U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1609

Part of Journal of Research of the National Bureau of Standards, Volume 33, October 1944

IONIZATION CONSTANT OF BORIC ACID AND THE pH OF CERTAIN BORAX-CHLORIDE BUFFER SOLUTIONS FROM 0° TO 60° C

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ABSTRACT

The ionization constant of boric acid was determined by the use of the electromotive force of cells without liquid junctions. Hydrogen and silver–silver-chloride electrodes were immersed in borax-sodium chloride solutions. To reduce the possibility of formation of polyborates, dilute solutions were used. The emf were measured at 5-degree intervals over the temperature range 0° to 60° C.

The negative common logarithm of the ionization constant (pK) of boric acid over the temperature range 0° to 60° C may be represented by the equation

$$\mathrm{p}K=2237.94/T+0.016883T-3.305,$$

where T is the absolute temperature.

The data indicate that the mean activity coefficients of the ions of sodium chloride and of sodium borate do not differ appreciably. The pH values for the solutions studied and for rounded values of the concentration are tabulated as functions of temperature and ionic strength. These solutions, which range in pH values from 8.934 to 9.465, can be used as standards in the calibration of glass-calomel and other electrometric pH equipment.

A discussion is given of the significance of the quantity a_i (commonly called the "distance of closest approach" of the ions) and its importance in the calculation of pH values, especially when the buffer ion is not univalent.

The changes in free energy, heat content, entropy, and heat capacity that accompany the ionization of 1 mole of boric acid are listed.

CONTENTS

I. INTRODUCTION

The proper adjustment of the degree of acidity or alkalinity has long been known to be important in the manufacture of many laboratory and commercial products. The control of pH [1] is now a requirement in certain medicinal preparations and in many Federal specifications.

The data reported here form a part of the program for the establishment of pH standards by the National Bureau of Standards. Provisional values for certain buffer solutions have already been published [1].[2]

Very few materials are suitable for use in the standardization of the pH scale in the alkaline range. Borax, $Na_2B_4O_7.10H_2O$, has been frequently used for this purpose, and the pH of solutions of this material, which is approximately 9.2 at 25° C, has been made to cover the range from 8 to 10.5 by the addition of known quantities of acid or base.

The dissociation of tetraborate ion in water to yield simpler ions is well established [2, 3], and measurements of the Raman spectra [3] indicate that the reaction

$$B_4O_7^{=}+3H_2O=2H_3BO_3+2BO_2^{-} \tag{1}$$

is complete. For the purpose of the investigation reported here, it is not important whether the free acid is orthoboric (H_3BO_3) or metaboric (HBO_2), as the concentration of the water in the solutions is not appreciably different. There appears to be some evidence [2] of the formation of tetraboric acid in concentrated solutions, particularly those in which the ratio of free boric acid to borate ion is greater than unity. This view, however, is not upheld by interpretation of the Raman data [3] that have been obtained for various mixtures of borax with hydrochloric acid and for borax with sodium hydroxide in approximately 0.2-*m* solutions. These data indicate that the formation of polyboric acids is probably less than 0.5 percent and that the equations

$$H_3BO_3+OH^{-}=BO_2^{-}+2H_2O, \tag{2}$$

and

$$H_3BO_3=H^{+}+BO_2^{-}+H_2O \tag{3}$$

represent the actual course of the reaction [4]. Additional data are needed before accurate pH values can be calculated for solutions which are more acid than those corresponding to equimolal ratios of boric acid and borate ion. A careful study of the freezing points of such acid solutions would help to clarify the picture.

In order to diminish as much as possible the effects of polyborate formation, the experimental measurements reported here were confined to equimolal ratios of boric acid and sodium borate, added as

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[1] The term pH is defined as the negative common logarithm of the product of the concentration of hydrogen ion in moles per thousand grams of water and the activity coefficient. Mathematically, $pH=-\log_{10}(m_H f_H)$.

[2] Figures in brackets indicate the literature references at the end of this paper.

borax. Likewise, the solutions used were as dilute as practicable, the maximum ionic strength [3] being 0.53.

II. DETERMINATION OF IONIZATION CONSTANTS BY USE OF CELLS WITHOUT LIQUID JUNCTIONS

In the determination of the ionization constant by the use of cells without liquid junctions, hydrogen and silver–silver-chloride electrodes are immersed in the buffer solution containing a known concentration of an alkali chloride. At any given temperature, the "single electrode potential" [4] at the silver–silver-chloride electrode is a function of the known molality of the chloride ion multiplied by the activity coefficient, and the corresponding potential at the hydrogen electrode, at 1-atmosphere pressure of hydrogen, is a function of the activity of the hydrogen ion. Essentially, the total electromotive force of such a galvanic cell depends upon the activity of the chloride ion and the pH of the solution under investigation. As the molality of the chloride ion is known and its activity coefficient may be calculated as shown later, the pH values of the solutions are thus obtained.

The galvanic cell may be represented as follows:

$$\mathrm{Pt}|\mathrm{H_2}(\mathrm{g},\ 1\ \mathrm{atm})|\mathrm{H_3BO_3}(m_1),\ \mathrm{NaBO_2}(m_2),\ \mathrm{NaCl}(m_3)|\mathrm{AgCl(s)}|\mathrm{Ag(s)}. \quad (4)$$

The symbols have their usual significance. The vertical lines indicate the separation of phases, and the commas set off the different components within the same phase.

When current is drawn from this cell, the reaction is

$$1/2\mathrm{H_2}(\mathrm{g},\ 1\ \mathrm{atm})+\mathrm{AgCl(s)}=\mathrm{Ag(s)}+\mathrm{H^+}+\mathrm{Cl^-}. \quad (5)$$

The electromotive force, the activity coefficients, and the concentrations are related by means of the equation

$$E=E^\circ-\frac{RT}{\boldsymbol{F}}\ln(a_\mathrm{H}a_\mathrm{Cl})=E^\circ-2.30259\frac{RT}{\boldsymbol{F}}\log(a_\mathrm{H}m_\mathrm{Cl}f_\mathrm{Cl}), \quad (6)$$

in which E is the measured emf, E° the potential of the silver–silver-chloride electrode against the normal hydrogen electrode in a solution of hydrochloric acid at unit activity, and R, T, and $\boldsymbol{F}$ are the gas constant, the absolute temperature, and the value of the Faraday, respectively.

The activity of the hydrogen ion is governed principally by the ionization constant of the buffer acid. The equilibrium constant of the reaction expressed in eq 3 is given by

$$K=\frac{a_\mathrm{H}a_\mathrm{BO_2}}{a_\mathrm{H_3BO_3}}=\frac{a_\mathrm{H}m_\mathrm{BO_2}f_\mathrm{BO_2}}{m_\mathrm{H_3BO_3}}. \quad (7)$$

In eq 7 the assumption is made that the activity of the unionized boric acid is equal to the molality.

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[3] The ionic strength is defined as $\mu=1/2\ \Sigma mz^2$, where m is the molality and z is the charge of each ion.

[4] The term is used here merely for convenience.

The hydrolysis of the borate ion causes a small change in the stoichiometric ratio $m_{H_3BO_3}/m_{BO_2}$ by increasing simultaneously the quantity of boric acid and decreasing that of the borate ion. The equations

$$m_{H_3BO_3}=m_1+m_{OH} \tag{8}$$

and

$$m_{BO_2}=m_2-m_{OH}, \tag{9}$$

in which m_1 and m_2 are the stoichiometric molalities of boric acid and of sodium borate, represent the equilibrium concentrations of these two substances in solution. The extent of the hydrolysis varies with the dilution and the temperature. From the values for the ionization constants of boric acid (K) and of water (Kw) and the molality of sodium borate (added as borax), it may be shown that eq 10,

$$m_{H_3BO_3}/m_{BO_2}=1+2K_w/(m_1+2m_{OH})K, \tag{10}$$

is applicable at any temperature. Tabular values of these corrections (table 1) may be interpolated for other temperatures and concentrations. The effect of the activity coefficients is negligible in these corrections.

