NBS

# Technical Note 271

# ELECTROCHEMICAL ANALYSIS: STUDIES OF ACIDS, BASES, AND SALTS BY EMF, CONDUCTANCE, OPTICAL AND KINETIC METHODS

## JULY 1964 TO JUNE 1965

Edited by Roger G. Bates

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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ISSUED SEPTEMBER 6, 1965

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

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Washington, D.C., 20402 - Price 60 cents

# FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964, reorganization. It consists at present of seven sections and about 85 technical personnel encompassing some 30 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences, and in turn the sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is highly important. In addition, however, it has been my experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information. At the National Bureau of Standards such publications fit logically into the category of Technical Note. In 1965 we plan to issue these summaries for all of our sections. The following is the first annual report on progress of the Electrochemical Analysis Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

# PREFACE

This is the first in a series of annual progress reports of the Electrochemical Analysis Section of the Analytical Chemistry Division. The report covers the fiscal year 1965, which began on July 1, 1964, and ended June 30, 1965.

As a discrete entity, the Electrochemical Analysis Section dates back to the late 1930's when a group was organized by the late S. F. Acree to investigate the electrochemistry of solutions, in particular the interactions of acids and bases. When the establishment of a national standard of acidity later became a major concern of the group, the name "pH Standards Section" was adopted. This title gave way to "Physical Chemistry Section", and, as the study of solvent effects on electrolyte processes became the primary objective about 1960, the name "Solution Chemistry Section" came into being. With the establishment of the Analytical Chemistry Division some three years later, the present name was authorized, in order to emphasize the place of the Section's activities within the frame-work of the Division's responsibilities.

The mission of the Section has been summarized as follows:

> "The Electrochemical Analysis Section conducts experimental and theoretical investigations of a) the properties of pure materials, especially weak and strong electrolytes, in aqueous and nonaqueous media; b) reversible and transport behavior at electrodes; and c) the application of these properties and phenomena to the development and improvement of analytical processes.
>
> "Specific programs include the establishment of standard reference materials and reference data for pure materials (dissociation constants, activity coefficients, conductivities, resistivities, electrode potentials, dielectric constants, rate constants, pH standards), measurement scales (pH and other acidity functions for the precise estimation of hydrogen ion), and analytical methods of improved sensitivity and accuracy."

A large share of the Section's efforts is directed currently toward an understanding of the behavior of acids, bases, and electrolytes in solution; to the measurement of the thermodynamic, transport, and kinetic properties of pure materials in solution; and to the electrical properties of pure liquids and solids. These fundamental investigations are designed to lead to a) the solution of measurement problems through the development of new and improved standard reference materials, b) the collection of useful data for pure materials, and c) the development and maintenance of a high competence in special areas of analysis within the purview of the Section.

It is the purpose of this report not only to review the individual projects of the Section but to convey as well an impression of the interrelationships of the separate activities as they fuse into a single Section program. The first goal could be achieved in a most satisfactory way by collecting together the published -- or soon to be published -- work of the staff as listed at the end of this document. The second aim, however, is more elusive. It can only be met by an integrated summary of the total Section effort, where accomplishment can be viewed against the backdrop of the mission, facilities, and personnel of the organizational unit.

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

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

Roger G. Bates, Chief
Electrochemical Analysis Section

Washington, D.C.
June 28, 1965

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July 1964 to June 1965

Edited by Roger G. Bates

## ABSTRACT

This survey of the activities of the Electrochemical Analysis Section, Analytical Chemistry Division, covers the period July 1964 to June 1965. An attempt is made to summarize a year's progress on the technical projects of the Section in such a way as to stress the program and capabilities of the organizational unit as a whole. Consequently, a description of facilities and equipment is presented first and is followed by brief summaries of the several lines of work currently under way. Emphasis is given to the reasons why each study was undertaken. The main areas of investigation include the study of acidity and solvent effects in water, deuterium oxide, and water-methanol solvents by emf methods; the development of reference indicator bases for nonaqueous media and reference materials for dielectric measurements; measurement of the thermodynamic properties of mixed salt solutions; and in-

vestigation of special problems in trace analysis by conductometric and kinetic methods. The survey concludes with lists of the members of the Section staff, publications and manuscripts produced during the year, and talks given by the staff.

# 1. FACILITIES AND EQUIPMENT

The Electrochemical Analysis Section occupies nine laboratories located in the east wing, fourth floor, of the Industrial Building. With the exception of two rooms maintained at constant temperature to assure the proper functioning of special equipment, all of the laboratories are of the "general-purpose" type.

The specialized equipment maintained and developed by the Electrochemical Analysis Section to support its mission within the Institute for Materials Research and the Standard Reference Materials program may be suitably classified in terms of the basic measurement methods involved. This is particularly so since considerably different methods are frequently used to obtain data from which comparable values of physicochemical constants or parameters for systems of analytical interest can be derived.

## A. Emf Methods

Precise measurement of the electromotive force of chemical systems using hydrogen electrodes or electrodes responsive to other ions provide data for standard reference potentials, for standard reference values of the acidity or basicity of buffer solutions, for dissociation constants, and for the derivation of the thermodynamic quantities associated with the processes studied.

The Section has three assemblies with which emf measurements with an uncertainty of 0.1 mV or less can be made in aqueous and semi-aqueous media over the temperature range 0 to 60 °C. Correspondingly, the pH of reference solutions can be determined to 0.003 unit with a precision of 0.001 unit or better. Considerable improvement has been made in these assemblies during the past year, particularly in regard to simplification of arrangement and operating procedures with improved convenience in bath-temperature control. The latter objective was accomplished by the installation of commercial temperature controllers utilizing the proportional mode of control and thermistor sensors.

High-impedance electrometers are available for potential measurements to 0.05 mV and pH to 0.02 unit with the glass electrode. A high-impedance electrometric apparatus utilizing a recording potentiometer with useful sensitivity of 0.02 mV is in the assembly and development stage. It is intended for studies of the sodium-ion response of special glass membranes.

### B. Spectrophotometric Methods

Three assemblies for precise measurement of changes in spectral absorption taking place in the near ultraviolet, visible, and near infrared are available for study of the properties of solutions of acids, bases, and salts in both aqueous and nonaqueous media. When sufficient colorimetric sensitivity exists, these instruments are useful for both quantitative and qualitative analysis for specific constituents or impurities.

These assemblies are built around the Beckman Model DU and Optica spectrophotometers and the Cary Model 14 recording spectrophotometer. They permit measurement of transmission and absorption in the wavelength range 200 to 3,000 nm. Under optimum conditions, the results may be accurate to 0.3 to 0.5 percent. A precision of 0.1 to 0.2 percent may be attained in the range 220 to 800 nm, with considerably less definition outside this interval. Sample-temperature control to 0.1 °C can be achieved near room temperature. The cell temperature in one instrument can be controlled in the range 15 to 35 °C by the circulation of water from a constant-temperature bath through a water-jacketed cell compartment designed in the Section. Another instrument is being provided with an electrically-heated cell compartment the temperature of which is controlled with the aid of a thermistor sensor. A considerable range of temperature above room temperature should be obtainable.

The spectrophotometric assemblies are in use for the determination of dissociation constants, the comparison of relative acidic strengths of acids and bases in various solvents, studies of rates of reaction, and for the development of methods for the detection of trace quantities of specific ions.

### C. Isopiestic Vapor Pressure Method

An independent approach to the determination of solvent activity and solute activity coefficients has been provided through construction of an isopiestic apparatus for the measurement of the vapor pressure of various simple and complex aqueous solutions at 25 °C. The method is simple and elegant both in principle and application, and the results obtained are in excellent agreement with those of other thermodynamic methods, where a comparison can be made. One assembly, consisting of constant-temperature bath, vacuum vessels, copper blocks, and silver dishes, is available.

### D. Resistance and Impedance Methods

#### 1. Conductance of Solutions

The conductivity of solutions of electrolytes is a definite function of the mobilities and charges of the ionic species present. It is therefore modified by changes in the temperature, viscosity, and dielectric constant of the medium. The factors affecting conductivity are not yet completely understood. Nevertheless, useful information on equivalent conductances of salts, conductances of individual ions, dissociation constants of electrolytes, and other quantities of both theoretical and practical importance can be obtained from the measurement of conductance as a function of concentration of electrolyte, temperature, and solvent properties.

Conductance phenomena are extremely sensitive to changes in ion concentrations and, hence, to the dissociation of the electrolyte present and to the extent of such reactions as neutralization and complexation. Alteration of the solvent has a profound effect as well. For these reasons, conductance measurements can often serve as a useful tool in chemical analysis.

A modified audio-frequency Jones bridge assembly with suitable conductivity cells and a precisely controlled constant-temperature oil bath are available for measurement of the conductance of electrolytes in aqueous and nonaqueous media. In addition, a precision capacitance-conductance bridge assembly and oil bath is available for general measurement of electrolytic conductance. Under optimum conditions, conductivities can be obtained with either of these two assemblies with a relative accuracy approaching 0.01 percent with a precision of about 0.001 percent over a temperature range of 0 to 80 °C.

### 2. Dielectric Constants of Liquids

A knowledge of the dielectric properties of the solvent is important in appraisal of the results of electrochemical measurements and to provide useful information regarding the structure of molecules and the condensed states of matter. Precise dielectric and conductance data of sufficient definition can serve as standard reference data and, where suitable, the materials may serve as accurate reference standards for other properties of concern.

The precision capacitance-conductance bridge assembled in the Section can be used to measure the static dielectric constants of semiconducting and nonconducting liquids at frequencies up to 100 kHz. Absolute measurements of the dielectric constant can be made with a precision of 0.02 percent to 0.1 percent over a temperature range from -30 to 130 °C.

A commercial transformer ratio-arm capacitance bridge with a range of $10^{-17}$ to $10^{-6}$ farad is also available for measuring the dielectric properties of low-loss dielectrics at frequencies up to 100 kHz. In combination with suitable three-terminal cells, it should permit the characteristic dielectric constants of well-defined reference and research materials to be determined with an accuracy of about 0.01 percent and dielectric loss to be determined to about 1 percent.

### 3. Resistivity of Metals

The resistivity of pure metals and alloys, or its reciprocal, the conductivity, is characteristic of a given metal composition, both in respect to its magnitude and to its dependence on temperature. As part of the Standard Reference Materials program, a Kelvin double bridge and accessory items are being acquired and assembled for use in characterizing metals and alloys through the resistivity and its temperature dependency.

### 4. Miscellaneous Special Methods

A sensitive dilatometer and associated apparatus exists for kinetic studies by an incremental volumetric method. Determinations of the volumetric change with a sensitivity approaching 2 parts in $10^7$ has been achieved and the method has been used with considerable success over the temperature range 15 to 40 °C.

A magnetic densimeter has been constructed for measurements of the density of pure liquids and solutions. It utilizes a closed system, and as little as 15 ml of sample is required. Operation of the instrument consists in finding the point at which a magnetic float is in buoyant equilibrium. The adjustment is accomplished by the calibrated regulation of an electromagnetic field. When suitable liquids are used, the densities obtained are estimated to be accurate to 0.0001 with a precision of 0.00005.

(C. G. Malmberg)

# 2. DESIGN OF AUTOMATED INSTRUMENTATION FOR EMF MEASUREMENTS

The design of an automated system for control, measurement, and data-handling in emf studies has been completed. This assemblage of equipment will make all adjustments and record all data concerned in a series of emf measurements, including time, barometric pressure, temperature, and emf. In addition, it will control accurately the temperature of the bath in which the cells are immersed, will decide when equilibrium has been reached in all of six cells (or any specified fraction of them), and will automatically change the bath temperature according to a flexible prearranged program. At the end of each run, the system will make available all of the pertinent data on a suitable print-out. Thus the new instrumentation will perform all of the functions that a human operator must now perform after the cells have been prepared, filled, and placed in the bath.

Moreover, such a system will have several advantages over human operation. Because it can operate unattended around the clock and over weekends, it will reduce the time to complete a run to about one-third of that now required, even when allowance is made for a 20-percent down-time factor. Because the system will make decisions on the basis of preprogrammed criteria, it will do away with errors of human judgment in arriving at a reliable conclusion as to when equilibrium has been reached. Each run will be completed in the shortest possible time, and consequently the system will make the most economical use of costly reagents (such as deuterium gas, for example) and will enhance the accuracy of data obtained for materials whose stability in solution is limited. Finally, because it will free the operator from the tedium of routine measurements, it will give him more time for the analysis of data and for the design of experiments which promise to yield the greatest possible amount of useful information.

The proposed instrumentation has considerable built-in flexibility and is readily adaptable to the performance of tasks other than routine emf measurements. At the heart of the proposed system is a computer and teleprinter-punch unit which will not only perform all of the data-logging and computation required for precise emf measurements but will be available for use on other routine computation jobs originating in the Section and Division, once programs for such tasks have been developed.

The sensors consist of a digital thermometer, a digital barometer (uncertainty of 0.01 mm in the range 0 to 800 mm), a digital voltmeter (accurate to 0.001 percent of full scale from -1.1 to +1.1 V), and a digital clock. These sensors are independent units and can be used individually or in combination in any type of physical experiment which can utilize them. The data can be handled according to any program which is within the capability of the computer.

Accordingly, if the emphasis of the work within the Section should change, or if it should prove desirable to use the system for more than one type of routine physical measurement, the probability is high that the system could easily be adapted to the change.

All of the major elements of this assembly are commercially available and have a service history which is considered acceptable. The total cost of the system would be approximately $55,000. This includes a 20-percent allowance for contingencies and 6 man-months of labor at $10 per hour for assembly, interfacing, and initial programming.

The basic design of the automated equipment was worked out by E. W. Hogue of the Measurement Engineering Division; Mr. Hogue also selected the components for the assembly. The design was later modified by D. R. Boyle of the Information Technology Division so as to make use of computer control.

(R. Gary)

## 3. MEASUREMENT OF ACIDITY

The Section has had primary responsibility over a period of 25 years for the development of a national standard scale of pH and for the selection and certification of suitable reference materials to provide experimental realization of this scale. The NBS scale utilizes the unit $-\log a_H$, where $a_H$ is the conventional hydrogen ion activity in each of the selected reference solutions. It has been endorsed, along with the closely-related British Standard scale, by the International Union of Pure and Applied Chemistry. Data provided by NBS research projects provide the experimental basis for the standard pH measurement procedures approved for use not only in the United Kingdom but also in Japan and on a less formal basis in most other industrialized countries.

The major research effort of the past year has been directed toward the definition of scales suitable for measurements of acidity in partially aqueous solvents and amphiprotic media in general. Special attention has been directed to 50 wt. percent methanol and to deuterium oxide, and one or more standard reference solutions for each of these media have been established.

### A. pH Standards

The search for new and better standard reference materials for pH measurements is a continuing activity. In addition, there are continual "maintenance tasks". These include 1) the examination and certification of new lots of materials before issuance, 2) the recheck of experimental data and recalculation of the reference data as "best" values of the natural constants are altered, and 3) the intercomparison of reference points to obtain a realistic evaluation of the accuracy with which the "practical" experimental pH scale can be fixed.

