and certification of potassium dihydrogen phosphate, disodium hydrogen phosphate, sodium bicarbonate, and sodium carbonate [11], these materials were added to the list of NBS Standard Reference Materials for the measurement of pH and pD. Potassium dihydrogen citrate promises to be a most useful reference material for acidity measurements both in H₂O and D₂O, and it is regrettable that no commercial source of this salt in pure form has yet been found. In anticipation of the issuance of this material, however, SRM numbers have already been assigned. Table 14 is a summary of the Standard Reference Materials for acidity measurements; although the potassium dihydrogen citrate is not yet available, it is listed in the table.


<table>
<thead>
<tr>
<th>SRM No.</th>
<th>pH Standards</th>
<th>SRM No.</th>
<th>pD Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>185d</td>
<td>Acid potassium phthalate</td>
<td>2186I</td>
<td>Potassium dihydrogen phosphate</td>
</tr>
<tr>
<td>186Ic</td>
<td>Potassium dihydrogen phosphate</td>
<td>2186II</td>
<td>Disodium hydrogen phosphate</td>
</tr>
<tr>
<td>186IIb</td>
<td>Disodium hydrogen phosphate</td>
<td>2190</td>
<td>Potassium dihydrogen citrate</td>
</tr>
<tr>
<td>187a</td>
<td>Borax</td>
<td>2191</td>
<td>Sodium bicarbonate</td>
</tr>
<tr>
<td>188</td>
<td>Potassium hydrogen tartrate</td>
<td>2192</td>
<td>Sodium carbonate</td>
</tr>
<tr>
<td>189</td>
<td>Potassium tetroxalate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>Potassium dihydrogen citrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>191</td>
<td>Sodium bicarbonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>192</td>
<td>Sodium carbonate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(R. G. Bates)

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C. Standard Materials for Conductivity Measurements

The oceanographic conductance standards discussed in Section 5 should find application as well in the calibration of conventional conductivity cells used in research. Although it is fundamentally desirable that such standards should be determined absolutely, e.g., in terms of the physical dimensions of a suitable cell and the absolute ohm, the difficulties of such a determination dictate that all sources of error should be systematically investigated. Several efforts in this direction have been described above. On the other hand, the general adoption of the Jones and Bradshaw [41] aqueous potassium chloride conductance standards for research on electrolyte solutions emphasizes the practical advantage of retaining these chemical standards even though they may be shown to be in error. We have adopted as a provisional reference the specific conductance datum of Jones and Bradshaw for 0.1 demal potassium chloride at 25 °C. As part of the development of accurate conductivity techniques, inconsistencies among the other eight standards of Jones and Bradshaw will be sought.

The adoption of a reference material (potassium chloride) for conductivity permits some specifications for purity to be set up. The mobilities of most inorganic ions are sufficiently similar that ionic impurities at the ppm level are not a serious source of error. Exceptions are the hydrogen and hydroxyl ions which have high mobilities in water. It can be shown that if the pH of 3.5 M potassium chloride or of 3.0 M sodium chloride is within 2 units of neutrality the contribution to the specific conductance is less than 10 ppm. This requirement is not particularly stringent but cannot be ignored. Nonelectrolyte impurities interfere only as a weighing error and are not serious at the ppm level.
Water, however, may be present at significant levels, especially in hygroscopic salts.

A comparison of 0.1 demal solutions was made between a commercial "ultrapure" sample of potassium chloride and a laboratory preparation that had been purified by the procedure of Pinching and Bates [42] and in addition had been treated by ion exchange to reduce other alkali metals to a negligible concentration. The conductance of the solution of the commercial sample was 0.07 percent lower than that prepared from the fused laboratory preparation of potassium chloride. When the commercial material was dried for three hours at 300 °C it lost 0.045 percent of its weight. The conductance of a 0.1 demal solution of the dried material was again 0.035 percent lower than that of the reference solution. Coulometric assay of the solutions showed that the former was also 0.036 percent lower in chloride. The discrepancy is believed to be due largely to mother liquor entrained in the crystals of the commercial specimen.