TABLE 1.—*Values for log* $(m_{H_3BO_3}/m_{BO_2})=\log\ (1+2K_w/(m_1+2m_{OH})K$, *(eq 10)*

Temperature	Concentration of borax in moles per 1,000 g water					
	0.002	0.005	0.010	0.015	0.020	0.025
°*C*						
0	0.0016	0.0007	0.0003	0.0002	0.0002	0.0002
5	.0022	.0009	.0004	.0003	.0002	.0002
10	.0030	.0012	.0006	.0004	.0003	.0003
15	.0041	.0016	.0008	.0006	.0004	.0003
20	.0056	.0023	.0011	.0008	.0006	.0004
25	.0074	.0030	.0015	.0010	.0008	.0006
30	.0098	.0039	.0020	.0013	.0010	.0008
35	.0128	.0052	.0026	.0017	.0013	.0010
40	.0167	.0068	.0034	.0023	.0017	.0014
45	.0215	.0087	.0044	.0029	.0022	.0018
50	.0276	.0113	.0057	.0038	.0029	.0023
55	.0351	.0144	.0072	.0048	.0036	.0029
60	.0442	.0182	.0092	.0062	.0046	.0037

Equations 6 and 7 may be combined to eliminate $\boldsymbol{a}_H$ and yield

$$pK=(E-E^\circ)/k+\log\ (m_{H_3BO_3}/m_{BO_2})+\log m_{Cl}+\log\ (f_{Cl}/f_{BO_2}), \tag{11}$$

where pK equals $-\log K$, and k is written for $2.30259RT/\boldsymbol{F}$.

The values of the quantities in the right-hand member of eq 11 are known except for the term log (f_{Cl}/f_{BO_2}). By transposition of the latter, the quantity p$K-\log\ (f_{Cl}/f_{BO_2})=pK'$, the apparent ionization constant, is obtained directly from the experimental data. Extrapolation of the data to zero concentration, at which all activity coefficients are unity, gives the values of pK for each temperature. The values of p$K-$pK' give the magnitude of log (f_{Cl}/f_{BO_2}) but not the activity coefficients of the individual ions.

The activity coefficient of an ion may be represented by any one of several equations, all of which involve certain concepts regarding the electrical field surrounding the ion, the dielectric constant of the medium, and other factors. The original Debye-Hückel expression [5],

$$\log f_i = -Az^2\mu^{1/2}, \tag{12}$$

involves the assumption that the ions behave as point charges. Later, Hückel [6] modified this equation on the supposition that there is a "distance of closest approach", a_i, of ions of opposite charges, and the semithermodynamic equation

$$\log f_i = \frac{-Az^2\mu^{1/2}}{1+Ba_i\mu^{1/2}} + \beta\mu, \tag{13}$$

was thus obtained. In more concentrated solutions or when approximate values of a_i are used [7], the inclusion of the second adjustable parameter β allows eq 13 to represent the experimental data more closely than does eq 12.

The complete expression for the ionization constant of boric acid is obtained by combining eq 11 and 13:

$$\mathrm{p}K - \beta^*\mu = (E-E^\circ)/k + \log\,(m_{\mathrm{H_3BO_3}}/m_{\mathrm{BO_2}}) + \log m_{\mathrm{Cl}} = \mathrm{p}K', \tag{14}$$

where pK and pK' are the negative common logarithms of the true and the apparent ionization constants. If all the assumptions made in the derivation of eq 14 are correct, a plot of the three terms to the right of the first equality sign in this equation against ionic strength should yield a straight line, the slope of which is $-\beta^*$. The value of the intercept at zero ionic strength gives pK. The use of eq 6 for computing the pH values and the method of calculating $\log f_{\mathrm{Cl}}$ for this case are discussed later.

III. EXPERIMENTAL TECHNIC

I. MATERIALS

All the chemicals used met the American Chemical Society specifications for reagent-grade materials. Borax (decahydrated sodium tetraborate) [5] was recrystallized twice [6] from conductivity water in a large Pyrex flask and the contents protected from atmospheric carbon dioxide by means of tubes containing Ascarite. The crystals on the Büchner funnel were washed once with ice cold conductivity water, twice with ethyl alcohol, and finally twice with ether. The material was then air-dried and bottled. The entire cycle of the washing and drying operations was completed in less than one-half hour after the crystals were first collected. The alcohol and the ether were freshly distilled from quicklime, in order to remove possible traces of acids and nonvolatile products, and were used the same day. This procedure for the preparation of borax containing exactly 10 molecules of water is recommended by Hurley [8].

The water content of several portions of the recrystallized material was determined by fusion of 12-g samples at 900° C to constant weight. An average value of 47.20±0.03 percent was found as compared with

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[5] The impurities listed by the manufacturer for this lot totalled 0.003 percent.

[6] The recrystallizations were made below 61° C to avoid formation of the pentahydrate.

the theoretical value of 47.24 percent. Eight months after preparation, analysis showed 47.27 ± 0.02 percent of water and 0.004 percent of carbon dioxide.[7] The alcohol-ether method is satisfactory for the preparation of this material. In addition, it is more convenient than drying moist borax over saturated sodium bromide [9] or saturated sodium chloride and sucrose solutions [10].

The fused borax was prepared in the manner described above, except that the washing with alcohol and ether and the air-drying were omitted. The crystals were warmed as quickly as possible to drive off the free water, and the temperature was then raised above the fusion point of the anhydrous borax. The results in tables 2, 3, and 4, show that both the hydrated and the fused material yield the same value for the ionization constant of boric acid to within an average of 0.0005 unit in pK.

Sodium chloride containing less than 0.01 percent of bromide was further purified by bubbling air through a concentrated, boiling solution of the salt, to which a slight excess of free chlorine had been added. The solution was made slightly acid (pH 5.5), and the bubbling was continued until a negative test for free halogen was obtained on a portion of the solution.[8] Freshly distilled ethyl alcohol was then gradually added to the cooled solution until the concentration of alcohol was approximately 80 percent.[9] The precipitated sodium chloride was filtered by suction, air-dried overnight, heated to 450° C for several hours, cooled, and bottled.

The specific conductance [10] of the water used was 0.8×10^{-6} mho at 25° C. The water was stored in an atmosphere of hydrogen.

Concentrated hydrochloric acid was diluted to correspond to the azeotropic mixture and redistilled in a Pyrex still. The middle third of the distillate was retained.

The hydrogen gas was freed from traces of oxygen by passage over heated palladinized asbestos.

2. SOLUTIONS

Weighted quantities of conductivity water, sodium chloride, and either decahydrated or fused borax were used to prepare accurately 2 liters of stock solution for each series of cell measurements. Proper corrections were made for the water of hydration of the borax. In each case the ionic strength of the stock solution was approximately 0.5. Hydrogen gas was used to force portions of this stock solution into a weight buret, from which known quantities were transferred to each of the 10 dilution flasks, *A* in figure 1, and the proper amount of conductivity water was added. These solutions were saturated with hydrogen gas and protected at all times from contact with the atmosphere. The weighings were corrected for the mass of hydrogen gas and water vapor in the space above the liquid in the dilution flask.[11] The final solutions contained stoichiometrically equal ratios

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[7] The analysis for carbon dioxide was performed by the Detergents, Cements, and Miscellaneous Materials Section of this Bureau.

[8] From the value of the several oxidation potentials involved [11] it should be possible to reduce the total bromide content to 0.001 percent or less.

[9] This fractional precipitation with alcohol has been applied by Hahn [12] for the removal of bromides from potassium chloride.

[10] The conductance measurements were performed by C. G. Malmberg, of the pH Standards Section.

[11] These corrections were of the order of 0.02 percent.

of boric acid to sodium borate (added together as borax) and approximately the same ratio of borate to chloride. The concentration of each component of these solutions was known to within ±0.05 percent. The concentrations, reduced to a vacuum basis, were expressed in moles per 1,000 g of water.

The effect of small quantities of carbon dioxide on the pH of these solutions can be calculated from the approximate ionization constant of boric acid (K_1 [2], and the first and second dissociation constants (K_2 and K_3) of carbonic acid [13] and of water (K_w) [14], together with the activity coefficients of the ions involved.