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

a. Method. Standard values for pH measurements, termed pH(S), are assigned to the NBS primary standard buffers by determination of the acidity function $p(a_H\gamma_{Cl})$ for a particular concentration of the buffer with different small concentrations of added soluble chloride. This function is derived from measurements of the emf of hydrogen-silver, silver chloride cells without liquid junction. The calculation utilizes the measured electromotive force, E, standard potential of the cell, E°, and other known quantities:

$$p(a_H\gamma_{Cl}) = \frac{(E - E^\circ) F}{RT \ln 10} + \log m_{Cl} \qquad (1)$$

in which $\gamma$ is the individual ionic activity coefficient on the molal scale, F is the Faraday, and m is molality. The function $p(a_H\gamma_{Cl})^\circ$ is evaluated by extrapolation of $p(a_H\gamma_{Cl})$

to zero concentration of chloride, and $pa_H$ is calculated by means of the equation

$$pa_H = p(a_H\gamma_{Cl})^\circ + \log \gamma_{Cl} \tag{2}$$

The Bates-Guggenheim convention is used to evaluate the individual ionic activity coefficient needed to obtain $pa_H$. This convention is based on the formula

$$\log \gamma_{Cl} = - \frac{A\ I^{1/2}}{1 + 1.5\ I^{1/2}} \tag{3}$$

where A is a constant of the Debye-Hückel theory and I is the ionic strength. The final step in the assignment of a standard reference value to the buffer solution is to identify $pa_H$ with pH(S) in the operational definition of the experimental pH value.

The partially completed study described in this section is part of a continuing project for the maintenance of the NBS standard pH scale, since the 0.05 m solution of potassium hydrogen o-phthalate is widely used for the standardization of pH assemblies. The main objective of the study is the re-examination of the pH of phthalate solutions, and the secondary objective or "by-product" is a redetermination of $K_1K_2$, the product of the first and second dissociation constants of o-phthalic acid. Values of $p(a_H\gamma_{Cl})$ are being determined at intervals of 5 degrees from 0 to 60 °C for five concentrations of potassium acid phthalate (NBS Standard 185d) in the range 0.01 to 0.1 molal with three different concentrations of added potassium chloride.

b. Procedures. The usual procedures used in this laboratory for precise electromotive force measurements have been followed, with a few exceptions. It is our usual practice to use palladium-coated hydrogen electrodes in phthalate solutions to avoid reduction of phthalate by platinum black. Better agreement between the pair of hydrogen electrodes in a cell was obtained at temperatures above 35 °C when the electrodes were conditioned, for a day before use, in oxygen-free 0.01 M hydrochloric acid. The cells were measured first at 25 °C, then from 0 to 35 °C in five-degree intervals in one continuous series. A different set of cells was prepared and measured at 25 °C, then from 40 to 60 °C. Final checks were always made at 25 °C. The general arrangement of equipment -- precision potentiometer, cell rack, and constant-temperature bath is shown in figure 1.

c. Results. At least four values of $p(a_H\gamma_{Cl})$ have been obtained for each of the five concentrations of potassium hydrogen phthalate with three concentrations of added potassium chloride and at 13 temperatures from 0 to 60 °C. The final least-squares treatment and extrapolation of the data are still incomplete. However, provisional results indicate that the pH(S) of 0.05 m potassium hydrogen

Figure 1. Equipment for the precise electromotive-force measurements on which pH standards are based.

phthalate at 25 °C is within 0.001 pH unit of the value of 4.008 assigned to this important reference solution on the basis of experimental data obtained nearly 20 years ago.

The provisional data and calculations for 25 °C are as follows:

| | | | |
|---|---|---|---|
| 0.05 m KH Phthalate, | 0.015 m KCl | $p(a_H\gamma_{Cl}) =$ | 4.0867 |
| 0.05 m KH Phthalate, | 0.01 | | 4.0896 |
| 0.05 m KH Phthalate, | 0.005 | | 4.0934 |
| 0.05 m KH Phthalate, | 0 | $p(a_H\gamma_{Cl})^\circ =$ | 4.0966 |

$-\log \gamma_{Cl}$ (eq.3) $= 0.0876$     $pa_H$(eq.2) $= 4.009$

(H. B. Hetzer)

## B. Standards for pH* in Methanol-Water Solvents.

The major purpose of this phase of the Section's activity has been the development and application of an acidity scale in amphiprotic solvents (media capable both of accepting and donating protons) containing water mixed with an organic liquid. Solvent mixtures of this sort are often used in research and industry to assure the solubility of slightly-soluble reactants or products. Without an acidity scale for these media, precise control of analytical and synthetic processes is impossible. A mixture of equal parts by weight of methanol and water was chosen as the first such medium for careful study, in view of its general usefulness in chemical and biochemical studies.

Operational pH numbers for solutions in many nonaqueous media can be measured with a pH meter using hydrogen (or glass) and calomel electrodes. This operational pH scale is defined as

$$\mathrm{pH(X)} = \mathrm{pH(S)} + \frac{E_X - E_S}{(RT \ln 10)/F} \qquad (1)$$

where pH(S) is the reference value for suitable aqueous reference solutions used to standardize the pH meter. In eq. 1, $E_X$ and $E_S$ are values of the emf of the pH cell with the electrodes immersed either in the standard (S) or in the unknown solution (X). The procedure for assigning values of pH(S) to aqueous standards has been described in section 3.A of this report.

### 1. Interpretation of pH(X) in Nonaqueous Media

The pH(X) determined by eq. 1 with aqueous standards will often be a reproducible number even when the solvent is not wholly aqueous. Thus it fulfills the primary requirement of an acidity scale for regulatory and control purposes. Abandonment of aqueous reference solutions in favor of reference solutions in the mixed solvent can be justified only if the interpretation of the data furnished and their correlation with acid-base phenomena are significantly improved.

It was shown recently [1] that the potential across the liquid junction: solution X in alcohol-$H_2O$|concentrated KCl (aq.) appears to be substantially constant even though the acidity of solution X changes over wide ranges, provided that the composition of the alcohol-water solvent remains unchanged. Furthermore, glass electrodes have been found to give nearly the theoretical response to hydrogen ions in alcohol-water mixtures when the water content is not too low. A consequence of this discovery is that the difference of $E_X - E_S$ obtained under optimum experimental conditions may be a valid measure of the relative hydrogen ion activity of the two media, or of pH(X) - pH(S) as expressed in logarithmic form in eq. 1. These optimum conditions for mixed solvents are, as in water, that the acidity of the solution be neither too high nor too low, that the ionic strength be moderate ($< 0.2$), and that the solute consist of simple buffer acids, bases, and salts. The assignment of a valid and usefu value to one or more reference solutions is then sufficient to define a new pH scale for that particular medium.

The unit designated $pa^*_H$ and defined by

$$pa^*_H = -\log m_H \cdot {}_s\gamma_H \qquad (2)$$

can be obtained by procedures similar to those on which aqueous pH standards have been based, utilizing a convention entirely analogous to eq. 3 of section 3.A.1. In eq. 2, the asterisk and the subscript s indicate that the quantity $a_H$ or $\gamma_H$ is referred to the standard state in the mixed solvent (s) rather than to that in water (w). It is now possible to set up an operational pH* scale for an amphiprotic or mixed solvent as has been done for pH in aqueous media:

$$pH^*(X) = pH^*(S) + \frac{E_X - E_S}{(RT \ln 10)/F} \qquad (3)$$

For the reference solutions selected, the pH*(S) is taken to be equal to $pa^*_H$ as determined by cells without a liquid junction. Under the optimum or "ideal" conditions, pH*(X) will then also have the dimensions of a conventional hydrogen ion activity or $pa^*_H$ in the particular solvent medium of concern.

## 2. Reference Solutions for 50 Wt. Percent Methanol

a. The Utility of Correction Factors. In work performed prior to the reporting period [1], it was shown that the difference between the pH(X) determined with aqueous standards and the pH*(X) determined with respect to reference solutions in an alcohol-water medium is nearly a constant under optimum experimental conditions. This constant was shown to be a combination of liquid-junction potentials and the medium effect (or transfer energy) for the hydrogen ion between the two solvents, water and the alcohol-water mixture. The value of the constant could be determined either from suitable emf measurements [1] or from pH-titration curves [2].

The derivation of pH* by the application of correction terms to pH values found with an assembly standardized in the usual way with aqueous reference solutions is undeniably attractive. It may be dangerous, however, for the asymmetry potential of the glass electrode may vary when the electrode is removed from one solvent and placed in another of widely different water activity. The safest procedure is to use reference solutions of the same solvent composition as the "unknown" or test solutions.

For this reason, $pa_H^*$ was determined for four buffer systems in 50 wt. percent methanol from 10 to 40 °C and over a range of buffer concentrations by the same methods used to obtain $pa_H$ for reference solutions in water. The procedure involved three steps, 1) the determination of ${}_sE°$, the standard emf of the hydrogen-silver chloride cell for the solvent 50-percent methanol, 2) the measurement of the acidity function $p_s(a_H\gamma_{Cl})$ for the reference solutions, and 3) the calculation of $pa_H^*$ from $p_s(a_H\gamma_{Cl})$ by application of a chosen convention.

b. Procedures. The four buffer systems selected were equimolal mixtures of

1) acetic acid, NaAc, and NaCl
2) sodium hydrogen succinate and NaCl
3) tris(hydroxymethyl)aminomethane and its hydrochloride
4) $KH_2PO_4$, $Na_2HPO_4$, and NaCl.

The chemicals used for the experiments were NBS Standard Reference Materials or reagent-grade materials, and some were further purified. "Spectro grade" methanol was used. Glacial acetic acid was purified by partial freezing and its purity checked by gas chromatography. The succinic acid and sodium succinate from which the sodium hydrogen succinate was prepared were assayed, and the purity of the tris(hydroxymethyl)aminomethane was also established by titration with a standard solution of distilled hydrochloric acid.

Appropriate stock solutions of the buffers were prepared in water. These were diluted with water and methanol to yield the desired concentration of the buffer in a 50-percent methanol-water medium. The ionic strength of each buffer system was varied from 0.01 to 0.1.

The emf of the cell

$Pt; H_2$(g., 1 atm), buffer in 50-percent MeOH, AgCl; Ag was measured over the range of temperatures from 10 to 40 °C at five-degree intervals. In order to obtain the standard emf ($_sE°$) of this cell, a series of measurements was also made from 10 to 40 °C in which the buffer was replaced by solutions of hydrochloric acid in 50-percent methanol. Further data at 25 °C in 10, 20, 45, and 70 wt. percent methanol were also obtained. The potentiometer and associated measuring equipment are shown in figure 2.

Figure 2. Equipment for the emf measurements on which pH* standards in methanol-water solvents are based.

c. Results. The standard emf ($_{s}E°$) of the cell was derived by accepted thermodynamic methods from the data for cells containing solutions of hydrochloric acid. The methods and the results have already been described [3,4]. The standard emf at 25 °C is summarized in table 1.

Table 1. Standard electromotive force of the hydrogen-silver chloride cell in methanol-water solvents at 25 °C.

| Wt. Percent Methanol | $_{s}E°$, V |
|---|---|
| 0 | 0.22234 |
| 10 | 0.21549 |
| 20 | 0.20901 |
| 45 | 0.19414 |
| 50 | 0.19067 |
| 70 | 0.16833 |

A knowledge of the standard emf permits the acidity function $p_s(a_H\gamma_{Cl})$ to be calculated for each of the reference buffer solutions for which emf data in methanol-water media were obtained. The calculation is similar in every way to the derivation of $p(a_H\gamma_{Cl})$ in aqueous solutions:

$$p_s(a_H\gamma_{Cl}) \equiv -\log\, _{s}(a_H\gamma_{Cl}) = \frac{E - {_{s}E°}}{(RT \ln 10)/F} + \log m_{Cl} \quad (4)$$

By adopting a formula (convention) analogous to that on which aqueous pH standards are based (eq. 3 of section 3.A.1), ${}_s\gamma_{Cl}$ could be evaluated and, hence, $pa_H^*$ values obtained from the experimental acidity functions:

$$pa_H^* = p_s(a_H\gamma_{Cl}) + \log {}_s\gamma_{Cl} \qquad (5)$$

The convention was modified to allow for the difference between the dielectric constants of the two solvents (water and methanol-water) and for the differences in the densities. The values of $pa_H^*$ obtained by eq. 5 were identified with pH*(S) in the operational definition of a practical scale of pH* (eq. 3).

A detailed description of the work, except for the measurements on buffers of tris(hydroxymethyl)aminomethane ("tris"), has been published [5]. The standard reference values in 50-percent methanol at 25 °C are collected in table 2. In addition to their application to the standardization of pH assemblies, these values are useful in the spectrophotometric determination of the dissociation constants of weak acids and bases in 50-percent methanol.

d. Consistency of the pH* Scale in 50-Percent Methanol. The internal consistency of the pH* scale defined by the four buffers in 50-percent methanol was examined by measurements of the cell

$$\text{Pt};H_2(\text{g., 1 atm}), \text{ buffer (1) in 50\% MeOH } \left| \begin{array}{c}\text{Satd.}\\ \text{KCl}\end{array} \right| \text{buffer (2) in 50\% MeOH}, H_2(\text{g., 1 atm}); \text{ Pt}$$

Table 2. Values of pH*(S) in 50% methanol at 25 °C.

| Ionic Strength | Buffer | | | |
|---|---|---|---|---|
| | Acetate | Succinate | Tris | Phosphate |
| 0.01 | 5.591 | 5.860 | 7.897 | 8.232 |
| 0.02 | 5.568 | 5.818 | 7.929 | 8.157 |
| 0.03 | 5.552 | 5.785 | 7.952 | 8.102 |
| 0.04 | 5.540 | 5.757 | 7.970 | 8.058 |
| 0.05 | 5.529 | 5.734 | 7.985 | 8.021 |
| 0.06 | 5.520 | 5.714 | 7.998 | 7.988 |
| 0.07 | 5.512 | 5.698 | 8.010 | 7.959 |
| 0.08 | 5.505 | 5.684 | 8.020 | 7.932 |
| 0.09 | 5.499 | 5.674 | 8.029 | 7.907 |
| 0.10 | 5.493 | 5.666 | 8.038 | 7.884 |

The assigned $pa_H^*$ values for the acetate and succinate buffers were found to be completely self-consistent, whereas the phosphate and tris buffers showed anomalies. With tris buffers, the discrepancy was sometimes as large as 0.05 pH unit. The residual liquid-junction error which causes the discrepancy seems to depend on the amount of chloride present in the buffer solution and also on the valence type of the buffer. More experimental work will, it is hoped, reveal a practical solution to this problem and lead to more accurate pH* measurements than are now possible.

(M. Paabo and R. G. Bates)

## C. Standards for pD in Deuterium Oxide

In an earlier section of this report, it was shown that standard reference solutions for measuring the practical pH can be provided for some solvents other than water. Since the assignment of pH values to a reference standard requires a considerable amount of careful work, the choice of solvents to receive first attention should be a judicious one.