(T. B. Hoover)

D. Acidimetric Assay of Bilirubin

1. General Considerations

Effort has been directed toward developing a stoichiometric assay procedure for bilirubin, which is urgently needed as a biological standard reference material. Bilirubin, which has a molecular weight of 584.7, has two carboxyl groups, suggesting that these functional groups might be titratable in a suitable system. Bilirubin was known to be very insoluble in water but quite readily soluble in dimethylsulfoxide (DMSO) and in strong alkali.
In alkaline aqueous solution it is readily degraded by oxygen and light. Consequently, titrations were carried out in closed vessels, under argon atmosphere, and shielded from direct light. Reagents were added through a septum by means of a hypodermic syringe. Efforts were made to avoid a pH greater than 10 and to keep exposure to stronger alkali as brief as possible consistent with complete solution of the sample.

2. Conductance Measurements

Exploratory measurements were made in dimethylformamide (solvent conductance $4 \times 10^{-7} \, \Omega^{-1} \, cm^{-1}$) and in DMSO (solvent conductance $4 \times 10^{-8} \, \Omega^{-1} \, cm^{-1}$). In both solvents bilirubin appeared to be a very weak electrolyte and the salt form differed little in equivalent conductance from the titrant (tetrabutylammonium hydroxide). Consequently, the end points of the titrations were barely detectable.

In the aqueous system, bilirubin was dissolved in an excess of 0.05 M sodium hydroxide and back-titrated with 0.05 M hydrochloric acid. Significant differences in the slopes of the titration curve were observed for the three major regions of the titration (free alkali, titration of bilirubin, and excess acid), but the transitions were highly rounded, preventing precise location of the end points. The large excess of strong electrolyte needed to dissolve the sample initially was a serious drawback in the conductometric technique.

3. Emf Titrations

One object of potentiometric titrations in water was to confirm published observations on the solubility, ionization, and pH at half neutralization of bilirubin [43]. An alkaline solution of bilirubin was back-titrated with 0.05 M hydrochloric acid while the pH was measured with a
combination glass-calomel electrode that had been standardized in phosphate buffer at pH 6.86. In confirmation of the above reference, the curves showed a single, sharp break at pH 8.3, when the acid form of bilirubin began to precipitate; the half-neutralization pH at 22.5 °C was 8.20. No separation of the two carboxyl groups was detectable. In the titration range in which bilirubin was precipitating, equilibrium was reached very slowly. After an addition of acid, the pH immediately decreased and required as long as half an hour to return to the equilibrium value, which was reproducible to ± 0.05 pH unit in different runs. In contrast to the published report [43], back titration with standard alkali did not retrace the equilibrium curve but always showed hysteresis in the direction of higher pH. The freshly precipitated bilirubin, however, redissolved more readily than the original sample. These results indicate that bilirubin, because of its extreme insolubility at pH less than 8, precipitates in a colloidal form that traps some of the ionic or salt form and only very slowly approaches a stoichiometric composition. Consequently, an indirect approach was adopted of dissolving the sample in a minimum of alkali and titrating only the excess base.

The most satisfactory procedure was to weigh the sample into the clean, dry cell under argon and add DMSO equivalent to 5 to 10 percent of the final volume. This was not enough to dissolve the sample completely but it wet and dispersed the bilirubin. Next, 0.05 M sodium hydroxide was added, equivalent to not more than 100 percent excess, and the solution was immediately diluted with sufficient water to cover the pH electrode. The standardized electrode was inserted and the cell contents were titrated by gravimetric additions of 0.02 M hydrochloric acid to pH 8 or until a definite break in the pH curve was reached.
The cell used for 2-3 mg samples of bilirubin is shown in figure 18. A similar cell having a capacity of 25 cm$^3$ was used for larger samples. In use, the cells were wrapped in aluminum foil as a light shield. The results of some titrations are summarized in table 15. Runs 10, 11, and 12 show that repetitive titrations of the same sample were reproducible to about 0.5 percent, even over a 24-hour period, indicating that instability of the bilirubin was not serious. The agreement between different samples is much poorer, and the causes of this lack of reproducibility are still under investigation.

Figure 18. Cell for the potentiometric titration of bilirubin.  