The equation

$$\boldsymbol{a}_H/f_H + m_{Na} = K_w/\boldsymbol{a}_H f_{OH} + m_1[1 + \boldsymbol{a}_H f_{BO_2}/K_1] + m_2[1 + 2K_3 f_{HCO_3}/\boldsymbol{a}_H f_{CO_3}]/[1 + K_3 f_{HCO_3}/\boldsymbol{a}_H f_{CO_3} + \boldsymbol{a}_H f_{HCO_3}/K_2] \quad (15)$$

represents the equilibrium conditions. m_{Na}, m_1, and m_2 represent, respectively, the total molality of sodium and of all forms of borates and carbonates. The addition of 0.2 mole percent of carbon dioxide to a solution 0.01m in borax lowers the pH by 0.002 unit. In view of the small carbonate content found for the recrystallized borax and the precautions taken to exclude contamination by atmospheric carbon dioxide, it is likely that any possible error from this source does not exceed 0.001 pH unit.

3. EQUIPMENT

The water thermostat, potentiometer, and accessory equipment and the method used in making the measurements in this work differ somewhat from a unit described previously [15]. All measurements were performed in a metal-lined constant-temperature room.

Figure 2 is a general view of the water thermostat, some of the cells (*A*) in position and connected to the hydrogen-supply manifold, the thermoregulator (*B*), and the cooling coil (*C*). The cooling coil and expansion valve for the bath are operated in parallel with a similar unit for cooling the room. For temperatures between 0° and 25° C, the diaphragm valve on the refrigerant line is adjusted to cool the bath slightly below the desired temperature, and a small amount of, heat is supplied electrically as required.

The temperature of the bath was read by means of a calibrated mercury-in-glass thermometer graduated to 0.2° C, and estimated to 0.02° with the aid of a small magnifier [12]. The uniformity of temperature within the bath was tested with a Beckmann thermometer at 20 different locations, corresponding to the positions of the electrodes when in use. At 0°, 25°, and 60° these deviations from the average temperature were respectively ±0.02°, ±0.01°, and ±0.03°. The variations of the temperatures of solutions inside the cells were approximately one-fifth the above.

The electromotive forces of the galvanic cells were measured in international volts. A precision type of potentiometer, a calibrated standard cell, and a sensitive galvanometer were employed. The emf cells have been described previously [15]. One of these cells, ready to be filled with the buffer solution, is shown in figure 1. The method of filling the cells is described later.

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[12] **An uncertainty of 0.02° in temperature corresponds to 0.0003 in pH or p*K*.**

4. ELECTRODES

The hydrogen electrodes were constructed from platinum foils 10 by 15 by 0.2 mm, to which were welded short pieces of platinum wire. A glass bead covering part of the wire and both sides of the foil at the weld[13] was fused to a 5-mm glass tube 3 inches long.

The electrodes were cleaned by boiling for 3 minutes in aqua regia (1 part of concentrated nitric acid and 3 parts of concentrated hydrochloric acid) diluted with an equal volume of water. They were first coated electrolytically with a thin layer of gold and then platinized according to the method of Popoff, Kunz, and Snow [16]. The electrodes were usually prepared before each series of determinations (a "run"), although electrodes from a previous run have occasionally been used. No differences larger than 0.02 mv were observed between electrodes freshly prepared, those used in previous runs, and spare electrodes that had been stored in water for a year or more.

The silver–silver-chloride electrodes were of the thermal-electrolytic type [17]. The older electrodes were made by igniting spheroidal masses of silver-oxide paste around platinum-wire spirals and weighed approximately 0.3 g after being chloridized. In the new ones, the silver-oxide paste was pressed within machine-wound platinum spirals 3 mm in diameter by 6 mm long and then ignited and chloridized. The mixture of silver and silver chloride weighed only 0.08 to 0.10 g and was found to reach equilibrium much more rapidly. Aging the electrodes of both forms overnight in a buffer-chloride solution sufficed to bring them to within 0.05 mv of each other. Where equilibrium is reached, they do not differ by more than 0.02 mv from each other after aging for a year or more.

The electrodes were usually prepared several days before each run, and after aging and checking in a dilute chloride solution were stored in distilled water until needed. Three electrodes of one kind, hydrogen or silver–silver-chloride, were mounted in one rubber stopper.[14]

5. PROCEDURE

The silver–silver-chloride electrodes were removed from the distilled water in which they had been immersed, dried superficially with filter paper, and soaked overnight in a portion of the proper buffer-chloride solution. When checked the next morning, the electrodes generally agreed to within 0.02 mv. The hydrogen and the silver–silver-chloride electrodes were then placed in the proper cell in which the normal atmosphere had been replaced by hydrogen.

The buffer solution in dilution flask *A* (fig. 1) was forced into the emf cell by means of hydrogen gas, and the stopcocks of the flask were then closed. The solution was expelled from the emf cell through stopcock *B* by means of pressure applied at *C* and the cell refilled. The solution was allowed to stand in the cell approximately 5 minutes before being discarded. This process was repeated three

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[13] Soft glass, Pyrex, and "lead sealing-in" glass were found to crack at the bead. Kimble "machine-made flint tubing" has the proper coefficient of expansion for this purpose, and platinum-to-glass seals made from this material will withstand considerable mechanical shock and repeated heatings to 400° C without cracking. Acknowledgment is made to the glassblowing shop of this Bureau for these tests.

[14] The mounting is most conveniently made by thoroughly cooling the rubber stopper in liquid air and drilling the holes in a drill press. The diameter of the drill should be 10 percent less than that of the glass tubing. By this method, a very clean, smooth bore is obtained.

or more times. After the last filling of the cell, solution flask *A* was removed and a connection to the hydrogen supply was substituted. A slow stream of hydrogen, corresponding to that used in the emf measurements, was passed through saturator bulb *D*, and the slight excess of solution above the electrodes in the hydrogen-electrode compartment was run to waste through stopcock *C*. A trap, *E*, was then attached to stopcock *C* and the cell placed in position in the bath (fig. 2) and connected to the hydrogen-supply manifold by means of a semiflexible copper tubing equipped with brass joints of standard taper. The silver–silver-chloride and hydrogen electrodes are shown at *F* and *G*.

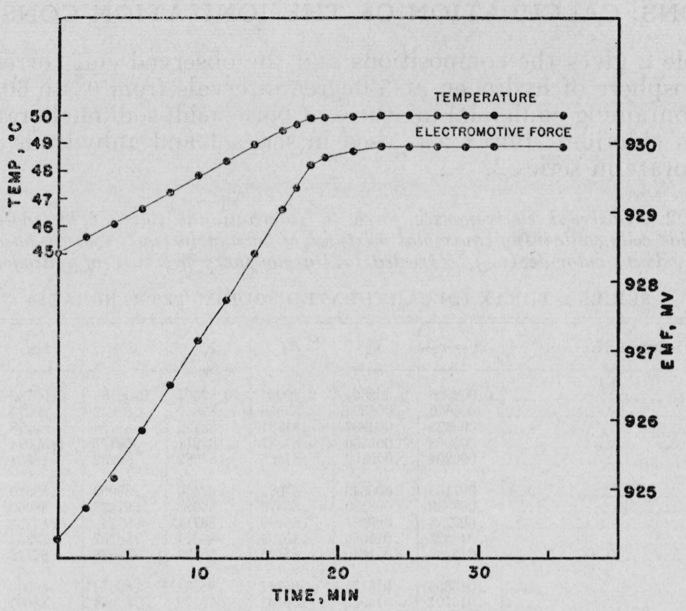

FIGURE 3.—*Typical data of the relation of time and temperature and electromotive force of the cells.*

The bath was heated from 45° to 50° C; the cells reached equilibrium with respect to electromotive force approximately 3 minutes after a new constant temperature in the bath had been attained.

The emf measurements of the 10 cells were first made at 25° C. Because the solutions were already saturated with hydrogen, equilibrium values for the emf were reached in about 2 hours. The bath was then cooled overnight to nearly 0° C; emf measurements were then made at this temperature and thereafter at 5° intervals up to 60° C. After the data had been taken at the highest temperature, the bath was cooled to 25° C and the emf again recorded. In all, three sets of measurements were made at 25° C. Generally, 3 days were required to complete the series of measurements. The emf data were corrected for the vapor pressure of water [18] and to 1 atmosphere of hydrogen [19]. Cells whose initial and final emf values at 25° C differed by more than 0.15 mv (0.0025 pH unit) were rejected as unsatisfactory.