There are a variety of reasons why it was felt that a series of reference standards for deuterium oxide would be valuable to the scientific community. From the practical point of view, deuterium oxide has moved rapidly from the status of a laboratory curiosity in 1930 almost to the status of a commercial solvent. It is found in ton quantities in many atomic energy installations where it is used as a coolant and a pile moderator, and where, incidentally, corrosion and the variables which control it are a constant concern. It is an indispensable tool of the biochemist who uses it in tracer studies of complex biochemical reactions and processes. Heavy water will no doubt find increasing application as it continues to become still more readily available.

The "acidity" measured in deuterium oxide is not the activity of hydrogen ion, $a_H$, but the activity of deuterium ion, $a_D$. And, similarly, while the practical pH scale for $H_2O$ is designed to reflect $a_H$, an analogous scale in $D_2O$

should reflect $a_D$. The experimental realization of this scale is called a practical pD scale.

### 1. Establishment of a pD Scale

The procedure for establishing such a scale parallels that used in constructing the practical pH scale. Values of the quantity $p(a_D\gamma_{Cl})$ are computed from emf measurements of the cell

$$\mathrm{Pt;D_2(g.),\ Reference\ solutions,\ MCl\ in\ D_2O,\ AgCl;\ Ag}$$

in which the $Pt;D_2(g.)$ electrode replaces the $Pt;H_2(g.)$ electrode used for studies in ordinary water. The emf of the cell is given by the equation

$$E = E° - k \log(a_D m_{Cl} \gamma_{Cl}) \qquad (1)$$

where E° (the "standard emf") is a constant characteristic of the cell reaction at a given temperature and at unit activity of the reactants and products, and k is written for (RT ln 10)/F.

The standard emf is, of course, different from the E° which pertains to the case of hydrogen. It therefore had to be evaluated before meaningful measurements could be made on the reference buffer systems. The evaluation was made from emf measurements of the cell

$$\mathrm{Pt;D_2(g.),\ DCl(m)\ in\ D_2O,\ AgCl;\ Ag}$$

at 5- or 10-degree intervals from 5 to 50 °C.

Details of the work have been published [6]. The values of E° are summarized in table 3.

Table 3. Values of E° for the deuterium-silver chloride cell in deuterium oxide from 5 to 50 °C.

| t, °C | E°, V. |
|---|---|
| 5 | 0.22528 |
| 15 | 0.21931 |
| 25 | 0.21266 |
| 35 | 0.20532 |
| 45 | 0.19733 |
| 50 | 0.19310 |

These measurements, as well as those taken subsequently on the reference solutions, were made in a cell of new design (figure 3).

### 2. Phosphate Buffer as a Standard Reference Solution

In choosing solutions to serve as possible reference standards for pD, the standard materials already used for the pH scale were considered to be prime candidates. Standard pD(S) values would be determined for them according to the usual NBS procedures.

The first system to be studied was the equimolal phosphate buffer system [7]. Measurements of the emf of the

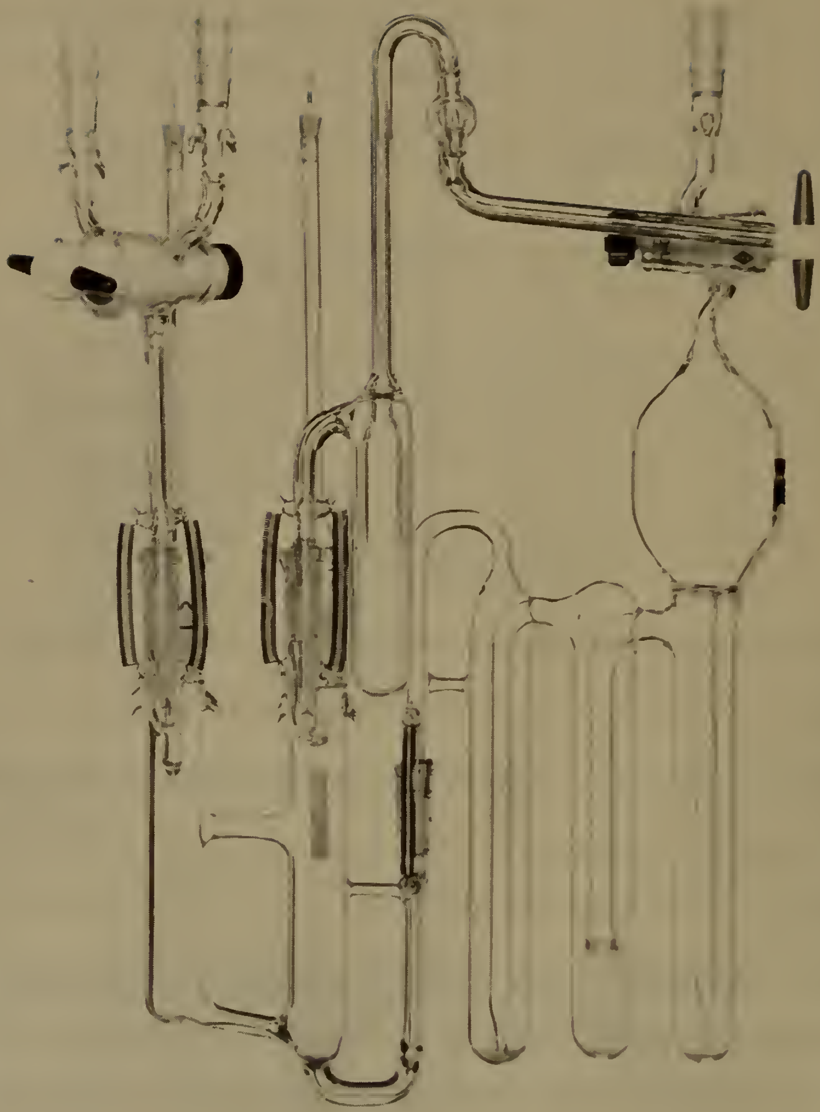


Figure 3. Emf cell for studies of solutions in deuterium oxide.

cell Pt;$D_2$(g.), $KD_2PO_4$(0.025 m), $Na_2DPO_4$(0.025 m), NaCl(m'), AgCl; Ag were made at 5-degree intervals from 5 to 50 °C and at several levels of m'. The emf (E) and the standard emf (E°) were used to compute values of the quantity $p(a_D\gamma_{Cl})$ which were extrapolated to the limit of $m_{Cl} = 0$, where the quantity may be designated $p(a_D\gamma_{Cl})$ :

$$p(a_D\gamma_{Cl})^\circ = (E - E^\circ)/k + \log m_{Cl}$$

To obtain a value for $-\log a_D \equiv pa_D$, the quantity $\gamma_{Cl}$ was evaluated from the expression

$$-\log \gamma_{Cl} = \frac{A' \, I^{1/2}}{1 + B' \, \mathring{a} \, I^{1/2}}$$

This expression differs from that used in the case of ordinary water in that the constants A' and B' are different. This is because the solvents differ in dielectric constant and density. The ion-size parameter å was taken to be the same in deuterium oxide as in ordinary water, namely 4.56 Å.

Values of $pa_D$ for the phosphate buffer system could then be computed, and these are shown in table 4. The practical significance of these values is that they can serve as reference values pD(S), for the calibration of equipment and procedures for measuring pD in other laboratories on an operational scale similar to that defined by eq. 1 of section 3.B. The accuracy of such measurements is

Table 4. Standard reference values of $pa_D$ for the solution $KD_2PO_4$ (0.025 m), $Na_2DPO_4$ (0.025 m) in heavy water.

| t, °C | $pa_D$ | t, °C | $pa_D$ |
|---|---|---|---|
| 5 | 7.537 | 30 | 7.411 |
| 10 | 7.504 | 35 | 7.397 |
| 15 | 7.475 | 40 | 7.386 |
| 20 | 7.450 | 45 | 7.380 |
| 25 | 7.429 | 50 | 7.377 |

probably subject to the same restrictions and precautions that pertain to pH measurements. Details of procedures for the use of commercial equipment such as the glass electrode to measure pD in heavy water will be the subject of further study.

### 3. Buffer System DAc (0.05 m), NaAc (0.05 m) in $D_2O$

This buffer system is not one of the five current NBS reference standards for pH. It was chosen for study, however, because it not only provides another point on the new pD scale but also because the data obtained might stimulate further work of theoretical importance by other workers. Acetic acid has often been used as a reference acid in the study of isotope effects.

The protium form of acetic acid, HAc, is a well-characterized material. The ionization of acetic acid in water has been the subject of several classic studies by well-known physical chemists.

In the determination of $pa_D$ for the solution $CH_3COOD$ (0.05 m), $CH_3COONa$ (0.05 m) in heavy water, the same procedure was followed as for the phosphate buffer. The $pa_D$ values obtained are shown in table 5 [8]. These values can be identified with pD(S) in an operational scale for pD measurement.

Table 5. Standard reference values of $pa_D$ for the solution $CH_3COOD$ (0.05 m), $CH_3COONa$ (0.05 m) in heavy water.

| t, °C | $pa_D$ | t, °C | $pa_D$ |
|---|---|---|---|
| 5 | 5.265 | 30 | 5.227 |
| 10 | 5.252 | 35 | 5.225 |
| 15 | 5.243 | 40 | 5.226 |
| 20 | 5.235 | 45 | 5.230 |
| 25 | 5.250 | 50 | 5.235 |

## 4. Future Programs

One of the criteria for a useful acidity scale is that it be internally consistent. This means that the difference between the practical pD values for any two standards measured individually in cells without liquid junction should agree with the difference observed when they are compared directly in the cell which is used for the overwhelming proportion of practical acidity measurements. The two systems already investigated, as well as others that will be studied from time to time, must be checked against each other in cells with liquid junction similar to the type used commonly for practical pH measurements (see section 3.B.2.d). This comparison has been initiated.

Since the glass electrode is the most convenient and widely used indicator electrode for hydrogen ion, the best way of adapting it to the measurement of deuterium ion requires study. The response of the glass electrode to deuterium ion in $D_2O$ has not yet been fully affirmed. The ultimate availability of several pD standards will make possible this series of experiments, essential in order to demonstrate the utility of the glass electrode in deuterium oxide.

In developing the pH scale, it was important to determine the limits within which the assumptions made in the formulation of the scale could reasonably be expected to be valid. The pD range within which reasonable constancy of the liquid-junction potential is maintained is not yet known and should be determined.

(R. Gary)

## D. Standard Emf of the Cell: $Pt;H_2(g.)$, HI, AgI; Ag from 0 to 50 °C

The standard electromotive forces of the analogous cells with hydrochloric acid and a silver-silver chloride electrode [9] and with hydrobromic acid and the silver-silver bromide electrode [10] have been determined previously. The silver-silver iodide electrode has some advantages over the other two, particularly its low solubility in ammonia and amine solutions. This makes it a very useful electrode with which to measure the dissociation constants of bases and the pH values of buffer solutions of high alkalinity.

Measurements of the emf of the cell

$$Pt;H_2(g.),\ HI\ (m),\ AgI;\ Ag$$

have been made [11] at 11 temperatures from 0 to 50 °C, and the standard emf (E°) evaluated at each temperature. The values of E° found can be expressed as a function of temperature by the equation:

$$E° = -\ 0.15242 - 3.19 \times 10^{-4}\ (t-25) - 2.84 \times 10^{-6}\ (t-25)^2,$$

where t is the temperature in degrees Celsius. A comparison with the earlier data of Owen [12], who used borax-buffered potassium iodide solutions, is given in table 6.

Table 6. Standard electromotive force (E°) of the cell $H_2$; HI (m), AgI; Ag from 0 to 50 °C in V.

| t, °C | E°, this work | E°, Owen [12] |
|---|---|---|
| 0 | -0.14637 | ---- |
| 5 | -0.14719 | -0.14717 |
| 10 | -0.14822 | -0.14810 |
| 15 | -0.14942 | -0.14925 |
| 20 | -0.15081 | -0.15067 |
| 25 | -0.15244 | -0.15230 |
| 30 | -0.15405 | -0.15401 |
| 35 | -0.15590 | -0.15591 |
| 40 | -0.15788 | -0.15792 |
| 45 | -0.15998 | ---- |
| 50 | -0.16219 | ---- |

The agreement is excellent at 5, 10, 30, 35, and 40 °C, but there are differences of 0.14 to 0.17 mV at intermediate temperatures.

Activity coefficients have been calculated up to 1 m at 10, 25, and 40 °C and those at 25 °C compared with those derived from isopiestic measurements [13]. The partial molal enthalpies ($\overline{L}_2$) of these solutions at 25 °C have also been derived. The results are given in table 7. The thermochemical calorie, (equivalent to 4.1840 J) is used here.

Table 7. Activity coefficients of HI at 10, 25, and 40 °C; $\bar{L}_2$ of HI at 25 °C.

| m | $\gamma_{\pm}$ (10 °C) | $\gamma_{\pm}$ (25 °C) | $\gamma_{\pm}$ (25 °C)[a] | $\gamma_{\pm}$ (40 °C) | $\bar{L}_2$ cal $mol^{-1}$ |
|---|---|---|---|---|---|
| 0.005 | 0.931 | 0.929 | - | 0.928 | 41 |
| 0.01 | 0.909 | 0.907 | - | 0.904 | 60 |
| 0.02 | 0.882 | 0.897 | - | 0.876 | 77 |
| 0.05 | 0.843 | 0.839 | - | 0.835 | 106 |
| 0.1 | 0.815 | 0.811 | 0.798 | 0.806 | 130 |
| 0.2 | 0.799 | 0.793 | 0.788 | 0.788 | 170 |
| 0.3 | 0.803 | 0.795 | 0.792 | 0.789 | 202 |
| 0.4 | 0.814 | 0.805 | 0.803 | 0.798 | 226 |
| 0.5 | 0.831 | 0.820 | 0.819 | 0.813 | 244 |
| 0.6 | 0.851 | 0.839 | 0.839 | 0.832 | 263 |
| 0.7 | 0.874 | 0.861 | 0.862 | 0.853 | 281 |
| 0.8 | 0.900 | 0.885 | 0.886 | 0.877 | 297 |
| 0.9 | 0.927 | 0.911 | 0.913 | 0.903 | 315 |
| 1.0 | - | - | 0.940 | - | - |

[a] From isopiestic data.

(H. B. Hetzer, R. A. Robinson)

# 4. INDICATORS AS REFERENCE BASES FOR ACID-BASE STUDIES IN INERT SOLVENTS

## A. The Need for New Reference Bases

Acid-base studies, such as the determination of relative acidic strengths and the determination of total acid content in nonaqueous solvents, have been impeded by shortcomings of presently obtainable reference bases. Ideally, a series of pure crystalline bases of graded strengths should be easily obtainable for chemical work in varied solvents, and the series would include strong bases which could be used without introducing water or alcohols. Two examples may be given of the limitations of reference bases now in common use:

1. Quaternary ammonium hydroxides or alkoxides, used when a very strong base is needed, are not available in a convenient form. Some are supplied as aqueous or alcoholic solutions, and in other cases the base has to be prepared from a halide. An additional disadvantage in their use is the inevitable introduction of water or alcohol into otherwise anhydrous systems.