(T. B. Hoover)
Table 15. Potentiometric titration of bilirubin.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Bilirubin (mg)</th>
<th>Total vol cm³</th>
<th>Net NaOH (μeq)</th>
<th>Apparent eq wt</th>
<th>Comments</th>
</tr>
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<tr>
<td>1</td>
<td>3.381</td>
<td>7.5</td>
<td>11.20</td>
<td>301.9</td>
<td>Water</td>
</tr>
<tr>
<td>2</td>
<td>2.000</td>
<td>7.5</td>
<td>6.95</td>
<td>287.8</td>
<td>Water</td>
</tr>
<tr>
<td>3</td>
<td>2.036</td>
<td>7.5</td>
<td>6.90</td>
<td>295.1</td>
<td>Water</td>
</tr>
<tr>
<td>4</td>
<td>2.080</td>
<td>7.5</td>
<td>6.80</td>
<td>305.9</td>
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<td>5</td>
<td>1.988</td>
<td>8.0</td>
<td>6.95</td>
<td>286.0</td>
<td>10% DMSO, to pH 8.0</td>
</tr>
<tr>
<td>6</td>
<td>2.116</td>
<td>9.0</td>
<td>7.306</td>
<td>289.6</td>
<td>10% DMSO, to pH 8.0</td>
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<tr>
<td>7</td>
<td>2.169</td>
<td>8.0</td>
<td>7.20</td>
<td>301.3</td>
<td>10% DMSO, to pH 8.0</td>
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<tr>
<td>8</td>
<td>2.360</td>
<td>8.0</td>
<td>7.82</td>
<td>301.8</td>
<td>Premixed 10% DMSO, pH 8.0</td>
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<tr>
<td>9</td>
<td>16.544</td>
<td>20.0</td>
<td>53.8</td>
<td>307.5</td>
<td>10% DMSO, pH 8.45</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>53.6</td>
<td>308.7</td>
<td>2nd titration</td>
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<td></td>
<td></td>
<td>54.3</td>
<td>304.7</td>
<td>3rd titration</td>
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<td>10</td>
<td>13.308</td>
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<td>41.83</td>
<td>318.1</td>
<td>Water, inflection pH 8.60</td>
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<td></td>
<td></td>
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<td>316.5</td>
<td>2nd titration 8.57</td>
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<td></td>
<td></td>
<td></td>
<td>41.96</td>
<td>317.2</td>
<td>4th (next day) 8.59</td>
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<tr>
<td>11</td>
<td>12.060</td>
<td>22.0</td>
<td>40.39</td>
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<td>5% DMSO, pH 8.50</td>
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<td>40.80</td>
<td>295.6</td>
<td>2nd titration 8.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40.73</td>
<td>296.1</td>
<td>3rd titration 8.46</td>
</tr>
<tr>
<td>12</td>
<td>15.863</td>
<td></td>
<td>52.88</td>
<td>300.0</td>
<td>5% DMSO, pH 8.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>52.99</td>
<td>299.4</td>
<td>2nd titration 8.45</td>
</tr>
</tbody>
</table>

a Theoretical value 292.3
E. A Standard for Ion-Selective Electrodes

It is anticipated that a Standard Reference Material, sodium chloride, will be issued in the near future, together with a provisional certification of values for the activities of sodium and chloride ions. When this first standard is made available, a detailed publication will be prepared describing methods for the standardization and use of ion-selective electrodes.

(B. R. Staples)
8. FOREIGN-CURRENCY PROGRAMS

The two projects sponsored by the Electrochemical Analysis Section at universities in India and financed through the provisions of Public Law 480 continued active during the reporting year. A brief description of these programs follows.

Properties of Electrolytes in Nonaqueous Media, Jadavpur University, Calcutta, Dr. M. N. Das and Dr. K. K. Kundu

(a) Standard potentials of the Ag-AgI electrode in ethylene glycol-water mixtures.

(b) Dissociation constants of tris(hydroxymethyl)-aminomethane in ethylene glycol.

(c) Studies in isodielectric media

1. Standard potentials of the Ag-AgBr electrode in propylene glycol-methanol solvent systems.

2. Autoprotolysis constants of propylene glycol-methanol solvent systems.

3. Standard potentials of the Ag-AgI electrode in propylene glycol-methanol solvent systems.

(d) Standard potentials of the Na-Na+ electrode in ethylene glycol-water systems.

Physicochemical Studies in Nonaqueous Solvents, Panjab University, Chandigarh, Professor R. C. Paul

Recent work is described in the following publication and manuscript:


Paul, R.C., Singla, J.P., Narula, S.P. Transference Numbers and Ionic Solvation of Some Alkali Salts in Dimethylformamide (in manuscript form).
9. IMPACT OF SECTION'S ACTIVITIES

The impact of the Section's activities on the technical and scientific public can best be judged in terms of the distribution of Section publications, number of invited talks, and requests for advice and consultation. In this connection, the following statistics, compiled for the calendar year 1968 unless otherwise indicated, are pertinent.