A study was made of the rapidity with which the temperature and the emf of the cell attained equilibrium when the temperature of the bath was raised 5 degrees. The results show that the new thermal equilibrium in the cell was reached in about 20 minutes, and that there was a lag of only about 3 minutes between the thermal and the electromotive force equilibria. A typical record of the data is shown in figure 3.

The three hydrogen and the three silver–silver-chloride electrodes in the same cell permit nine measurements of the emf. Side reactions and abnormal states of electrodes affecting unequally the emf are revealed quickly. The data from such electrodes were rejected.

IV. ELECTROMOTIVE FORCES OF GALVANIC CELLS CONTAINING BORAX-SODIUM CHLORIDE BUFFER SOLUTIONS; CALCULATION OF THE IONIZATION CONSTANT

Table 2 gives the compositions and the observed emf corrected to 1 atmosphere of hydrogen at 5-degree intervals from 0° to 60° C for cells containing equimolal mixtures of boric acid, sodium borate, and sodium chloride. Borax was used in series 1 and anhydrous sodium tetraborate in series 2.

Table 2.—*Observed electromotive force in international volts of hydrogen–silver-chloride cells containing equimolal mixtures of boric acid* (m_1), *sodium borate* (m_2), *and sodium chloride* (m_3), *corrected to 1-atmosphere pressure of hydrogen*

SERIES 1. BORAX (DECAHYDRATED SODIUM TETRABORATE)

Solution No.	$m_1=m_2$	m_3	E_0	E_5	E_{10}	E_{15}	E_{20}
1	0.002906	0.002695	0.89086	0.89607	0.90183	0.90780	0.91375
2	.003660	.003394	.88559	.89057	.89637	.90211	.90797
3	.005323	.004937	.87701	.88192	.88759	.89328	.89896
4	.005963	.005530	.87387	.87911	.88477	.89044	.89613
5	.006204	.006106	.87165	.87682	.88239	.88801	.89369
6	.007163	.006643	.87001	.87486	.88053	.88610	.89169
7	.008830	.008189	.86475	.86988	.87523	.88069	.88628
8	.009313	.009165	.86190	.86711	.87247	.87795	.88343
9	.011227	.011050	.85763	.86271	.86797	.87337	.87874
10	.012767	.011840	.85626	.86137	.86636	.87173	.87705
11	.013384	.013171	.85367	.85834	.86374	.86903	.87434
12	.016101	.014932	.85101	.85572	.86084	.86607	.87134
13	.017902	.017618	.84669	.85170	.85672	.86187	.86701
14	.022415	.020788	.84318	.84783	.85278	.85784	.86303
15	.026859	.026434	.83754	.84224	.84699	.85192	.85691

SERIES 1—Continued

Solution No.	E_{25}	E_{30}	E_{35}	E_{40}	E_{45}	E_{50}	E_{55}	E_{60}
1	0.91955	0.92541	0.93119	0.93705	0.94284	0.94839	0.95386	0.95918
2	.91420	.91989	.92572	.93154	.93729	.94308	.94859	.95397
3	.90479	.91050	.91616	.92191	.92755	.93320	.93873	.94419
4	.90186	.90739	.91306	.91878	.92438	.93003	.93560	.94097
5	.89932	.90489	.91057	.91618	.92178	.92732	.93287	.93831
6	.89720	.90273	.90829	.91394	.91943	.92507	.93055	.93607
7	.89188	.89731	.90279	.90830	.91384	.91941	.92487	.93025
8	.88892	.89435	.89988	.90536	.91085	.91655	.92172	.92704
9	.88418	.88956	.89507	.90046	.90588	.91131	.91667	.92196
10	.88258	.88793	.89333	.89876	.90415	.90960	.91491	.92020
11	.87969	.88500	.89044	.89575	.90109	.90643	.91166	.91692
12	.87656	.88187	.88712	.89245	.89772	.90308	.90837	.91359
13	.87223	.87735	.88265	.88784	.89308	.89835	.90346	.90867
14	.86811	.87315	.87832	.88355	.88871	.89397	.89909	.90423
15	.86198	.86699	.87192	.87697	.88203	.88707	.89200	.89704

TABLE 2.—*Observed electromotive force in international volts of hydrogen-silver-chloride cells containing equimolal mixtures of boric acid* (m_1), *sodium borate* (m_2), *and sodium chloride* (m_3), *corrected to 1-atmosphere pressure of hydrogen*—Con.

SERIES 2. ANHYDROUS SODIUM TETRABORATE

Solution No.	$m_1=m_2$	m_3	E_0	E_5	E_{10}	E_{15}	E_{20}
16	0.003381	0.003403	0.88539	0.89099	0.89666	0.90247	0.90834
17	.005680	.005716	.87308	.87848	.88399	.88964	.89535
18	.007497	.007545	.86659	.87189	.87735	.88289	.88846
19	.009436	.009496	.86128	.86647	.87184	.87719	.88268
20	.009960	.010023	.85992	.86516	.87043	.87582	.88129
21	.014233	.014323	.85158	.85662	.86176	.86693	.87225
22	.015343	.015440	.84987	.85481	.85995	.86516	.87045
23	.018524	.018642	.84553	.85054	.85540	.86061	.86581
24	.020574	.020705	.84322	.84806	.85293	.85809	.86326

SERIES 2—Continued

Solution No.	E_{25}	E_{30}	E_{35}	E_{40}	E_{45}	E_{50}	E_{55}	E_{60}
16	0.91391	0.92013	0.92603	0.93183	0.93760	0.94331	0.94897	0.95428
17	.90083	.90672	.91238	.91799	.92364	.92921	.93475	.94016
18	.89406	.89968	.90529	.91083	.91632	.92186	.92728	.93265
19	.88802	.89363	.89916	.90464	.91011	.91554	.92092	.92629
20	.88671	.89230	.89781	.90325	.90869	.91411	.91953	.92481
21	.87759	.88295	.88828	.89359	.89885	.90415	.90940	.91468
22	.87571	.88099	.88627	.89151	.89675	.90208	.90723	.91233
23	.87103	.87616	.88140	.88661	.89170	.89702	.90214	.90733
24	.86824	.87353	.87868	.88388	.88898	.89416	.89925	.90430

Values of the negative common logarithm of the apparent constant, pK', defined in eq 14, are given in table 3. In calculating these quantities the E° values of Harned and Ehlers [20] were used. Recalculations of $2.30259RT/F$ and of A and B in the Debye-Hückel equation have been made by Manov, Bates, Hamer, and Acree [21].

TABLE 3.—*Values of the negative logarithm of the apparent ionization constant,* pK', *of boric acid from 0° to 60° C in equimolal mixtures of boric acid, sodium borate, and sodium chloride*

SERIES 1. BORAX

Solution No.	Ionic strength	pK'_0	pK'_5	pK'_{10}	pK'_{15}	pK'_{20}	pK'_{25}
1	0.005600	9.5104	9.4331	9.3712	9.3195	9.2709	9.2245
2	.007054	9.5132	9.4333	9.3737	9.3195	9.2711	9.2332
3	.010260	9.5173	9.4388	9.3795	9.3270	9.2777	9.2356
4	.011493	9.5084	9.4371	9.3785	9.3264	9.2782	9.2349
5	.012309	9.5105	9.4385	9.3791	9.3268	9.2791	9.2349
6	.013805	9.5167	9.4395	9.3825	9.3299	9.2811	9.2354
7	.017019	9.5104	9.4401	9.3788	9.3259	9.2787	9.2359
8	.018477	9.5067	9.4387	9.3786	9.3268	9.2784	9.2342
9	.022277	9.5091	9.4401	9.3795	9.3276	9.2788	9.2354
10	.024607	9.5138	9.4457	9.3808	9.3289	9.2796	9.2382
11	.026555	9.5123	9.4371	9.3803	9.3279	9.2792	9.2356
12	.031032	9.5176	9.4441	9.3832	9.3305	9.2820	9.2370
13	.035520	9.5098	9.4431	9.3823	9.3289	9.2794	9.2355
14	.043203	9.5168	9.4447	9.3840	9.3301	9.2826	9.2376
15	.053293	9.5170	9.4478	9.3840	9.3308	9.2816	9.2378