2. Aliphatic amines, commonly employed when a weaker reference base will serve, are liquids when of low molecular weight. Solid aliphatic amines have been prepared by introducing heavy alkyl groups, but the additional bulk of these groups makes the nitrogen atom less accessible to acidic molecules.

With concerted efforts, it should be possible to develop better reference bases. For example, quinuclidine ($C_7H_{13}N$) appears to be superior in two respects to triethylamine (one of the most frequently used aliphatic amines): It is a solid, and it is a little more reactive (probably because the nitrogen is more exposed). However, it is hard to obtain because an economical procedure for its synthesis has not yet been worked out.

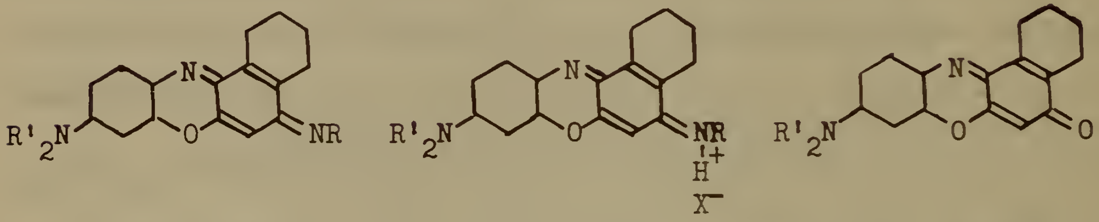
An obvious place to look for strong reference bases is among compounds in which cation formation is favored by resonance. The relatively high basicity of 1,3-diphenylguanidine can be attributed to stabilization of the cation form by resonance. Other useful solid bases should be found among guanidines containing aralkyl and alkyl groups. Development work in this area is badly needed.

Indicator bases, another group of compounds in which cation formation is favored by resonance, offer well-known advantages. One is the high molar absorptivity which is characteristic of these compounds, making them very sensitive reagents. Another advantage is that the principal absorption bands ordinarily do not overlap absorption bands of solvents and dissolved acids. Little developmental work has been done in this area. This report summarizes exploratory studies using several indicators of the Nile Blue group.

## B. Indicators of the Nile Blue Group

### 1. Structure and Terminology

When using acid-base indicators in non-ionizing solvents it is necessary to specify whether the indicator is employed as the salt or as the corresponding base or acid. Figure 4 shows the general structural formulas of the indicators under discussion, as the base (I) and as a salt (II) formed by adding an acid HX to the base. A related indicator, known as an "oxazone", is also shown (III).



(I) BASE (II) SALT (III) OXAZONE

Figure 4. General formulas of indicators of the Nile Blue group. Unless otherwise noted, $R' = C_2H_5$.

In all but one of the indicators under discussion, $R' = C_2H_5$. The identities of R in the salts used and the corresponding common names (in parentheses) were as follows: (1) H (Nile Blue A); (2) $C_2H_5$ (Nile Blue BX); (3) $C_6H_5CH_2$ (Nile Blue 2B); (4) p-$ClC_6H_4CH_2$ (4-Chlorobenzyl Diethyl

Nile Blue); (5) $C_6H_5$ (Phenyl Diethyl Nile Blue). The common names applied to the salts are used for the corresponding bases, but with the word "base" or "anhydro-base" appended. On comparing the three structural formulas it can be seen that the salts or bases just mentioned are related to the same oxazone ("Nile Blue Oxazone").

One of the anhydro-bases used differed from these compounds with respect to the nature of both R and R': R = $\underline{p}$-$CH_3C_6H_4$ and R' = $\underline{n}$-$C_3H_7$. Its common name is "$\underline{p}$-Tolyl Dipropyl Nile Blue Base".

The "common names" mentioned have been adopted as everyday substitutes for the very cumbersome systematic terminology. As an example, the systematic chemical name for Nile Blue A Base is "9-diethylamino-5-iminobenzo/$\underline{a}$/-phenoxazine".

## 2. Preparation of the Indicators

Ordinarily indicators of the Nile Blue group are prepared as the salts (II) by condensation reactions (described in literature on dyes), then converted to the bases (I) by treatment with alkali. The oxazone (III) can be prepared either by a condensation reaction or by heating an aqueous solution of the salt with an excess of acid. Purification of the products is accomplished by techniques familiar to the organic chemist.

Nile Blue A and Nile Blue 2B have long been supplied commercially in impure grades. Pure materials were needed for our investigations. Most of them were obtained by gift and were samples of materials that had been synthesized for possible medical applications [14].

## C. Determining Relative Strengths of Acids in Inert Solvents by Spectrophotometry

In comparatively inert solvents like benzene and acetonitrile (which were the solvents of major interest), the relative strengths of acids are measured in terms of their comparative affinities for the reference base which has been selected; see, for example, reference [15]. The best numerical criterion is the value of the equilibrium constant for 1:1 association of the base (symbolized by B) and the acid (symbolized by HA). If the tendency toward formation of BHA is small, overlapping association reactions will probably occur -- for example, formation of $(HA)_2$ or of $B(HA)_2$. When the tendencies for such competing associations are unknown, a flexible program of measurements must be adopted. In this work, a fixed concentration of the indicator base (usually of the order $10^{-5}$ $\underline{M}$) was mixed with systematically varying amounts of the acid.

It is desirable, whenever possible, to continue the experiment to the stage where complete conversion of base to salt may be considered to have occurred. Entire absorption curves are obtained, so that any spectral shifts indicative of competing associations will not be overlooked. When favorable experimental conditions have been employed, association constants can be calculated from spectral data and the stoichiometry. Only materials of high purity were used, and precautions were taken to exclude moisture (even though traces were not likely to affect the results of most experiments).

### 1. Relative Acidic Strengths in Acetonitrile Using Phenyl Diethyl Nile Blue Base

The type of spectrophotometric data obtained is illustrated in figure 5. The absorption curve marked "0" was obtained for Phenyl Diethyl Nile Blue Base in acetonitrile ($8 \times 10^{-5}$ $\underline{M}$). The other curves were obtained using solutions with the same concentration of base but differing amounts of two monobasic acids -- hydrogen chloride and anhydrous diphenyl phosphate. The curve obtained for the solution which contained 4.0 equivalents of diphenyl phosphate ($3.2 \times 10^{-4}$ $\underline{M}$) plus additional solid acid probably corresponds closely to the "limiting" curve (the curve obtained when all of the base has been converted to a salt). In the experiments testing the reactivity of diphenyl phosphate, known amounts of the solid acid were mixed with the base. In the experiments testing the reactivity of hydrogen chloride, known amounts of the base and of the corresponding chloride were used.

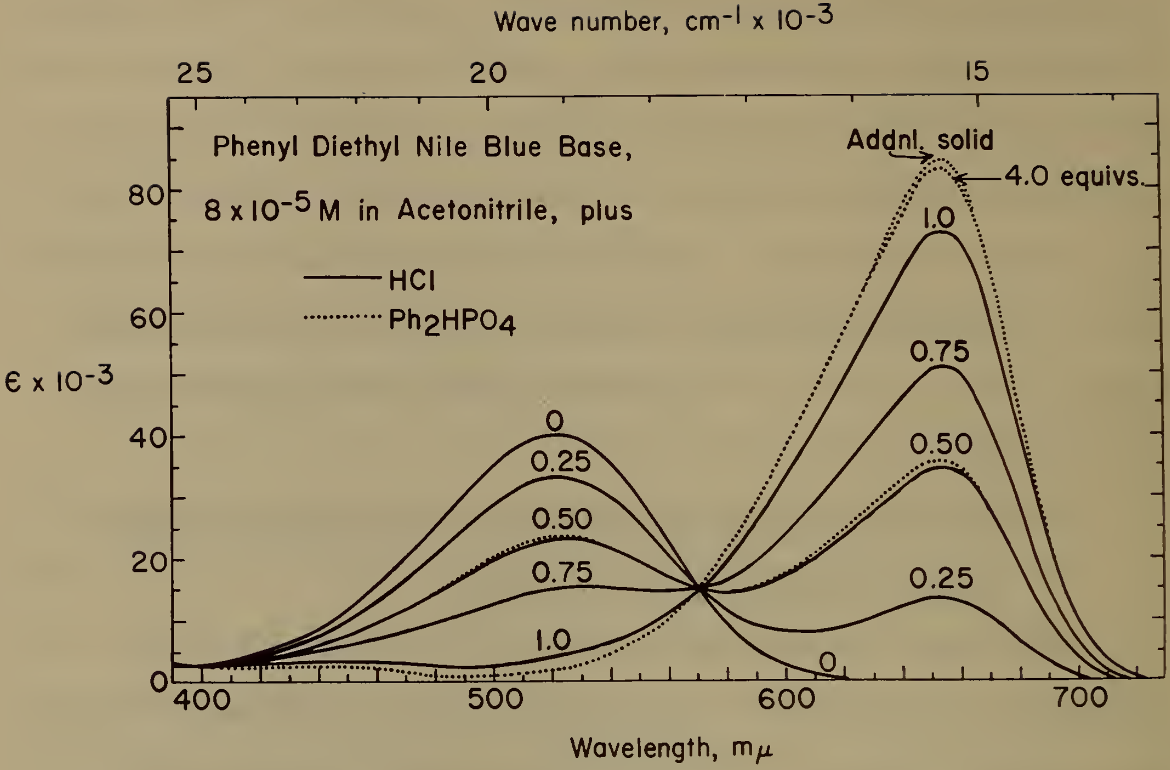


Figure 5. Spectrophotometric curves obtained with Phenyl Diethyl Nile Blue Base.

These preliminary results justify the following conclusions:

(1) The base and acid combined in 1:1 ratio. This conclusion is supported by the spectral evidence that salt formation was nearly complete on adding one equivalent of the acid. Also, the sharp isosbestic point near 570 mμ (570 nm) indicates the probable absence of competing associations, such as formation of $B(HA)_2$.

(2) Hydrogen chloride and diphenyl phosphate do not differ greatly in proton-donor ability.

## 2. Relative Acidic Strengths in Benzene Using Tolyl Dipropyl Nile Blue Base

Figures 6 and 7 present results obtained in studying the comparative reactivities in benzene of three strong acids and five moderately strong acids. Trichloroacetic acid, diphenyl phosphate, and trinitro-*m*-cresol (figure 6) associate fairly readily with Tolyl Dipropyl Nile Blue Base. Trichloroacetic acid is more reactive than trinitro-*m*-cresol in benzene, in keeping with its lower pK value in water.

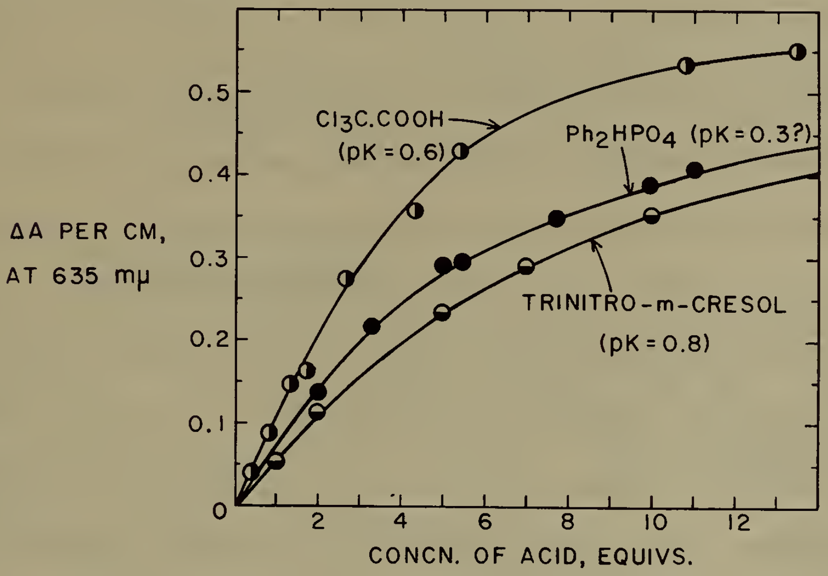


Figure 6. Comparative reactivities of acids in benzene, as measured by their tendencies toward association with Tolyl Dipropyl Nile Blue Base: Trichloroacetic acid, diphenyl phosphate, and trinitro-*m*-cresol.

Diphenyl phosphate seems to be intermediate in strength. The very low aqueous pK value given in parentheses, taken from the literature, was determined under unfavorable conditions and is probably only a rough approximation to the true value. The shapes of the curves in figure 6, and also the well-defined isosbestic points which were observed in the complete absorption curves, indicate that the base is associated with these acids in 1:1 ratio in the concentration range shown. Equilibrium constants were calculated for the associations involving diphenyl phosphate and trinitro-m-cresol; the respective log $K_{\text{assocn.}}$ values were 4.4 and 4.13.

The curves shown in figure 7 which were obtained with the five moderately strong acids, have an S-shape that is more evident when the data are plotted with an expanded horizontal axis. With the possible exception of the reaction involving o-chlorobenzoic acid, overlapping reactions (probably including formation of both BHA and $B(HA)_2$ but chiefly the latter) seem to have occurred under the experimental conditions used. The order of apparent strengths of these five acids in benzene does not parallel exactly the relative order in water (see aqueous pK values given in parentheses). The presence of internal hydrogen bonding in compounds such as o-chlorobenzoic acid is one explanation for this.

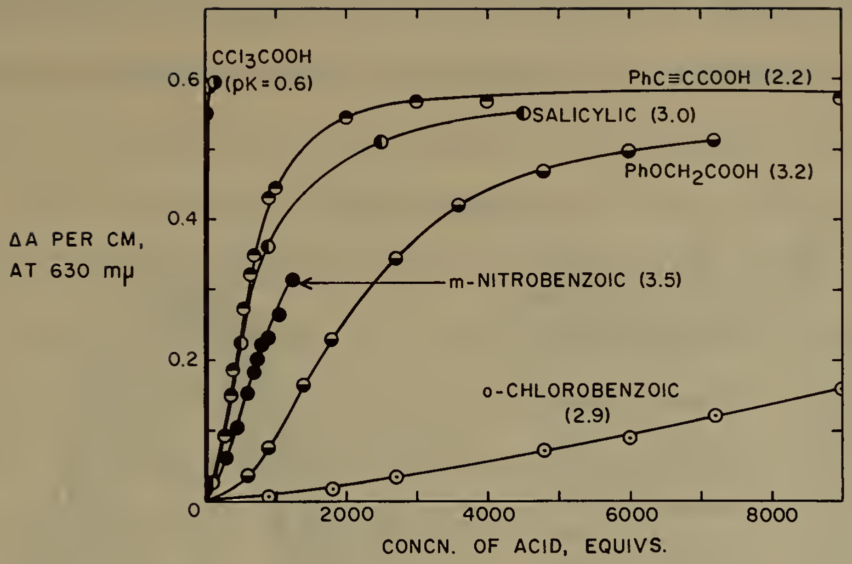


Figure 7. Comparative reactivities of acids in benzene, as measured by their tendencies toward association with Tolyl Dipropyl Nile Blue Base: Phenylpropiolic, salicylic, m-nitrobenzoic, phenoxyacetic, and o-chlorobenzoic acids.