Reprints requested ......... 681
Manuscripts reviewed for outside journals .......... 22
Project proposals reviewed ........ 2
Significant consultations .......... 27
    federal and state agencies 8
    industries 13
    universities 6
Committee memberships .......... 16
Publications (7/68 to 6/69) .......... 11
Talks (7/68 to 6/69) .......... 21
    scientific societies 12
    universities 3
    industries 2
    government agencies 4
10. PERSONNEL

Roger G. Bates, Section Chief
Marguerite Raudenbush, Section Secretary

Conductance Measurements

Electromotive Force and Acidity Measurements

pH, Ion-selective electrodes

B. R. Staples
M. Alfenaar (July to Sept.)
from University of Utrecht, Holland
J. T. Clark, Jr.
(July to Sept.)
guest worker from
Clarkson College of Technology
R. S. Carter, Jr.
(June to Aug.)
guest worker from
Landon School

Heavy water, mixed solvents

M. Paabo
H. P. Thun (Oct. to July)
guest worker from
University of Ghent, Belgium

Nonaqueous solvents

E. S. Etz (July to Sept.)
from Clarkson College of Technology

Consultant

D. Rosenthal, Clarkson College of Technology
11. COMMITTEE MEMBERSHIPS

R. G. Bates

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

Councilor, American Chemical Society, representing the Division of Analytical Chemistry.

Member, ACS Council Committee on Publications.

Chairman, Undergraduate Awards Committee
ACS Division of Analytical Chemistry.

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

Member, Commission on Electrochemistry, IUPAC.

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

Associate Member, Commission on Electroanalytical Chemistry, IUPAC.

Chairman, Subcommittee on Physicochemical Symbols and Terminology, Committee on Physical Chemistry, NRC.

Member, Committee Y1, Abbreviations for Science and Engineering, U.S.A. Standards Institute.

Member, Committee Y10, Letter Symbols, U.S.A. Standards Institute.

Member, Board of Editorial Advisers, Analytica Chimica Acta.

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

Member, Museum Committee (NBS).

T. B. Hoover

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

B. R. Staples

Member, Ad Hoc Division Committee on Electronic Data Systems, Analytical Chemistry Division, NBS.
12. PUBLICATIONS AND MANUSCRIPTS, JULY 1968 TO JUNE 1969

1. Bates, R.G. (Ed.)
   Electroanalytical Analysis Section: Summary of Activities, July 1967 to June 1968,
   NBS Technical Note 453 (July 1968).

2. Davis, M.M.

3. Bates, R.G.
   Equilibrium Properties of Acids and Bases in Amphiprotic Mixed Solvents, in Hydrogen-Bonded

   Thermodynamics of Hydrochloric Acid in 95 Volume
   Per Cent (92.41 Mass Per Cent) Ethanol from
   E.M.F. Measurements at 5 to 50 °C,

5. Paabo, M., Bates, R.G.
   Standards for a Practical Scale of pD in Heavy Water,

   Two New Standards for the pH Scale,

7. Hoover, T.B.
   The N-Methylpropionamide-Water System. Densities
   and Dielectric Constants at 20-40°,

8. Staples, B.R., Atkinson, G.
   Structure and Electrolyte Properties in Bolaform
   Electrolytes. III. The Hydrodynamics of Potassium
   Salts of Several Rigid Bolaform Disulfonic Acids in
   Dioxane-Water Mixtures at 25°

   Intracellular pH,

11. Bates, R.G.

12. Bates, R.G.

13. Bates, R.G.
Hydrogen Ions
Encyclopaedia Brittanica (In press).


15. Paabo, M., Bates, R.G.

16. Bates, R.G.

13. TALKS, JULY 1968 TO JUNE 1969


14. LIST OF REFERENCES


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    Electrolyte Solutions, 2nd ed., appendix 8.10

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    In Hydrogen-Bonded Solvent Systems (A. K. Covington
    and P. Jones, Eds.), p. 49.
[31] Franks, F., Ives, D.J.G.
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    Determination of pH, Theory and Practice, Chapter 7.
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[41] Jones, G., Bradshaw, B.C.
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[43] Overbeek, J.T.G., Vink, C.L.J., Deenstra, H.
JOURNAL OF RESEARCH reports National Bureau of Standards research and development in physics, mathematics, chemistry, and engineering. Comprehensive scientific papers give complete details of the work, including laboratory data, experimental procedures, and theoretical and mathematical analyses. Illustrated with photographs, drawings, and charts.

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