TABLE 3.—*Values of the negative logarithm of the apparent ionization constant,* pK', *of boric acid from 0° to 60° C in equimolal mixtures of boric acid, sodium borate, and sodium chloride*—Continued

SERIES 1—Continued

Solution No.	Ionic strength	pK'_{30}	pK'_{35}	pK'_{40}	pK'_{45}	pK'_{50}	pK'_{55}	pK'_{60}
1	.005600	9.1837	9.1465	9.1141	9.0866	9.0584	9.0320	9.0078
2	.007054	9.1907	9.1554	9.1232	9.0959	9.0718	9.0464	9.0230
3	.010260	9.1954	9.1595	9.1281	9.0999	9.0757	9.0516	9.0302
4	.011493	9.1927	9.1575	9.1263	9.0987	9.0744	9.0514	9.0289
5	.012309	9.1941	9.1596	9.1272	9.1003	9.0750	9.0521	9.0306
6	.013805	9.1943	9.1583	9.1270	9.0990	9.0750	9.0514	9.0318
7	.017019	9.1946	9.1585	9.1261	9.0999	9.0762	9.0533	9.0327
8	.018477	9.1941	9.1597	9.1275	9.1011	9.0801	9.0532	9.0318
9	.022277	9.1953	9.1617	9.1292	9.1028	9.0786	9.0556	9.0345
10	.024607	9.1980	9.1630	9.1315	9.1050	9.0813	9.0577	9.0371
11	.026555	9.1955	9.1619	9.1293	9.1026	9.0779	9.0538	9.0332
12	.031032	9.1976	9.1618	9.1301	9.1031	9.0795	9.0569	9.0363
13	.035520	9.1942	9.1604	9.1276	9.1012	9.0772	9.0529	9.0331
14	.043203	9.1960	9.1611	9.1299	9.1032	9.0801	9.0563	9.0368
15	.053293	9.1978	9.1606	9.1282	9.1015	9.0772	9.0521	9.0316

SERIES 2. ANHYDROUS SODIUM TETRABORATE

Solution No.	Ionic strength	pK'_{0}	pK'_{5}	pK'_{10}	pK'_{15}	pK'_{20}	pK'_{25}
16	.006784	9.5108	9.4422	9.3802	9.3272	9.2787	9.2335
17	.011397	9.5084	9.4401	9.3798	9.3238	9.2792	9.2346
18	.015042	9.5090	9.4411	9.3812	9.3290	9.2808	9.2386
19	.018931	9.5107	9.4425	9.3828	9.3289	9.2809	9.2365
20	.019982	9.5091	9.4422	9.3811	9.3283	9.2804	9.2382
21	.028556	9.5099	9.4423	9.3815	9.3275	9.2797	9.2374
22	.030782	9.5111	9.4421	9.3819	9.3292	9.2812	9.2382
23	.037166	9.5128	9.4465	9.3825	9.3311	9.2831	9.2398
24	.041279	9.5157	9.4470	9.3842	9.3326	9.2849	9.2400

SERIES 2—Continued

Solution No.	Ionic strength	pK'_{30}	pK'_{35}	pK'_{40}	pK'_{45}	pK'_{50}	pK'_{55}	pK'_{60}
16	.006784	9.1963	9.1623	9.1299	9.1029	9.0778	9.0550	9.0300
17	.011397	9.1962	9.1612	9.1282	9.1018	9.0764	9.0533	9.0313
18	.015042	9.1988	9.1645	9.1321	9.1046	9.0800	9.0562	9.0346
19	.018931	9.1974	9.1635	9.1313	9.1048	9.0797	9.0563	9.0357
20	.019982	9.1988	9.1646	9.1322	9.1055	9.0806	9.0580	9.0362
21	.028556	9.1977	9.1628	9.1307	9.1033	9.0785	9.0552	9.0353
22	.030782	9.1976	9.1624	9.1296	9.1024	9.0785	9.0541	9.0319
23	.037166	9.1989	9.1643	9.1321	9.1037	9.0808	9.0568	9.0370
24	.041279	9.2006	9.1653	9.1336	9.1059	9.0815	9.0576	9.0364

In figure 4 are plotted the values of the negative logarithm of the apparent ionization constant, pK', for temperatures of 0°, 25°, and 60° C as a function of the ionic strength of the solution. Except at the greatest dilutions, the points at each of the temperatures lie on a straight line within the limits of experimental error. The extrapolation to zero ionic strength was made readily[15] and the value of pK thus obtained.

In table 4 are given the values of pK, K, and β^* at temperatures from 0° to 60° C. At 0°, 25°, and 60° C, calculations were made separately of the pK, K, and β^* values obtained by using borax and anhydrous sodium tetraborate. Table 4 shows that the agreement is well within 0.001 pK unit and that the degree of hydration of the salt is immaterial.

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[15] The extrapolation was made by the method of least squares.

TABLE 4.—*Summary of values for* pK, β^*, *and* K *from 0° to 60° C*

Temperature	pK	β^*	$K\times10^{10}$	Remarks [1]
°*C*				
0	9.5082	−0.17	3.10	Borax.
0	9.5074	.15	3.11	Fused borax.
5	9.4374	.19	3.65	Average value.
10	9.3785	.11	4.18	Do.
15	9.3255	.12	4.73	Do.
20	9.2780	.10	5.27	Do.
25	9.2342	.07	5.83	Borax.
25	9.2337	.16	5.84	Fused borax.
30	9.1947	.07	6.39	Average value.
35	9.1605	.05	6.91	Do.
40	9.1282	.05	7.44	Do.
45	9.1013	.05	7.92	Do.
50	9.0766	.07	8.38	Do.
55	9.0537	.04	8.84	Do.
60	9.0310	.08	9.31	Borax.
60	9.0310	.14	9.31	Fused borax.

[1] The average values for pK, β^*, and K at the temperatures other than 0°, 25°, and 60° C are those for the solutions of borax and of anhydrous sodium tetraborate given in tables 2 and 3, and in figure 4.

In view of the greater ease of preparation, however, it is recommended that borax, prepared as described earlier in this paper, be used instead of the fused material as suggested previously [1].

The equation

$$\mathrm{p}K=2237.94/T+0.016883T-3.305, \qquad (16)$$

where T is 273.16 plus the temperature in degrees centigrade, reproduces the experimental variation of pK with absolute temperature to within 0.001 unit[16] except at the two extreme temperatures where

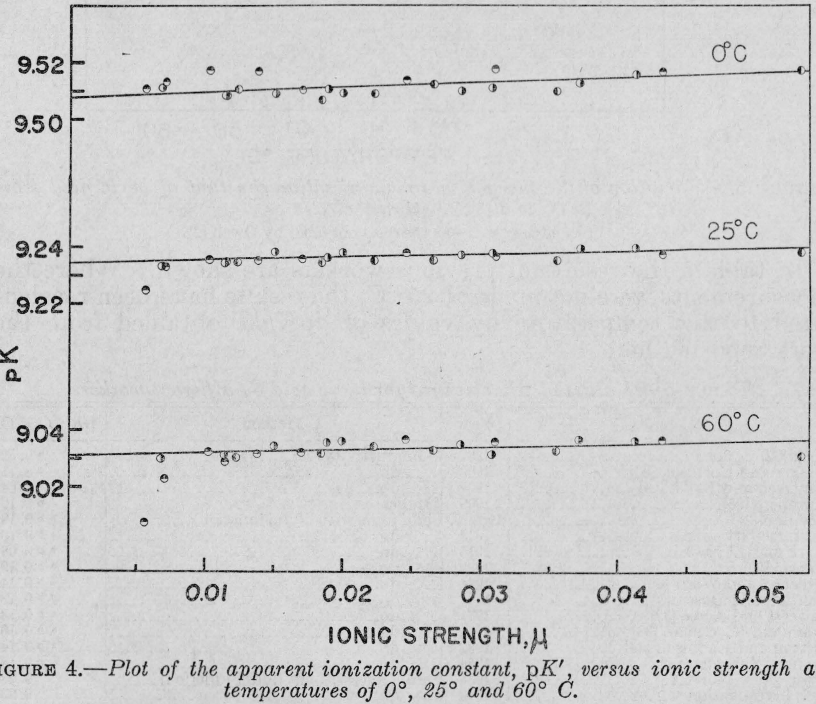

FIGURE 4.—*Plot of the apparent ionization constant,* pK', *versus ionic strength at temperatures of 0°, 25° and 60° C.*

The two series of determinations in which decahydrated borax was used are represented by ◐ and ◓; data for the fused borax are indicated by ◑.