### 3. Nile Blue Oxazone

The oxazone differs from the two anhydro-bases just discussed in (a) being a weaker base, and (b) possessing a marked fluorescence in solution. This fluorescence is quenched by adding a strong acid.

### 4. Solvatochromism vs. Halochromism

Hantzsch [16] coined the two terms "solvatochromism" and "halochromism" to distinguish between two kinds of color changes of indicator dyes. The first term refers to the bathochromic or hypsochromic shifts of spectral absorption curves caused by changing the solvent, and the second term applies to color changes which accompany salt formation.

Halochromic shifts are illustrated in figure 5. Solvatochromism is illustrated in figure 8. The solvation shifts

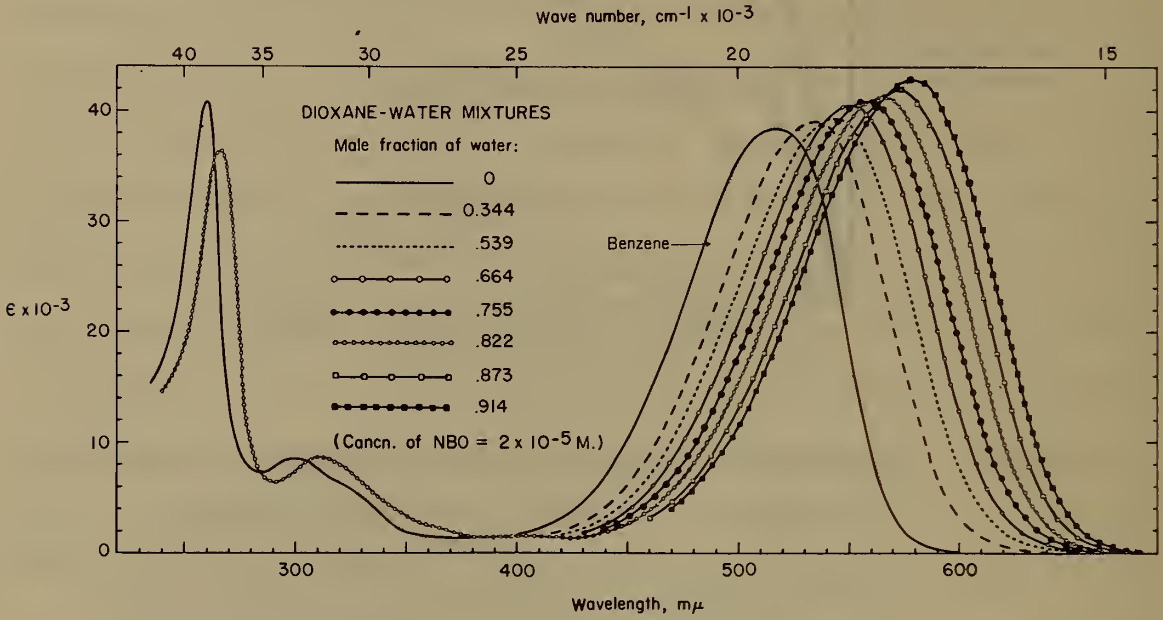


Figure 8. Solvent effects on absorbance of Nile Blue A oxazone.

were produced by adding water, in progressively larger amounts, to dioxane solutions of Nile Blue Oxazone. Analogous shifts were observed on changing from a single solvent such as benzene to more polar solvents, for example acetonitrile and methyl sulfoxide. The anhydro-bases referred to above also exhibit solvatochromism, but the phenomenon is more noticeable when the fluorescent oxazone is used.

Solvatochromism occurs very widely. Solvatochromic shifts have been employed as "empirical parameters" of the relative polarities of solvents; for example, see reference [17]. Most compounds used in deriving such parameters are much more solvatochromic than the Nile Blue group of indicator bases. However, it is apparent that well-marked isosbestic points like those shown in figure 5 cannot be expected if the solvent composition is allowed to change in the process of salt formation.

This last point seems worth stressing, because analytical titrations and various non-spectrophotometric procedures are often carried out with changing solvent composition. Changes in the medium could be responsible for the puzzling results sometimes obtained.

## D. Nonaqueous Titrations Using Indicators of the Nile Blue Group

Nile Blue Oxazone can be used as an indicator in certain titrations with perchloric acid in acetic acid solution, but in general it is less satisfactory than Crystal Violet. However, the fluorescence might be an advantageous property in some applications.

Interesting results have been obtained in using some of the Nile Blue type indicators (as the salts) in nonaqueous titrations. A representative sampling of results is presented in table 8.

Table 8. Relative acidities of some indicator dyes in water and nonaqueous solvents.

| Water[a] | 50 wt. % Methanol[b] | 4:1 Benzene-methanol[c] |
|---|---|---|
| Bromophenol Blue (3.8) | Bromophenol Blue | PHENYL DIETHYL NILE BLUE |
| Bromocresol Purple (6.0) | Bromocresol Purple | Bromophenol Blue |
| Bromothymol Blue (6.8) | Bromothymol Blue | NILE BLUE 2B |
|  | PHENYL DIETHYL NILE BLUE | Bromocresol Purple |
|  | 4-CHLOROBENZYL DIETHYL NILE BLUE | NILE BLUE A |
| NILE BLUE 2B (7.9?) | NILE BLUE 2B | Bromothymol Blue |
| *m*-Cresol Purple (8.4) |  | *p*-Naphtholbenzein |
| *p*-Naphtholbenzein (9.1) |  | *m*-Cresol Purple |
| NILE BLUE A (9.7) | NILE BLUE A |  |
|  | NILE BLUE BX |  |

[a] Value in parentheses is mid-point of pH range.

[b] From approximate pH* value at titration end-point.

[c] From approximate emf at titration end-point [18].

### 1. Comparative Acidities of Indicators in Water and 50 Wt. Percent Methanol

Two broad classes of indicators are represented in Table 8 -- "uncharged" acids (sulfonephthaleins, p-naptholbenzein) and "cation" acids (the Nile Blue group). Not all of the indicators listed have been tested in all three of the solvents represented. So far as comparative behavior in water and 50 wt. percent methanol is concerned, the following tentative conclusions may be drawn: (1) The acidities follow the same relative order in these two solvents. (2) In 50 wt. percent methanol the Nile Blue group of five salts fall in the expected order of decreasing acidity. This order is based on the known effects of substituents R on the basicity of nitrogen.

### 2. Comparative Acidities of the Indicators in 4:1 Benzene-Methanol

The relative positions of Nile Blue 2B and Nile Blue A with respect to uncharged acids are very different from the positions observed for solutions in water or in aqueous methanol. The shifted order makes possible differentiating titrations of strong and weak acids in benzene-methanol [18].

(M. M. Davis)

# 5. SOLVENT EFFECTS ON ACID-BASE PROCESSES OF ANALYTICAL INTEREST

Many chemical processes that occur in solution are essentially interactions between acids and bases. These processes include the synthesis of many organic chemicals and drugs, for example, as well as enzymatic and related physiological operations of importance in clinical studies and in medical research.

It is often desirable to conduct these operations in solvents that are not wholly aqueous, either because the reactants are not sufficiently soluble in water or because a particular nonaqueous solvent has a favorable effect upon the extent of the reaction or the rate at which the reaction proceeds. Although some of these changes are quite profound, they are very little understood.

## A. Behavior of Cation Acids in Alcohol-Water Solvents

It seems clear that the effects produced by a change in the character of the solvent medium are the result of increases or decreases in the strength of the acids and bases which take part in the reactions. The decrease in the strength of weak uncharged acids when the medium is altered by the addition of an organic solvent, producing a decrease of the dielectric constant, is well recognized. This effect can be explained readily, in qualitative fashion, by the electrostatic influence of the lowered dielectric constant on the work of separating the ions.

The behavior of positively charged weak acids such as ammonium ion and the protonated forms of the common amine bases is less easy to explain. When these acids (designated $BH^+$) dissociate in the medium SH as shown by the equation

$$BH^+ + SH = SH_2^+ + B$$

the number of ions remains unchanged. Hence, electrostatic terms should be without substantial influence on the position of equilibrium. Nevertheless, the general pattern of the solvent effect of methyl alcohol on weak acids of this type is an initial increase of strength when the alcohol is added to a water-rich solvent. This increase continues up to a methanol concentration between 60 and 80 wt. percent, where the ionization constant (K) goes through a maximum and then falls rapidly as the amount of water in the solvent becomes small.

### 1. Dissociation of Tris(hydroxymethyl)aminomethane in 50 Wt. Percent Methanol

In an earlier study performed in this laboratory [19], the solvent effect of methanol on the dissociation constants of anilinium-type indicators was examined by a spectrophotometric method. In order to clarify the factors responsible for the rather peculiar form of the pK curve as methanol is added to aqueous solutions of cationic acids, a study of the pK value of protonated tris(hydroxymethyl)aminomethane ("tris") in 50 wt. percent methanol was undertaken. These measurements were made by an accurate emf method and extended over a temperature range (10 to 40 °C) sufficiently wide to permit the enthalpy and entropy changes on dissociation to be derived as well as the pK values.

In essence, the acidity function $p(a_H\gamma_{Cl})$ for buffer solutions composed of tris and its hydrochloride in 50-percent methanol was determined by measuring the emf of hydrogen-silver chloride cells, for which the standard emf was already known (section 3.B). An "apparent" pK value was then obtained by substitution of the acidity function into the expression for the dissociation constant of the acid $\text{tris}\cdot H^+$; the true pK was found by extrapolation of the apparent values to zero ionic strength. The change of pK with temperature enables the thermodynamic quantities associated with the dissociation process to be derived readily. These procedures are set forth in somewhat more detail in section 5.B, where isotope effects in heavy water are discussed.

The results obtained for the pK of protonated tris [20] in 50-percent methanol are compared in table 9 with those earlier found in water [21]. The corresponding values of the enthalpy ($\Delta H°$) and entropy ($\Delta S°$) changes are also given. For comparison with the latter, $\Delta H°$ and $\Delta S°$ for the dissociation of ammonium ion and methylammonium ion in 60 wt. percent methanol [22] are given in parentheses. These are the only thermodynamic data available for the dissociation of a cationic acid in methanol-water solvents.

Table 9. pK and related thermodynamic quantities for the dissociation of protonated tris(hydroxymethyl)aminomethane in 50-percent methanol from 10 to 40 °C.

| t. °C | pK (water) | pK (50-percent MeOH) |
|---|---|---|
| 10 | 8.516 | 8.273 |
| 15 | 8.361 | 8.113 |
| 20 | 8.213 | 7.962 |
| 25 | 8.072 | 7.818 |
| 30 | 7.934 | 7.681 |
| 35 | 7.802 | 7.550 |
| 40 | 7.676 | 7.426 |
| ΔH°(25 °C) | 47.7 kJ $mol^{-1}$ | 47.9 kJ $mol^{-1}$<br>52.6 ($NH_4^+$)<br>53.5 ($MeNH_3^+$) |
| ΔS°(25 °C) | 5.4 J $deg^{-1} mol^{-1}$ | 10.9 J $deg^{-1} mol^{-1}$<br>11.8 ($NH_4^+$)<br>- 6.4 ($MeNH_3^+$) |

### 2. Dissociation of Ammonium Ion in Methanol-Water Mixtures

Standard emf data for the cell at other methanol-water solvent compositions exist only at 25 °C, so thermodynamic data (apart from pK) cannot be obtained. Nevertheless, it was of interest to determine the course of the pK curve for ammonium ion at 25 °C from pure water (pK = 9.245) through 60 percent methanol (pK = 8.591). The results obtained thus far are summarized in table 10.

Table 10. pK values for the dissociation of ammonium ion in methanol-water solvents at 25 °C.

| Wt. Percent Methanol | pK |
|---|---|
| 0 | 9.245 |
| 20 | 9.044 |
| 50 | 8.687 |
| 60 | 8.591 |
| 70 | 8.571 |

### 3. Nature of the Solvent Effect on Cation Acids

As a first step toward explaining these results, the electrostatic approach was examined. If the ions $BH^+$ and $SH_2^+$ were identical in size and contour, the work of charging a mole of each in the same medium would be equal. A change of the solvent would therefore be without influence on the dissociation constant and the amount of energy absorbed or released when a mole of $BH^+$ ions dissociates. If the ions are of different sizes, different amounts of energy are required to charge the two ions, and, consequently, the dissociation energy will vary with the solvent. A further refinement can be introduced by assuming a reasonable variation of the dielectric constant from the region of dielectric saturation at the surface of the ion outward to a distance of 4 Å where the effective dielectric constant of the solvent is believed to approach the macroscopic dielectric constant of the solvent.

Although this electrostatic calculation is able to explain some increase in the strength of cationic acids when methyl alcohol is added to the aqueous solvent, the predicted increase is always far less than that actually observed. Furthermore, the deviations are too large to be explained by the recognized oversimplifications in the method of calculation used. Similar attempts to explain the decrease in strength for uncharged acids likewise produce predicted strengths that are lower than is actually observed, yet it is significant that the deviations are approximately the same for acids of the two charge types in a solvent of fixed composition. This observation makes it appear that a "basicity parameter" characteristic of the solvent should be superimposed upon the electrostatic parameters in order to explain fully the solvent effect [19].

The unexplained enhancement in strength suggests that the basicity of the medium is increased when methyl alcohol is added to water, passes through a maximum, and then decreases as the composition approaches pure methyl alcohol. At first thought, this observation is surprising, for water molecules are believed to be more basic than methanol molecules. At room temperature, however, a considerable part of the water exists in a clustered structure. If methanol were to cause a breakdown in the clustered structure of the water, an increase in the total basicity of the medium could result. It is hoped that further work now underway, as well as studies elsewhere of the structure-breaking properties of the alcohols, will shed some light on the validity of this proposed mechanism.

(R. G. Bates)

## B. Isotope Effect on the Dissociation of Acetic Acid and Dihydrogen Phosphate in Heavy Water

In section 3.C of this report, the electrometric method for determining $p(a_H\gamma_{Cl})$ of acetate and phosphate buffer solutions in deuterium oxide as solvent was described. This was part of work designed to establish a pD scale in deuterium oxide analogous to the pH scale in ordinary water. The same experimental measurements yielded the dissociation constant of acetic acid and the second dissociation of phosphoric acid in deuterium oxide at temperatures from 5 to 50 °C, together with the associated thermodynamic quantities, namely the changes in entropy, enthalpy, and heat capacity, on ionization of the acid [7,8]. A general view of the constant-temperature bath and measuring equipment used for emf studies with the deuterium gas electrode in deuterium oxide solutions is shown in figure 9.