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[16] The constants of this equation were obtained by the method of least squares.

the discrepancies are approximately 0.006 unit. The results are expressed graphically in figure 5, where the values of Owen [2] are included for comparison.

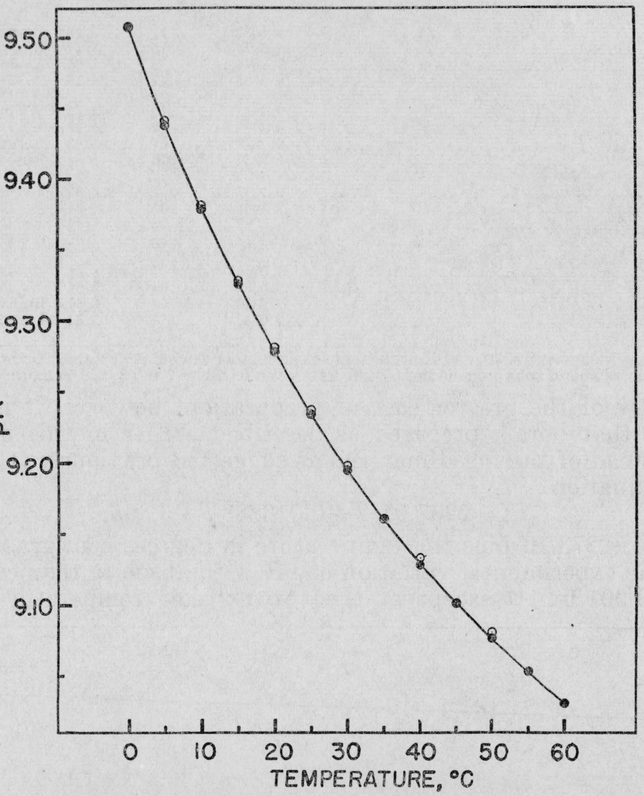

FIGURE 5.—*Variation of the thermodynamic ionization constant of boric acid from 0° to 60° C. (closed circles).*

The open circles represent the data obtained by Owen [2].

In table 5 the results of previous workers are shown. Where the measurements were not made at 25° C, the results have been recalculated to this temperature by values of dpK/dT obtained from the work reported here.

TABLE 5.—*Values of* pK *obtained for boric acid by different workers*

Reference	Year	Method	pK at 25° C
Bock [22]	1887	Conductivity	[a] 9.52
Walker and Cormack [23]	1900	do	[a] 8.71
Hantzsch and Barth [24]	1902	do	8.64
Lundberg [25]	1909	Indicator	[b] 9.19
Sørensen [26]	1909–10	emf (cells with liquid junction)	[a] [b] 9.19
Palitzsch [27]	1915	do	[a] [b] 9.19
Clark and Lubs [28]	1916	do	[a] [b] 9.08
Menzel [29]	1922	do	[a] [b] 9.19
Prideaux and Ward [30]	1924	do	[a] [b] 9.14
Kolthoff and Bosch [31]	1927	do	[a] [b] 9.13
Fawcett and Acree [32]	1931	do	[a] [b] 9.13
Hahn and Klockman [33]	1931	do	[a] [b] 9.10
Britton and Robinson [34]	1932	do	[a] [b] 9.14
Branch, Yabroff, and Bettman [35]	1934	do	[b] 9.185
Owen [2]	1934	emf (cells without liquid junction)	9.236
This investigation	1943	do	9.234

[a] Values corrected to 25° C by use of dpK/dT obtained from this investigation.
[b] Includes possible errors due to salt effects.

V. pH VALUES OF BORAX-SODIUM CHLORIDE MIXTURES

Equation 6 may be rearranged to give

$$\mathrm{pH} = (E - E^{\circ})/k + \log m_{\mathrm{Cl}} + \log f_{\mathrm{Cl}}, \tag{17}$$

from which pH values of the solutions may be calculated when $\log f_{\mathrm{Cl}}$ is known.

In the derivation of eq 13 the parameter a_i was regarded as the sum of the radii of oppositely charged ions in contact. For simple binary salts such a mechanical picture is easily understood, but in more complex solutions each pair of oppositely charged ions can be expected to give rise to different values of a_i. The assumption customarily made is that eq 13 can be applied to each ion of a complex mixture, and for an anion x of charge z, the quantity $\log (f_{\mathrm{Cl}}/f_x)$ is generally expressed by the equation

$$\log (f_{\mathrm{Cl}}/f_x) = \frac{(z^2-1)A\mu^{1/2}}{1+Ba_i\mu^{1/2}} + \beta^*\mu. \tag{18}$$

The use of eq 18 involves the concept that the logarithm of the ratio of activity coefficients can be expressed by the use of "average" values for a_i and for β^*. Under these conditions, the "distance of closest approach" tends to lose its physical significance, and it, as well as the "salt effect term" β^*, become constants whose values are obtained empirically by a process of curve fitting.[17]

When the anion of the buffer acid is univalent, eq 18 reduces to

$$\log (f_{\mathrm{Cl}}/f_x) = \beta^*\mu, \tag{19}$$

in which β^*, as before, is an "average" value for the betas of the two constituents. This use of cells without liquid junctions therefore yields no direct information concerning a_i.[18] The practical solution to this difficulty lies in the experimental determination of the degree of curvature of the plot of pK' as a function of μ (eq 14). A linear relationship will be found only if the values of a_i for the two ions are equal. Examination of the data in figure 4 shows that this condition exists for the solutions studied here. At 0°, 25°, and 60° C the average deviations of the experimental points from linearity are ±0.0011, ±0.0009, and ±0.0014 pK unit, which correspond, respectively, to ±0.06, ±0.05, and ±0.09 mv in emf. These deviations are of the same order of magnitude as the experimental errors and show no significant trend with increasing ionic strength. Calculations indicate that the a_i values for borate and for chloride ions therefore differ by 0.2 A or less, which corresponds to a maximum uncertainty of 0.0008 in pH for the most concentrated solution at the highest temperature.

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[17] This concept is strikingly borne out by recent emf measurements made in this laboratory on the second dissociation constant of phenolsulfonic acid [36]. In order to obtain a linear relationship between pK' and μ, it was found necessary to set a_i equal to 8 angstrom units (A), a value considerably higher than the 4 to 5 A found for other acid-salt mixtures [37, 38]. In the calculation of the pH of a solution, an uncertainty may be introduced when this "average" value for a_i is used in eq 13 and 17 in place of the actual value for the chloride ion. Additional experimental work on activity coefficients in mixtures of salts is necessary before improvements can be made in our present methods of calculating pH. The correct value for a_i for use in such cases probably lies between that for hydrochloric acid alone and that which is found necessary to give a linear relationship between pK' and μ. At an ionic strength of 0.05, the difference in the choice between a_i values of 5 and 8. A corresponds to a possible uncertainty of −0.013 unit in the absolute value of the pH. At present there are no adequate theoretical methods for calculating the magnitude of these effects.

[18] This situation applies to all buffer acids (or bases) in which only the first ionization constant is involved, regardless of the number of species derivable by further ionization. For multivalent anions, values of a_i (and of β) are obtainable from the experimental data and apply only to the particular mixture studied. The assumption is generally made, however, that the a_i values for the uni- and the bivalent ions of the same acid are equal.