The dissociation constant of acetic acid in deuterium oxide is defined by the equation:

$$K = \frac{m_D\, m_{Ac}}{m_{DAc}} \cdot \frac{\gamma_D\, \gamma_{Ac}}{\gamma_{DAc}} \qquad (1)$$

The acidity function $p(a_D\gamma_{Cl}) \equiv -\log(m_D\gamma_D\gamma_{Cl})$ has been obtained from the cell measurements described earlier. Substitution of $m_D\gamma_D$ from eq. 1 gives

$$p(a_D\gamma_{Cl}) = pK + \log\frac{m_{Ac}}{m_{DAc}} + \log\frac{\gamma_{Ac}}{\gamma_{Cl}\gamma_{DAc}} \qquad (2)$$

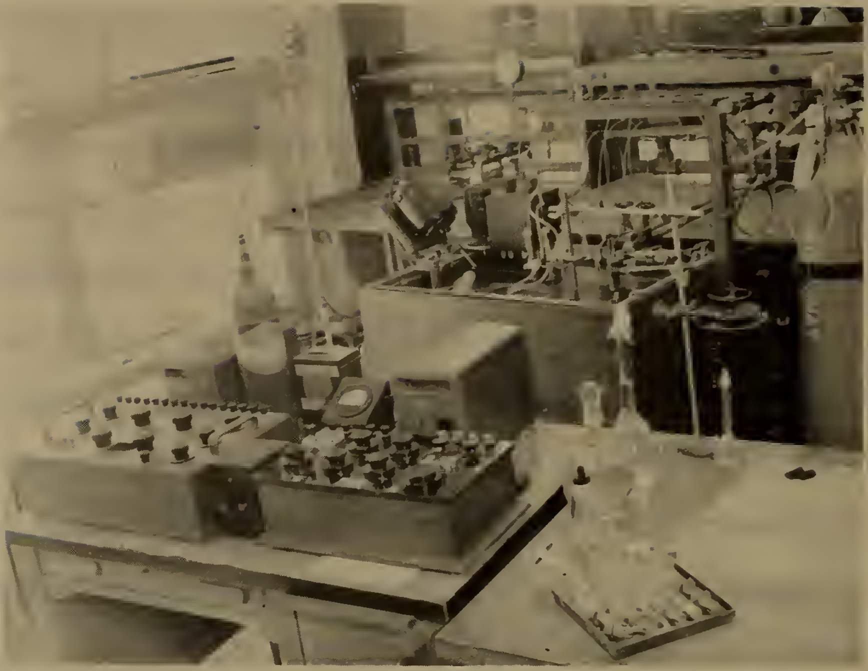


Figure 9. Equipment for emf studies in deuterium oxide solutions.

In these experiments the concentrations of acetic acid and sodium acetate were equal, so that

$$p(a_D\gamma_{Cl}) = pK + \log \frac{\gamma_{Ac}}{\gamma_{Cl}\gamma_{DAc}} \qquad (3)$$

(In dilute solutions, the ionization of acetic acid destroys the equality $m_{DAc} = m_{Ac}$ and requires the application of a small correction.)

Inasmuch as acetate ions and chloride ions have the same charge, $\gamma_{Ac}$ and $\gamma_{Cl}$ will have almost the same value; DAc, an undissociated molecule, will have an activity coefficient close to unity. Hence $p(a_D\gamma_{Cl})$ hardly varies with concentration and pK can be found as the limiting value of a plot of $p(a_D\gamma_{Cl})$ against the total ionic strength.

The calculation is not so easy for the second constant of phosphoric acid,

$$D_2PO_4^- \leftrightarrows H^+ + DPO_4^=, \ K_2$$

even if, as in the present case,

$$m_{D_2PO_4^-} = m_{DPO_4^=}$$

Now,

$$pK_2 = p(a_H\gamma_{Cl}) - \log \frac{\gamma_{DPO_4^=}}{\gamma_{Cl^-}\ \gamma_{D_2PO_4^-}} \qquad (4)$$

The activity coefficient term can, however, be approximated by a Debye-Hückel expression and the right-hand side extrapolated to zero concentration in order to obtain $pK_2$ for phosphoric acid in the deuterium oxide solvent.

Dissociation constants of both of these acids have been measured from 5 to 50 °C. The results are given in table 11, where the data in deuterium oxide as solvent are compared with those for water as solvent.

The results for both acids can be fitted to the equation

$$pK = \frac{A_1}{T} - A_2 + A_3T$$

Table 11. The dissociation constant of acetic acid and the second dissociation constant of deuteriophosphoric acid in deuterium oxide from 5 to 50 °C.

| t, °C | Acetic acid | | Phosphoric acid | |
|---|---|---|---|---|
| | pK in $D_2O$ | pK in $H_2O$ | $pK_2$ in $D_2O$ | $pK_2$ in $H_2O$ |
| 5 | $5.346_3$ | 4.7701 | $7.884_6$ | 7.2810 |
| 10 | $5.334_3$ | 4.7628 | $7.849_9$ | 7.2545 |
| 15 | $5.323_6$ | 4.7581 | $7.823_3$ | 7.2324 |
| 20 | $5.316_8$ | 4.7558 | $7.798_6$ | 7.2145 |
| 25 | $5.313_0$ | 4.7558 | $7.779_6$ | 7.2005 |
| 30 | $5.310_0$ | 4.7581 | $7.766_7$ | 7.1902 |
| 35 | $5.309_3$ | 4.7624 | $7.754_7$ | 7.1834 |
| 40 | $5.311_8$ | 4.7688 | $7.748_4$ | 7.1800 |
| 45 | $5.316_7$ | 4.7770 | $7.743_3$ | 7.1799 |
| 50 | $5.324_5$ | 4.7871 | $7.743_5$ | 7.1828 |

Thus, by standard thermodynamic methods, the changes in enthalpy, entropy, and heat capacity on dissociation can be derived. Values at 25 °C in heavy water and ordinary water are given in table 12.

Table 12. Thermodynamic quantities for the dissociation of acetic acid and phosphate ion in water and in deuterium oxide*.

| | DAc in $D_2O$ | HAc in $H_2O$ | $D_2PO_4^-$ in $D_2O$ | $H_2PO_4^-$ in $H_2O$ |
|---|---|---|---|---|
| $\Delta H°$ (cal mol$^{-1}$) | 275 | - 98 | 1376 | 987 |
| $\Delta S°$ (cal deg$^{-1}$ mol$^{-1}$) | -23.4 | -22.1 | -31.0 | -29.6 |
| $\Delta C_p°$ (cal deg$^{-1}$ mol$^{-1}$) | -38.6 | -36.6 | -58.4 | -54.1 |

* 1 cal = 4.1840 J

(R. A. Robinson)

### C. Improved Spectrophotometric Techniques: Design and Construction of a Controlled-Temperature Cell Block

In the spectrophotometric method for determining the dissociation constant of a weak acid or base, measurements are made, at a given wavelength, of the absorption of light by a solution containing the acid in its undissociated state, another solution in which the acid is completely dissociated into its ions, and a third solution containing both forms. The light absorption measurements give information about the relative proportions of each species present in this last solution. The resulting dissociation constant is known to be dependent on the temperature, and it is important to have some provision for temperature control. This may be accomplished by making the measurements in a temperature-controlled room or by thermostating the cells containing the solutions. Improvement in the latter operation has been achieved.

A thermostated cell block was constructed using the metal cell holder supplied with the spectrophotometer. The holder has provisions for four cells, and a heater was placed in each of the outer cell positions. The heaters were formed by winding 7 ft. of 26 B and S nichrome wire, insulated with glass spaghetti, onto each of two aluminum blocks. The complete heaters fitted snugly into the cell holder. The heater windings were connected in series.

A thermistor cemented to the cell holder served as a sensor in a temperature-control circuit. A second thermistor, used for temperature measurement, was mounted on a movable metal bracket so that it could be placed in the solution in one of the cells or moved aside when solutions were being changed. Leads from the heaters and thermistors terminate in a six-pin socket mounted on the cell holder; the leads from a corresponding six-pin plug were passed through a hole in the lid of the cell compartment.

The resistance of the measuring thermistor is determined using a D.C. Wheatstone bridge. The leads from the regulating thermistor are connected to the input of a commercial electronic proportional temperature controller. The heaters constitute the load for this controller. Provision is made for connecting a 100- or 250-ohm ballast load in series with the heaters.

Using this apparatus, the temperature of the solutions can be regulated between room temperature and 50 °C with a constancy of 0.01 °C. The prototype of this cell block is shown in figure 10.

Figure 10. Controlled-temperature cell block for spectrophotometric measurements.

(B. J. Steel)

# 6. AQUEOUS SOLUTIONS OF MIXED SALTS

The Section's program of research on the properties of aqueous mixtures of pure salts has been assisted by a grant from the Office of Saline Water of the U.S. Department of the Interior.

## A. Methods and Procedures

In general, this research is carried out by the isopiestic method of vapor pressure measurement. This method consists essentially in comparing the vapor pressure of solutions containing two or more salts with the vapor pressure of a solution of a single salt (the "reference" salt).

The apparatus is shown in figure 11. Small silver cups with close-fitting hinged lids are placed, with lids raised, on a heavy copper block. The block and cups are placed in a vacuum desiccator which has a spherical joint in the center of the top. Through the spherical joint passes a glass rod with a "T" on the end. Above the spherical joint is the vacuum control stopcock. The spherical joints, when greased, permit the rotation of the glass rod which in turn rotates the light wire frame which holds open the lids of the cups. A gap in the wire frame permits the lids of the cups to fall one by one as the glass rod in the top of the desiccator is turned. Thus the lids of the cups can be closed before the vacuum of the desiccator is broken. During the experiment the desiccator is immersed in a thermostat.

Figure 11. Isopiestic vapor pressure apparatus, showing the silver dishes and the copper block in the desiccator.

A typical determination is carried out in the following way. Two stock solutions, each containing one of the two salts to be mixed, are prepared. Mixtures of the stock solutions in different proportions are then prepared by weight. The solutions so prepared are weighed into the silver cups which are placed on the copper block (precooled to reduce vapor loss) inside the desiccator. The desiccator is evacuated and placed in the thermostat. It is gently rocked by a mechanical arrangement in the thermostat in order to prevent the formation of concentration gradients in the solutions as they equilibrate with one another.

When the solutions have equilibrated, the lids on the cups are closed, the vacuum in the desiccator is broken, and the cups are reweighed. As the cups lose only about 0.0001 g of vapor per minute, it is easy to correct the weights to the time the vacuum was broken. In each determination, three of the 11 cups in the desiccator contain a solution of an electrolyte such as potassium chloride whose thermodynamic properties are well known. This solution is the standard or "reference" solution.

Many of the simple salt systems which are of the greatest general interest can be studied easily and precisely by the isopiestic method. This method provides the same kind of data as the measurement of the emf of cells. The determination of the thermodynamic properties of mixtures of electrolytes in solution by the measurement of emf of cells is, however, restricted by the availability of suitable electrodes. It would be difficult, for instance, to devise an emf method for the determination of the properties of the mixture water-sodium chloride-potassium chloride. However, this simple system can be studied with relative ease by the isopiestic method.

## B. Results

The first system studied within the reporting period was the system water-glycine-potassium chloride. For this system there were indeed some electrometric data in the literature covering a narrowly restricted range of concentrations. A broader range of data was desired, and furthermore it was desirable to test, with experimentally determined values of the solubility of each component, both the underlying theory and the accuracy of the isopiestic method.

In a paper published early this year [23],data were reported for the system water-glycine-potassium chloride which agreed excellently with prior electrometric data for a restricted range of concentrations. The new data on the activity coefficients of the constituents of the system also predicted in a most satisfactory way the solubility of each of the components in the presence of the other.

Two other papers [24,25] explored the properties of mixtures of sodium chloride with barium chloride and of potassium chloride mixed with the barium chloride. These two systems behave quite differently. Thus the isopiestic ratio in the system sodium chloride-barium chloride is a linear function of the ionic concentration, whereas in the system potassium chloride-barium chloride the same two quantities bear a non-linear relationship to one another.

When the total ionic strength is unity, addition of sodium chloride to barium chloride solutions is found to increase the activity coefficient of barium chloride, and the addition of barium chloride to sodium chloride solutions reduces the activity coefficient of sodium chloride. Thus the activity coefficients tend to come closer to one another. In the system potassium chloride-barium chloride, the activity coefficients of both salts are depressed.

At a total ionic strength of about 2.5, the activity coefficients of sodium and barium chlorides in mixtures of these salts display a slight reversal of the tendency for the activity coefficients to come together. The separation effect on the activity coefficients of potassium and barium chlorides at this ionic strength is still more marked. The type of behavior exhibited in the potassium chloride-barium chloride system is atypical and must indicate unusual ionic interactions in this system.

A fourth paper [26] deals with an additivity rule for the vapor pressure lowering of aqueous solutions containing an alkali metal chloride and an alkaline earth metal chloride. It is found that the vapor pressure lowering of an aqueous solution containing two salts A and B can be compounded additively from the vapor pressure lowerings of a solution containing A alone and a solution containing B alone. The additivity rule disclosed in this paper is that the vapor pressure lowering of the mixture of alkaline metal chlorides and alkaline earth metal chlorides is the sum of the respective vapor pressure lowerings for the salts, each taken at the total ionic strength of the mixed solution.

In some instances the additivity of vapor pressure is valid to within 0.5 percent. Six systems were examined in this paper, and the greatest deviation from additivity amounted to 2.0 percent.

A fifth paper [27] deals with the osmotic and activity coefficients of tris(hydroxymethyl)aminomethane, a compound of interest both as an acidimetric standard and as a biological buffer substance. This base behaves as an almost ideal solute even at high concentrations. The activity coefficients of its hydrochloride are similar to those of ammonium chloride up to 1 molal, and even in concentrated solutions the differences are small. It is concluded that ion-pair formation is not marked.

(V. E. Bower)

# 7. BEHAVIOR OF SODIUM-RESPONSIVE GLASS ELECTRODES

The purpose of this investigation is to determine some of the advantages and limitations of sodium-responsive glass electrodes for the analysis of sodium ions in solution and for the determination of thermodynamic data for solutions of sodium salts in mixed solvents.

## A. Method of Application

If a sodium-responsive glass electrode and a silver-silver chloride electrode are placed in a solution of sodium chloride to form the cell:

$$\text{Glass} \,||\, \text{NaCl (m), AgCl; Ag}$$

the emf of the cell should be given by:

$$E = E' - \frac{2\ RT}{F} \ln a_{\pm} \tag{1}$$

In eq. 1, $a_{\pm}$ is the mean ionic activity of sodium chloride in the solution and E' includes contributions from the standard potential of the silver-silver chloride electrode, the potential of the internal reference electrode, and the asymmetry potential of the glass electrode.