Accurate measurements of the activity coefficients of sodium chloride solutions from 15° to 45° C are available from the recent work of Janz and Gordon [39]. The numerical values obtained for a_i by these authors have been recalculated [19] to conform to the preferred values of A and B [21] and are 4.4, 4.4, 4.4, and 4.3 A, respectively, at 15°, 25°, 35°, and 45° C. The average, 4.4 A, has been used here to calculate the pH of borax-sodium chloride buffer soutions from 0° to 60° C.[20]

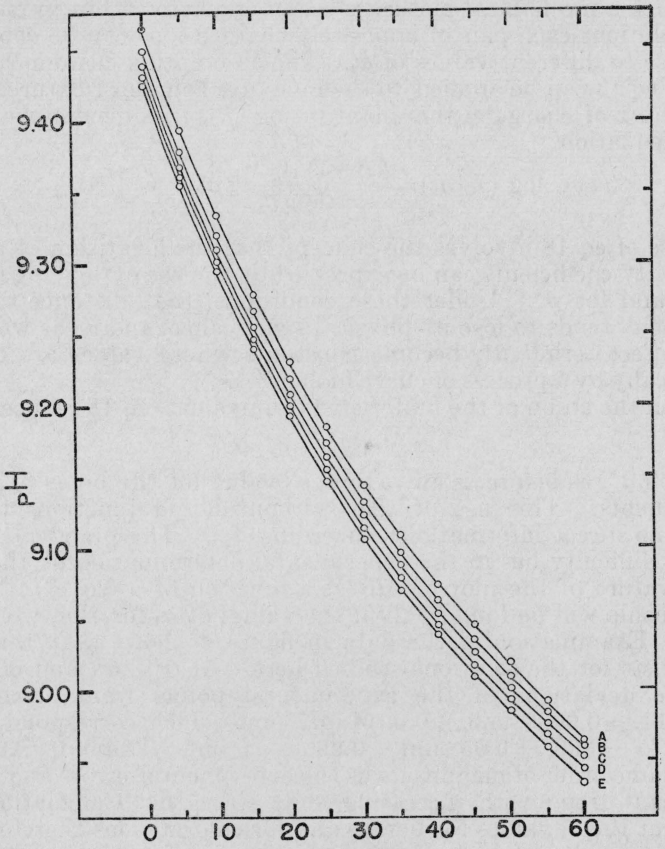

FIGURE 6.—pH *values of equimolal mixtures of boric acid, sodium borate, and sodium chloride from 0° to 60° C at ionic strengths of 0.01 (A), 0.02 (B), 0.03 (C), 0.04 (D), and 0.05 (E), respectively.*

In table 6 the pH values are given for the solutions in series 1 and 2, arranged in order of increasing ionic strength. The pH values from

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[19] The quantities A, B, a_i and β must be self-consistent in order to express correctly the experimentally determined values of the activity coefficients.

[20] Although the a_i values for the chloride and borate ions in this mixture are equal, there is a possible objection to the assumption that the a_i for the mixture is the same as that for pure sodium chloride. Consideration of the work of Güntelberg [40], Hawkins [41], Harned [42], and others on the activity coefficients of mixtures indicates that the above objection is not serious and is unlikely to give rise to uncertainties exceeding 0.002 pH unit.

0° to 60° C at integral ionic strengths are given in table 7 and are presented graphically in figure 6. The values in both tables are regarded as accurate to 0.003 pH unit.

TABLE 6.—pH *values of borax-sodium chloride mixtures from 0° to 60° C*

Solution No.	Ionic strength	0°	5°	10°	15°	20°	25°
16	0.006784	9.473	9.404	9.341	9.287	9.238	9.192
17	.011397	9.461	9.392	9.331	9.275	9.230	9.185
4	.011493	9.461	9.389	9.330	9.277	9.229	9.184
5	.012309	9.461	9.389	9.329	9.276	9.228	9.183
6	.013805	9.465	9.387	9.330	9.277	9.228	9.181
18	.015042	9.455	9.387	9.327	9.274	9.226	9.182
7	.017019	9.454	9.383	9.322	9.268	9.221	9.177
8	.018477	9.448	9.379	9.320	9.267	9.218	9.173
19	.018931	9.451	9.382	9.323	9.269	9.220	9.175
20	.019982	9.448	9.380	9.320	9.267	9.218	9.175
9	.022277	9.445	9.375	9.316	9.263	9.214	9.170
10	.024607	9.447	9.378	9.314	9.262	9.212	9.170
11	.026555	9.443	9.367	9.312	9.258	9.210	9.165
21	.028556	9.439	9.370	9.311	9.256	9.208	9.165
22	.030782	9.438	9.367	9.309	9.255	9.207	9.163
12	.031032	9.444	9.369	9.310	9.256	9.208	9.162
13	.035520	9.432	9.364	9.305	9.250	9.201	9.156
23	.037166	9.433	9.365	9.304	9.251	9.203	9.159
24	.041279	9.432	9.362	9.302	9.249	9.201	9.156
14	.043203	9.432	9.358	9.300	9.245	9.198	9.152
15	.053293	9.424	9.353	9.292	9.238	9.189	9.145

Solution No.	Ionic strength	30°	35°	40°	45°	50°	55°	60°
16	0.006784	9.152	9.116	9.081	9.051	9.022	8.994	8.964
17	.011397	9.145	9.108	9.073	9.045	9.017	8.990	8.964
4	.011493	9.141	9.105	9.072	9.042	9.015	8.989	8.962
5	.012309	9.141	9.105	9.071	9.042	9.014	8.989	8.963
6	.013805	9.139	9.102	9.069	9.039	9.013	8.987	8.963
18	.015042	9.142	9.106	9.073	9.043	9.016	8.990	8.965
7	.017019	9.135	9.098	9.064	9.036	9.010	8.985	8.961
8	.018477	9.132	9.097	9.064	9.036	9.012	8.984	8.959
19	.018931	9.135	9.101	9.067	9.039	9.011	8.986	8.962
20	.019982	9.135	9.100	9.067	9.038	9.011	8.987	8.962
9	.022277	9.129	9.095	9.061	9.033	9.007	8.982	8.958
10	.024607	9.129	9.094	9.061	9.033	9.007	8.982	8.958
11	.026555	9.125	9.091	9.057	9.029	9.002	8.977	8.952
21	.028556	9.125	9.090	9.056	9.027	9.000	8.976	8.953
22	.030782	9.122	9.087	9.053	9.024	8.998	8.973	8.947
12	.031032	9.122	9.086	9.053	9.025	8.999	8.976	8.951
13	.035520	9.115	9.081	9.047	9.019	8.993	8.968	8.944
23	.037166	9.118	9.083	9.050	9.020	8.995	8.971	8.947
24	.041279	9.116	9.081	9.048	9.019	8.993	8.968	8.943
14	.043203	9.110	9.075	9.043	9.015	8.990	8.966	8.942
15	.053293	9.105	9.068	9.034	9.006	8.980	8.955	8.930

TABLE 7.—pH *values of borax-sodium chloride buffers at rounded values of the ionic strength*

Temperature	Ionic strength				
	0.01	0.02	0.03	0.04	0.05
°C					
0	9.465	9.449	9.439	9.431	9.425
5	9.394	9.379	9.368	9.361	9.355
10	9.334	9.320	9.310	9.302	9.295
15	9.278	9.267	9.256	9.247	9.240
20	9.231	9.219	9.208	9.200	9.193
25	9.185	9.174	9.164	9.155	9.147
30	9.144	9.132	9.123	9.114	9.106
35	9.109	9.097	9.088	9.079	9.070
40	9.073	9.063	9.054	9.046	9.039
45	9.046	9.035	9.026	9.017	9.009
50	9.019	9.009	9.001	8.993	8.985
55	8.992	8.984	8.976	8.968	8.959
60	8.964	8.960	8.953	8.944	8.934

Each of the solutions in table 7 may be used as a pH standard. An error of 1 percent in the total concentration corresponds to less than 0.001 in pH, and it is therefore permissible to make up the solution to a total volume of 1 liter instead of weighing out the water separately. A solution composed of 0.01 mole (3.814 g) borax and 0.02 mole (1.169 g) sodium chloride per liter of solution is readily prepared and has a pH of 9.155 at 25° C.