If the emf of the cell is measured for different concentrations of NaCl, then, provided E' is constant,

$$E_2 - E_1 = \Delta E = 2.303 \times \frac{2\ RT}{F} \log \frac{(a_{\pm})_1}{(a_{\pm})_2} \tag{2}$$

Thus, provided $a_\pm$ is known for one solution which can be used as a reference, $a_\pm$ can be determined in other solutions. As a reference solution it is convenient to use an aqueous solution of sodium chloride, since values of mean ionic activity coefficients $\gamma_\pm$ for these solutions are already tabulated in the literature. Hence $a_\pm = m\,\gamma_\pm$ is known for the reference. Since the factor 2.303 RT/F is 0.05916 at 25 °C,

$$\Delta E = 0.11832 \log \frac{a_\pm}{(a_\pm)_{ref}} \qquad (3)$$

Thus, in order to determine log $a_\pm$ with a precision of 0.001, $\Delta E$ must be measured with a precision of better than 0.1 mV. It is also essential that E' remain constant during the determination. The initial problem, therefore, is to measure the emf of the cell with a precision of 0.05 mV and to determine whether the emf of the cell is constant for a reasonable period of time (E' constant).

## B. Procedures

The cell potentials were measured using a precision potentiometer. Because of the high impedance of the cell containing a glass electrode, an expanded-scale pH meter was used as a null detector. The feedback circuit of this meter had been modified to further increase its sensitivity.

The output of the meter was fed into a 1 mV recorder in order to study easily the time-dependence of the measured emf. The sensitivity of the circuitry was adjusted so that 0.05 mV out of balance corresponded to a recorder deflection of 0.1 in. Initially, electrical noise was very troublesome, but with close attention to shielding and the use of an isolating transformer in the a.c. supply circuit, the noise could be reduced to less than 0.02 mV. The thermostat and measuring equipment are shown in figure 12.

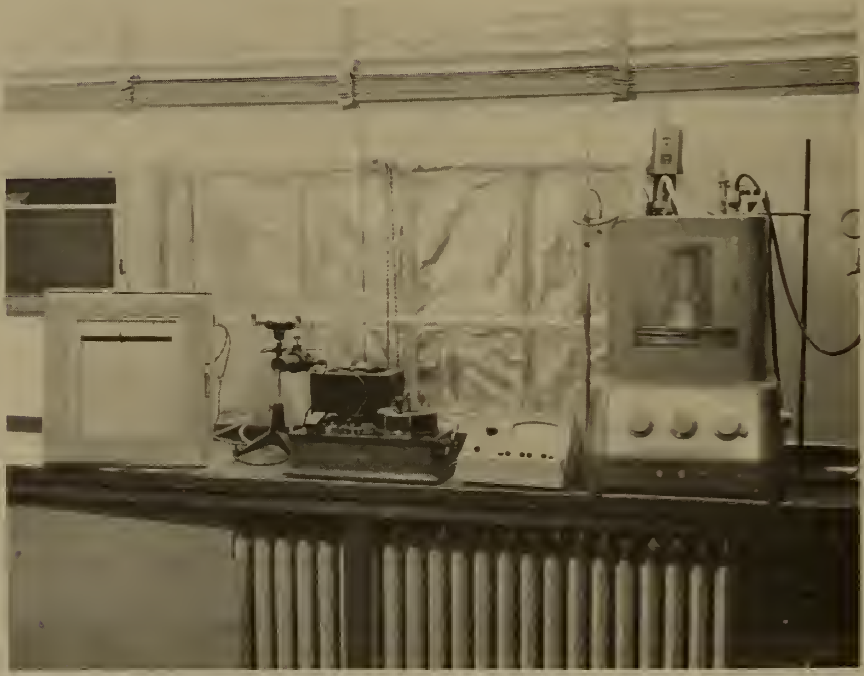


Figure 12. Equipment for studies of the behavior of sodium-responsive glass electrodes.

The measuring circuit was tested by measuring the emf of a standard cell in series with a 100-megohm resistor. The emf of the cell agreed to ± 0.02 mV with that determined using a low-resistance potentiometer circuit. Further, the emf was constant for up to 1 hour, showing that there is negligible drift in the pH meter.

### C. Results

This project is new, and only preliminary results have thus far been obtained. When measurements were made on the glass electrode cells, thermostated at 25° ± 0.01 °C, the emf showed a marked time dependence. In some cases, the cell emf drifted at a rate of 1 mV per minute and, although this rate decreased with time, the cells did not attain a steady emf within several hours. It was eventually shown that this drift could be eliminated by rapidly stirring the solution in the cell. If the stirring was stopped, the emf immediately began drifting again. This effect is present to a smaller extent in new electrodes and is being investigated further.

As a test of the response of the electrodes, the emf of the cells was measured as a concentrated stock solution of sodium chloride was added in weighed aliquots to a stirred solution of sodium chloride in the cell. The results of a typical run are shown in table 13. It can be seen that errors up to 0.25 mV are present in these measurements.

Table 13. Comparison of observed and calculated responses of a sodium-sensitive glass electrode at 25 °C

| Molality of NaCl | log $a_\pm$ | 0.11832 $\Delta$ log $a_\pm$ | $\Delta E$ |
|---|---|---|---|
| 0.06355 | -1.2897 | (Reference) | |
| 0.12005 | -1.0359 | $0.0300_3$ | $0.0300_6$ |
| 0.15043 | -0.9461 | $0.0106_2$ | $0.0106_5$ |
| 0.17380 | -0.8886 | $0.0068_0$ | $0.0066_0$ |
| 0.19539 | -0.8421 | $0.0055_0$ | $0.0052_5$ |

The best type of silver-silver chloride electrode to use in these measurements is being investigated. The thermal-electrolytic type of electrode is rather sluggish in response, probably because of its porous nature. Electrodes formed by electrodepositing silver chloride onto silver wire or chemically deposited silver are being tested.

(B. J. Steel)

## 8. CONDUCTOMETRIC DETERMINATION OF TRACES OF WATER

During the past year, work has been initiated on the application of conductance techniques to the determination of traces of water in gases. The objectives have been oriented toward the development of a simple, inexpensive instrument for the determination of hydrogen in the micro-elemental analysis of organic compounds. To be useful in this context, it is necessary to determine 0.5 to 5 mg of water with an error not greater than 0.01 mg.

The detection scheme was based on the great sensitivity of the conductance of solutions of sulfuric acid in acetic acid to small amounts of water [28]. It has been found that the fractional increase of the specific conductance of solutions of 0.02 to 0.04 M $H_2SO_4$ is about 850 times the weight fraction of water added [29]. Qualitatively, the effect depends on the relative acidities of the constituents, namely $H_2SO_4 > HOAc > H_2O$. Sulfuric acid is a weak acid in this solvent, contributing relatively few protons to the acetic acid. Water is sufficiently basic to accept protons readily from sulfuric acid but not from the solvent. It was predicted that propionic acid would provide an even more sensitive system.

## A. Apparatus

The prototype model of the instrument consists basically of three elements: an absorption-circulation system for transferring water from the gas stream to the electrolyte, the conductance cells, and the electrical measuring system. The absorption system and conductance cell are shown in figure 13.

Figure 13. Conductometric cell for the determination of small amounts of water in a gas stream.

The absorber consists of a vertical helix of 2-mm glass capillary tubing. Gas bubbles entering the bottom of the helix push liquid ahead as they rise and contact the wetted wall. At the top, the spent gas is vented through a drying tube. It was originally intended that the absorber would also provide circulation of the electrolyte through the conductance cells by gravity flow down the tube at the center of the helix. The flow rate proved to be too slow, however, requiring 2 to 3 minutes for one complete circuit of the apparatus. Consequently, an enclosed glass magnetically-actuated pump is now being constructed to provide rapid circulation and mixing of the cell contents. The four-way stopcock provides either for flow through both conductance cells in series or for closing the reference cell and continuing circulation through the indicating cell. The instrument holds 15 cc. of electrolyte.

The two conductance cells are formed by three parallel stainless steel disks separated by 1/16-in. polytetrafluoroethylene gaskets. The middle disk is a common electrode for both cells, and the liquid flow connections are made to both outside disks. This construction provides for a good thermal contact between the cells, for low cell constants (about 0.005), and for small volumes.

The electrical measuring system is a simple Wheatstone bridge. The cells constitute adjacent arms so that it is the ratio of the conductances which is measured. Since the effects of polarization and temperature changes are nearly the same in each cell, these are largely cancelled. One of the two low-potential corners of the bridge is connected to the common electrode and the other to the slider of a 1000-ohm, 10-turn precision potentiometer which, with 5000-ohm end coils, is connected across the outside electrodes.

## B. Results

### 1. Prototype Instrument

a. Water Content of Carrier Gas. In trials with the gas-lift absorption-circulation system, the cell resistance did not reach a constant value after additions of water. After 10 to 15 minutes of circulation, the conductance continued to increase at a uniform rate. This drift rate was equivalent to approximately 400 ppm by volume of water in the "super dry" tank nitrogen used as the carrier gas. Prior passage of the gas through a bed composed of a molecular sieve (size 4A) reduced the drift to a value corresponding to about 150 ppm of water, and this value was also characteristic of tank argon. The drift in conductance also depended on the water content of the electrolyte. Argon or pre-dried nitrogen apparently removed water from solutions of sulfuric acid in propionic acid when more than 300 ppm (by weight) of water was present. In any combustion procedure, no more than one liter of carrier gas should be required to sweep the products into the analyzer, and hence the correction for moisture in the gas can probably be made negligible.

b. Calibration. Of several methods of calibration which were investigated, the most satisfactory was the direct addition of liquid water by weight from a micropipet. Pipets have been made of 5 µl capacity and a 40-mg tare. The calibration results can be expressed in terms of the response factor, F, which is the ratio of the fractional change of specific conductance to the weight fraction of water added to the electrolyte system. The expected value of F was 850, but calibrations of 0.0096 M and 0.0190 M sulfuric acid solutions gave values in the range 415-490. Accordingly, conductances of the systems water-sulfuric acid-organic acid were examined in more detail.

## 2. Fundamental Data

a. Materials. Reagent-grade acetic and propionic acids were distilled through a fractionating column. Approximately 0.4 M sulfuric acid stock solutions were made from concentrated $H_2SO_4$ and were standardized potentiometrically against potassium acid phthalate. An acetic acid solution, 0.0386 M in $H_2SO_4$, and propionic acid solutions 0.052, 0.086, and 0.209 M in $H_2SO_4$ were prepared by dilution. Additions of water were made by weight.

b. Conductances. The conductances of the solutions were measured with conventional conductance equipment at 25 °C. Cells having constants of 0.0616 and 0.001075 were used. The molar conductance of the acetic acid solution was 0.0637 $ohm^{-1}\ cm^2\ mole^{-1}$, about 50 percent higher than the literature value [28]. Water was added in amounts up to 0.18 percent and the resistance (R) measured. A plot of log R *vs*. ppm $H_2O$ showed appreciable curvature. The initial slope corresponded to F = 524, while the slope at the highest water content corresponded to F = 331.

The specific conductance of the solvent propionic acid was $5 \times 10^{-11}$ $ohm^{-1}$ $cm^{-1}$. Molar conductances of the three sulfuric acid solutions increased with concentration from $8.8 \times 10^{-6}$ to $5.4 \times 10^{-5}$ $ohm^{-1}$ $cm^{-1}$, reflecting the extremely slight ionization of the electrolyte. The effect of water on the conductance of each of these solutions was qualitatively similar to that in acetic acid. Values of F for the initial additions of water are shown in table 14.

Table 14. Effect of water on the conductance of solutions of sulfuric acid in propionic acid.

| $H_2SO_4$, *M* | 0.052 | 0.086 | 0.209 |
|---|---|---|---|
| $F_o$ | 621 | 1091 | 1162 |

As expected, F is appreciably larger in propionic acid than in acetic acid. The conductance data for one of these solutions are shown in table 15.

Table 15. Conductance of Water and 0.209 M sulfuric acid in propionic acid at 25 °C (Cell constant: 0.001075).

| Added Water, ppm | Cell Resistance | |
|---|---|---|
| | Measured | Calculated |
| 0 | 95,490 | (95,490) |
| 45.0 | 91,711 | ---- |
| 66.4 | 88,400 | 88,653 |
| 129.2 | 83,940 | ---- |
| 240.9 | 77,960 | 74,606 |
| 421.7 | 68,740 | 64,093 |
| 1095.0 | 44,801 | 42,025 |
| 2018.8 | 28,809 | 28,542 |

## 3. Revision of Instrumentation

The unexpected non-linearity of the water response is inconvenient in an instrument intended to provide a direct analytical result. The circuit shown in figure 14 compensates to a considerable extent for the observed behavior. In this diagram, D represents the potentiometer setting, in ohms, and $R_2$ is the resistance of the reference cell.

When initially balanced, the resistance of the indicating cell, R, is equal to $R_2$, and D = 0. As water is added, $R_2$ remains constant, and the decrease in R is compensated

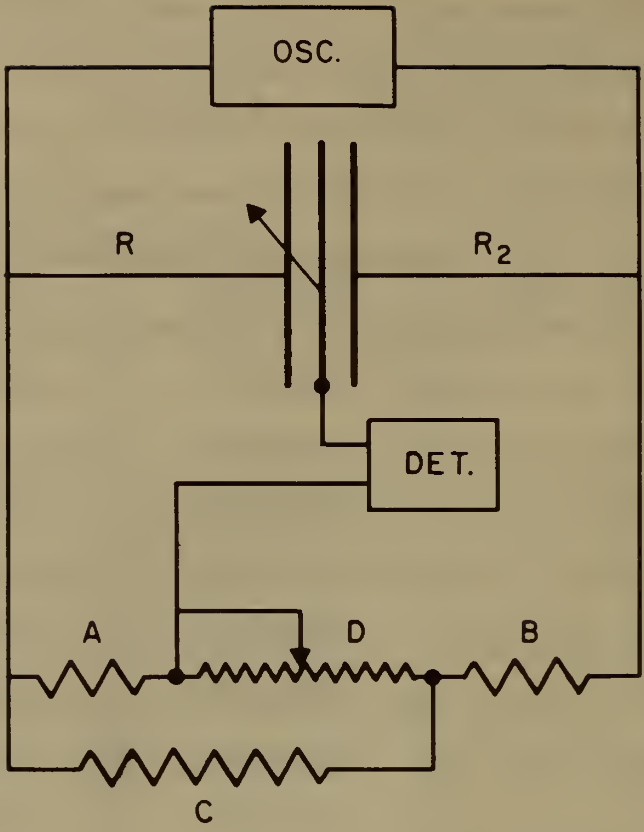


Figure 14. Circuit designed to compensate for the non-linear relationship between conductance and amount of water.

by increasing D. It is readily shown that, for this circuit

$$\left(\frac{d \ln R}{d D}\right)_{D=0} = S_o = \frac{(B + C)}{B(A + C)} \qquad (1)$$

where A, B, and C represent the resistances of the elements identified on the figure. The initial slope $S_o$ is related to the initial value of F by

$$S_o = -F_o/(dD/dW) \qquad (2)$$

where dD/dW is a scale factor relating the dial reading to water content.