Electrometric pH equipment such as glass-calomel and hydrogen-calomel assemblies and special glass electrodes for determining the pH of highly alkaline materials may be calibrated by means of these solutions. During the past 2 years several hundred comparisons have been made between the pH of a 0.05-*m* solution of potassium acid phthalate (NBS Standard Sample 84 a) and borax-chloride solutions, using various commercial vacuum-tube pH meters. In practically all cases the calibrations of the meter with phthalate and with borax, performed by using these two standards in either order, agreed to within 0.01 pH unit, the limit of error of the best instrument. However, if the glass electrode was old or had been mishandled, the pH-emf relationship departed from linearity, and the agreement between the calibrations then differed by as much as 0.06 unit.

VI. RELATED THERMODYNAMIC QUANTITIES

Values expressed in international joules of the changes in free energy, entropy, heat content, and heat capacity which accompany the ionization of 1 mole of boric acid at infinite dilution [21] can be computed from the following general equations [43], together with the appropriate numerical values from eq 16:

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[21] In accordance with the convention regarding the hydration of solutes at infinite dilution [43], the respective values for orthoboric and metaboric acid are identical.

$$\Delta F^\circ = -RT \ln K = 2.30259RT\mathrm{p}K = 42836 + 0.32315T^2 - 63.264T \tag{20}$$
$$\Delta S^\circ = -(\partial \Delta F^\circ / \partial T)_P = -0.64631T + 63.3 \tag{21}$$
$$\Delta H^\circ = \Delta F^\circ + T\Delta S^\circ = 42836 - 0.32315T^2 \tag{22}$$
$$\Delta C^\circ_P = (\partial \Delta H^\circ / \partial T)_P = -0.64631T \tag{23}$$

The value of R used throughout this paper is that of Cragoe [44]; 8.3127 int. j deg^{-1}. For comparison with data in the literature, the calorie is taken equal to 4.1833 int. j [45]. The derived thermodynamic quantities are given in table 8.

TABLE 8.—*Derived thermodynamic quantities for the process:* $H_3BO_3(aq) = H^+(aq) + BO_2^-(aq)$

Temperature	Δ_P°		Δ_P°		Δ_P°		Δ_P°	
° C	*Int. j*	*cal*	*Int. j*	*cal*	*Int. j*	*cal*	*Int. j*	*cal*
0	49, 667	11, 873	18, 723	4, 476	−113. 3	−27. 1	−176. 5	−42. 2
5	50, 242	12, 010	17, 833	4, 263	−116. 5	−27. 9	−179. 8	−43. 0
10	50, 832	12, 151	16, 926	4, 046	−119. 7	−28. 6	−183. 0	−43. 7
15	51, 439	12, 296	16, 002	3, 825	−122. 9	−29. 4	−186. 2	−44. 5
20	52, 062	12, 445	15, 063	3, 601	−126. 2	−30. 2	−189. 5	−45. 3
25	52, 701	12, 598	14, 107	3, 372	−129. 4	−30. 9	−192. 7	−46. 1
30	53, 356	12, 755	13, 136	3, 140	−132. 7	−31. 7	−195. 9	−46. 8
35	54, 028	12, 915	12, 148	2, 904	−135. 9	−32. 5	−199. 2	−47. 6
40	54, 715	13, 079	11, 144	2, 664	−139. 1	−33. 3	−202. 4	−48. 4
45	55, 419	13, 248	10, 124	2, 420	−142. 4	−34. 0	−205. 6	−49. 2
50	56, 139	13, 420	9, 088	2, 172	−145. 6	−34. 8	−208. 9	−49. 9
55	56, 875	13, 596	8, 036	1, 921	−148. 8	−35. 6	−212. 1	−50. 7
60	57, 627	13, 775	6, 967	1, 665	−152. 1	−36. 3	−215. 3	−51. 5

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WASHINGTON, June 20, 1944.

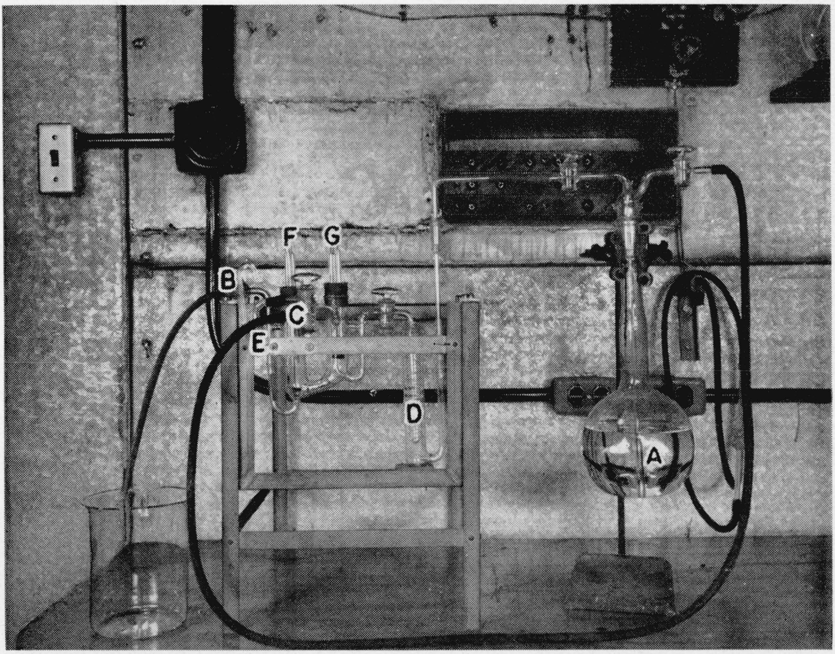

Figure 1.—*Electromotive force cell in position for filling, showing solution flask A, overflow stopcocks B and C, saturator D, trap E, and electrodes F and G.*

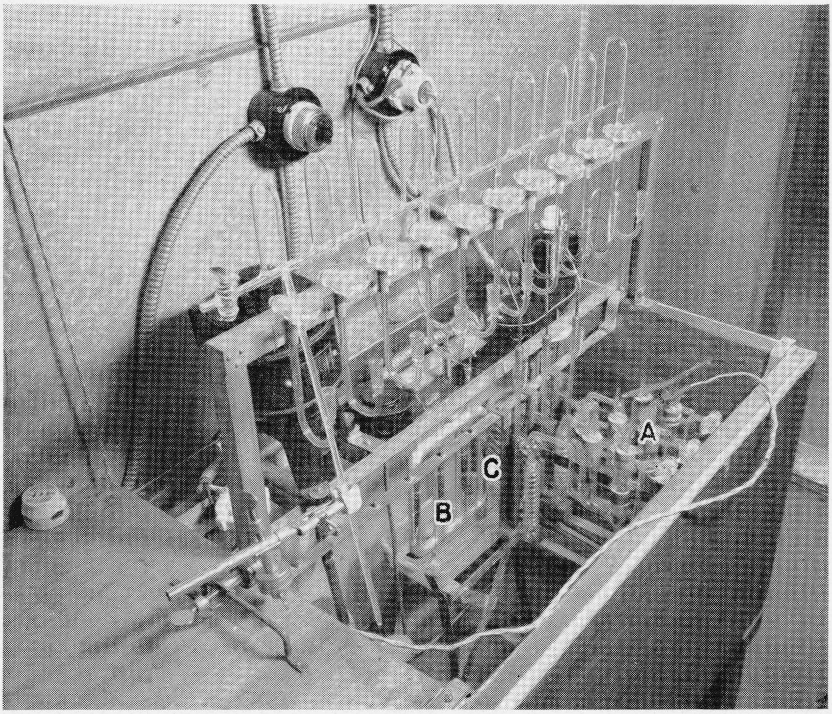

FIGURE 2.—*General view of the bath, showing electromotive force cells, A, connected to the hydrogen-supply manifold by means of the semiflexible copper tubing, the thermoregulator B, and the cooling coil, C.*