It will be remembered that F was defined in terms of the change in specific conductance and therefore is opposite in sign to S. The working volume of the absorber plus indicating cell is 10 cc, so that 100 mg of water provides a concentration of 1 percent. For the system described in Table 15, $F_o$ is 1162 and, hence, $-S_o = 0.01162$ in order to represent 1 percent water by 1000 ohms in D. At the initial balance condition, $B = AC/(A+C)$, and this relation requires that $-AS_o = (2A-C)/(A+C)$. Based on an arbitrary choice of 1.5 for $-AS_o$, $A = C = 129.1$ and $B = 64.5$. These values were used to calculate the third column of Table 15. The agreement with the observed data could be improved by a small change in $F_o$.

(T. B. Hoover)

## 9. REFERENCE MATERIALS FOR DIELECTRIC MEASUREMENTS

### A. Tertiary Butanol

Tertiary butyl alcohol is an amphiprotic solvent of low dielectric constant which is completely miscible with water and most other common solvents. This substance is easily acquired in reasonable purity and appears to be stable up to its boiling point of 82.5 °C. It has a sharp melting point at about 25.6 °C and so it lends itself conveniently to purification by fractional distillation and stepwise recrystallization. The purified compound has a conductivity of less than $10^{-10}$ $\text{ohm}^{-1}$ $\text{cm}^{-1}$ at 30 °C. Samples are easily produced with conductivities well below $10^{-8}$ $\text{ohm}^{-1}$ $\text{cm}^{-1}$, and these can be used with minimal conductivity error in dielectric constant measurements.

In view of these characteristics, accurate measurement of the dielectric constant of this alcohol can serve to establish it as a convenient reference standard for comparative measurements, provided consistent values can be obtained on independent samples. Along with the measurement of the dielectric constant ($\epsilon$) of the pure alcohol and its aqueous mixtures now in progress, comparative data have been obtained on samples from three commercial sources. Values at 25 and 30 °C obtained by a bridge method are shown in table 16, along with the measured melting points and respective conductivities ($\gamma$). Included are determinations made both by comparative and absolute methods.

The results show considerable consistency, and the usefulness of this compound as a standard reference material appears promising. Furthermore, the melting point of tertiary butanol has been proposed as a fixed reference point for temperature measurements and could conceivably be established as such.

Table 16. Dielectric constant of samples of tertiary butyl alcohol at 25 and 30 °C; conductivity at 30 °C.

| Sample No. | m.p., °C | $\epsilon_{25}$ | $\epsilon_{30}$ | $\gamma_{30}$ |
|---|---|---|---|---|
| | | | | μmho $cm^{-1}$ |
| 1A1 | | | 11.444 | 0.0050 |
| 1C1 | | | 11.436 | 0.0016 |
| 2A | $25.6_0$ | $12.46_2$ | 11.446 | 0.0021 |
| 2AB | | $12.46_0$ | 11.445 | $0.0008_3$ |
| 2AA1 | $25.6_0$ | $12.45_8$ | 11.444 | $0.00006_3$ |
| 3AB | $25.6_6$ | | 11.447 | $0.0001_5$ |

## B. Benzene

Benzene has long been used as a standard reference liquid in investigations of dielectric properties. It is not well suited for this purpose, inasmuch as water is appreciably soluble in benzene and influences its dielectric constant. The results of recommended procedures for drying benzene are in effect not entirely consistent. Furthermore, in many cases they are extremely time-consuming, extending to a period of months or more.

Some comparisons of the effectiveness of four drying agents were made using a common commercial lot of benzene. This material was purified by distillation and recrystallization and dried with non-indicating Drierite until a melting point of 5.52 °C was attained. Representative results for the dielectric constant of benzene, shown in table 17, indicate that Drierite and molecular sieves have satisfactory drying rates.

Table 17. Effect of drying benzene on the dielectric constant at 30 °C.

| Drying time (days) | Drying agent or condition | | | | | |
|---|---|---|---|---|---|---|
| | Undried | Wet at 22 °C | Drierite | Molecular sieves | $CaH_2$ | Silica gel |
| 0 | 2.2670<br>2.2665 | 2.2740 | | | | |
| 1 | | | 2.2631 | | | |
| 3 | | | | 2.2626 | | |
| 4 | | | | 2.2625 | 2.2637 | 2.2648 |
| 5 | | | 2.2629 | | 2.2634 | 2.2646 |
| 7 | | | 2.2627 | | | |
| 10 | | | 2.2627 | 2.2626 | 2.2634 | |
| 0 | Dried stock + $CaH_2$ | | | | | |
| 2 | 2.2626 | | | | | |

The differences evident in table 17 are sufficiently large to explain the scatter of the dielectric constants of benzene reported in the literature. If the literature value of 0.54 g/l is taken for the solubility of water in benzene, the data suggest a sensitivity in $\epsilon$ of $2 \times 10^{-4}$ units per 0.01 g of water.

These measurements are made with the three-terminal cell shown in figure 15. It has a working capacity of 21 pf with a liquid volume of about 5 ml and is suitable for use with most low-loss liquids. The capacitance-conductance bridge assembly and constant temperature baths employed are shown in figure 16.

Figure 15. Three-terminal cell for measurements of dielectric constants.

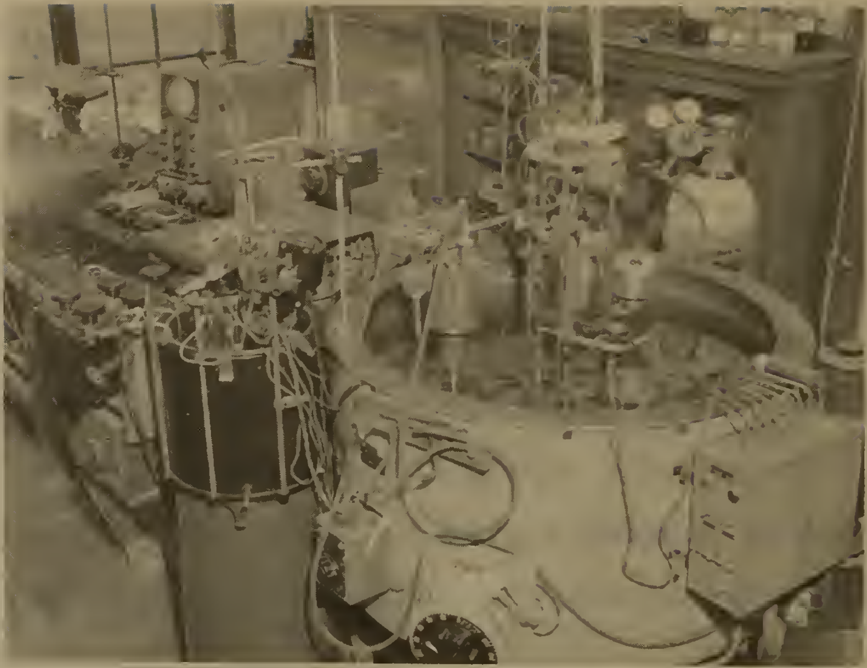


Figure 16. Capacitance-conductance bridge assembly and constant-temperature baths for precise measurements of the dielectric constants of liquids.

C. Dimethylsulfoxide-Water Mixtures

Analysis of the data obtained on dimethylsulfoxide and its aqueous mixtures over the temperature range -5 to 75 °C is in progress. A satisfactory interpretation of the results will require further time.

(C. G. Malmberg)

## 10. KINETIC METHODS OF ANALYSIS

The Section's program dealing with the effect of a change in medium (or environment) on the kinetics of reactions has been redirected in part. In conjunction with the considerable Division effort in trace analytical procedures, emphasis is now being placed on the application of kinetic measurements to analytical problems.

Reaction-rate methods are important in analytical chemistry because many quantitative determinations can be based on measurements of rate. For example, in the analysis of a mixture containing two or more closely related compounds (such as isomers), use can be made of the fact that these compounds undergo the same type of reaction with an added reagent, but at different rates. Likewise, catalyst concentrations can be determined from the rates of catalyzed reactions.

Trace concentrations of many ions can be determined from the catalytic effects of the ions on certain reactions. The sensitivity of these methods is, generally, quite high; however, the reaction chosen is frequently subject to catalysis by other ions. This lack of specificity is a major problem, and experiments are designed to remedy this defect by choosing conditions such that the importance of these interferences is minimized. An understanding of the reaction mecnanism can aid in achieving this goal.

Trace amounts of cobalt can be determined from studies of the rate of reaction between Alizarin Red (a 1,2-dihydroxyanthraquinone dye) and hydrogen peroxide. The usefulness of this method is being examined, and the conditions necessary for high sensitivity and accuracy are being studied.

## A. <u>Experimental</u>

The rate of reaction between Alizarin Red and hydrogen peroxide was determined by observing the decrease in absorption of the dye with time. All spectra were recorded, and all of the absorption measurements were made with the aid of the recording spectrophotometer shown in figure 17.

The water used was obtained by passing the general laboratory distilled supply through a mixed bed ion-exchange column. The disodium hydrogen phosphate solution was prepared from salt available as an NBS Standard Reference Material. An aqueous solution containing 10 percent sodium hydroxide was subjected to electrolysis employing a mercury pool cathode and platinum gauze anode.

## B. <u>Preliminary Results</u>

The rate of the cobalt-catalyzed reaction passes through a maximum value at a pH of about 11.1 in buffer solutions composed of disodium hydrogen phosphate and sodium hydroxide. The rate of the uncatalyzed reaction was studied in the presence of $0.5 \times 10^{-3}$ <u>M</u> to $1.5 \times 10^{-3}$ <u>M</u> disodium ethylenediaminetetra-acetate and was found also to pass through a maximum value at a pH of 11.1 in the same buffer solutions.

Figure 17. Spectrophotometer used to measure the rate of the reaction between Alizarin Red and hydrogen peroxide.

The reaction is first-order both with respect to the dye and hydrogen peroxide at the pH where the maximum occurs. The magnitude of the difference in the rates between the catalyzed and uncatalyzed reactions is such that a sensitivity of $0.1 \times 10^{-9}$ $\underline{M}$ cobalt can be attained. However, erratic results and a lack of satisfactory reproducibility when cobalt is present poses a serious problem.

All experiments that have been performed up to the present time suggest that most of the trouble is due to adsorption of cobalt by the surface of the container in which the reaction is taking place. This process begins when cobalt is added to the reaction vessel and continues while the reaction is occurring; hence the cobalt concentration and the rate of the reaction change during a run.

A polytetrafluoroethylene (Teflon) surface appears to present less of a problem in this respect than do either borosilicate (Pyrex) glass or polyethylene (Nalgene) surfaces. The suitability of organo-silicon coated surfaces is being investigated. Residual impurities in the water and reagents and contamination from containers do not noticeably affect the reproducibility as long as the stock solutions are prepared in the same containers and the number of such containers is held to a minimum. Residual impurities will, however, limit the sensitivity of the method.

Future experiments will be designed to study the tolerance of the reaction to the effects of certain interferences. Attempts will be made to improve the precision of the method at high sensitivities.

(R. K. Wolford)

# 11. PERSONNEL

Electrochemical Analysis Section, Roger G. Bates, Chief
R. A. Robinson, Assistant Chief

Group I. Electromotive Force and
Optical Measurements of Acidity

V. E. Bower
R. Gary
H. B. Hetzer
M. Paabo
R. A. Robinson
B. J. Steel, On leave from the University of
Adelaide, South Australia.

Group II. Conductance Techniques

T. B. Hoover

Group III. Dielectric Measurements

C. G. Malmberg

Group IV. Spectroscopic Techniques for Nonaqueous Media

M. M. Davis

Group V. Isopiestic Vapor Pressure Measurements

V. E. Bower
R. A. Robinson

Group VI. Kinetic Techniques

R. K. Wolford

Group VII. Solubility Techniques

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

Section Secretary

M. Raudenbush

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J. Research NBS. (In Press).

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for pH Control in 50 Wt. % Methanol from 10 to 40 °C.
Anal. Chem. (In Press).

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Amphiprotic and Mixed Solvents.
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2. Bates, R.G., "Acids and Bases in Alcohol-Water Solvents", American Chemical Society, Hawaii Section, University of Hawaii, Honolulu, Hawaii. August 3, 1964.

3. Bates, R.G., "pH Measurements in Amphiprotic Solvents", Gordon Research Conference on Analytical Chemistry, New Hampton, New Hampshire. August 17, 1964.

4. Bates, R.G., "Acid-Base Behavior in Amphiprotic Solvents", Chemistry Seminar, Rutgers University, New Brunswick, New Jersey. October 29, 1964.

5. Robinson, R.A., "Thermodynamic Properties of Multicomponent Solutions", Office of Saline Water, Department of Interior, Mellon Institute, Pittsburgh, Pennsylvania. November 12, 1964.

6. Bates, R.G., "Acids, Bases, and Buffers", Symposium on Current Concepts of Acid-Base Measurements, New York Academy of Sciences, New York, N.Y. November 23, 1964.

7. Bates, R.G., "Acidity and Basicity", Joint Board on Science Education, Randall Junior High School, Washington, D.C. December 16, 1964.

8. Bates, R.G., "Acid-Base Interactions in Alcohol-Water Solvents", Chemistry Seminar, University of Pennsylvania, Philadelphia, Pennsylvania. February 24, 1965.

9. Bates, R.G., "pH Standards", Course on "Advances in Instrumental Analysis", Walter Reed Army Institute of Research, Walter Reed Army Medical Center, Washington, D.C. March 11, 1965.

10. Robinson, R.A., "Thermodynamics of Multicomponent Systems", Department of Chemistry, University of South Carolina, Columbia, South Carolina. March 12, 1965.

11. Bates, R.G., "Acids and Bases in Alcohol-Water Solvents", Research Seminar, Rohm and Haas Company, Philadelphia, Pennsylvania. March 24, 1965.

12. Bates, R.G., Paabo, M., Woodhead, M., Robinson, R.A. "Behavior of Weak Bases in Methanol-Water Solvents", American Chemical Society, National Meeting, Detroit, Michigan. April 7, 1965.

13. Davis, M.M., "Titrimetric and Equilibrium Studies Using Indicators Related to Nile Blue A", American Chemical Society, National Meeting, Detroit, Michigan. April 8, 1965.

14. Robinson, R.A., "Properties of Mixed Salt Solutions", Rensselaer Polytechnic Institute, Troy, N.Y. April 12, 1965.

15. Bates, R.G., "Behavior of Acids and Bases in Methanol-Water Solvents", Chemistry Seminar, University of Kentucky, Lexington, Kentucky. April 30, 1965.

16. Gary, R., "Reference Solutions for a pD Scale", Chemical Society of Washington, University of Maryland. May 7, 1965.

17. Bates, R.G., "The Conceptual Basis of Practical pH Measurements in Water and Other Amphiprotic Solvents", Chemical Institute of Canada, McGill University, Montreal, P.Q., Canada. June 1, 1965.

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