pH VALUES OF CERTAIN PHOSPHATE-CHLORIDE MIXTURES, AND THE SECOND DISSOCIATION CONSTANT OF PHOSPHORIC ACID FROM 0° TO 60° C

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ABSTRACT

Measurements of the electromotive forces of galvanic cells composed of hydrogen and silver–silver-chloride electrodes in aqueous chloride-phosphate solutions were made at 5-degree intervals from 0° to 60° C. The solutions were mixtures of sodium chloride, disodium hydrogen phosphate, and either sodium or potassium dihydrogen phosphate; three ratios of the molalities of the two phosphate salts were employed, and a wide range of concentrations was covered. The second dissociation constant was evaluated from the experimental data. The values of the negative logarithm of the constant at each of the 13 temperatures studied may be computed from the following equation:

$$pK_2 = 1979.5/T - 5.3541 + 0.019840T,$$

where T is in degrees Kelvin.

For each temperature, the heat and entropy of dissociation, the change of heat capacity, and the free-energy change accompanying the dissociation of 1 mole of $H_2PO_4^-$ were computed from the variation of the second dissociation constant with temperature.

The pH value of each solution was calculated. The pH values from 0° to 60° C of mixtures of sodium (or potassium) dihydrogen phosphate, disodium hydrogen phosphate, and sodium chloride, in which $m_{H_2PO_4} = m_{Cl}$ and the ratio of the molality of $H_2PO_4^-$ to that of HPO_4^- lies between 0.2 and 5.0, are given by the equation

$$(pH)_t = (pK_2)_t - \log (m_{H_2PO_4}/m_{HPO_4}) - 3A\sqrt{\mu}/(1 + Ba_i\sqrt{\mu}),$$

where μ is the ionic strength. These solutions are proposed as pH standards in the range 6.4 to 7.4.

CONTENTS

I. INTRODUCTION

In the preparation of many commercial products the rapidity and efficiency of the processes depend upon the accurate control of the acidity, or alkalinity, of aqueous solutions. Such control is now a regulatory requirement in certain medicinal preparations and in paper and leather manufactured for the Government. Among other applications, one of particular importance is the avoidance of corrosion and embrittlement of boiler walls and tubes by the control of the acidity of boiler water.

It is important to have recognized pH standards for the control of operations and products and for the calibration of the necessary laboratory and plant equipment, and several such standards have been proposed. The National Bureau of Standards is engaged in developing precise pH standards to cover the useful pH ranges and in making them available for scientific and industrial work. A list of standard buffers and their provisional pH values at 20°, 25°, and 30° C has recently been prepared [1].[1]

Buffer solutions prepared from anhydrous potassium dihydrogen phosphate (KH_2PO_4) and anhydrous disodium hydrogen phosphate (Na_2HPO_4) are among the most suitable standards for the pH range 6 to 8. Both substances are readily prepared in a state of high purity. Neither substance will take up moisture from an atmosphere whose relative humidity does not exceed 40 percent at 25° C. The pressure of water vapor in equilibrium with a system containing solid potassium dihydrogen phosphate and its saturated solution at this temperature is 22.76 mm (96-percent relative humidity) [2]. Anhydrous disodium hydrogen phosphate and the dihydrate are in equilibrium at 25° C with water vapor at a partial pressure of 9.80 mm (relative humidity of 41 percent) [3]. Absorbed moisture was readily lost when the salts were dried for 2 hours at 110° to 120° C.

The first step in the accurate determination of the pH values of mixtures of phosphate salts at several temperatures is the measurement of the ionization, or dissociation, constants of phosphoric acid. The second dissociation constant has been studied at 18° C by several investigators, by the use of cells with liquid junction. The earlier results varied widely. More recently, Bjerrum and Unmack [4] used cells with liquid junction at 18°, 25° and 37° C. Nims [5] extended the range of temperature and calculated the constant from measurements of cells without liquid junction at 5-degree intervals from 20° to 50° C.

It is the purpose of this paper to report a determination of the pH values of some phosphate solutions, the second dissociation constant of the acid, and related thermodynamic quantities, at 5-degree intervals from 0° to 60° C.
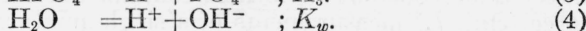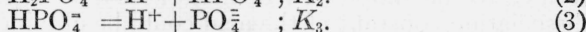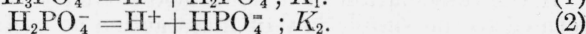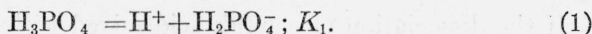
II. METHOD

1. DISSOCIATION OF PHOSPHORIC ACID IN WATER

The distribution of hydrogen among the primary, secondary, and tertiary phosphate ions and the water is determined by the relative

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

amounts of these several species and by the magnitudes of the mass-action constants,[2] K, for the following equilibria:

$$H_3PO_4 = H^+ + H_2PO_4^-; K_1. \tag{1}$$
$$H_2PO_4^- = H^+ + HPO_4^=; K_2. \tag{2}$$
$$HPO_4^= = H^+ + PO_4^{\equiv}; K_3. \tag{3}$$
$$H_2O = H^+ + OH^-; K_w. \tag{4}$$

When a 0.1 M solution of phosphoric acid is titrated with 0.1 M alkali solution the titration curve [6] of figure 1 is obtained. In the
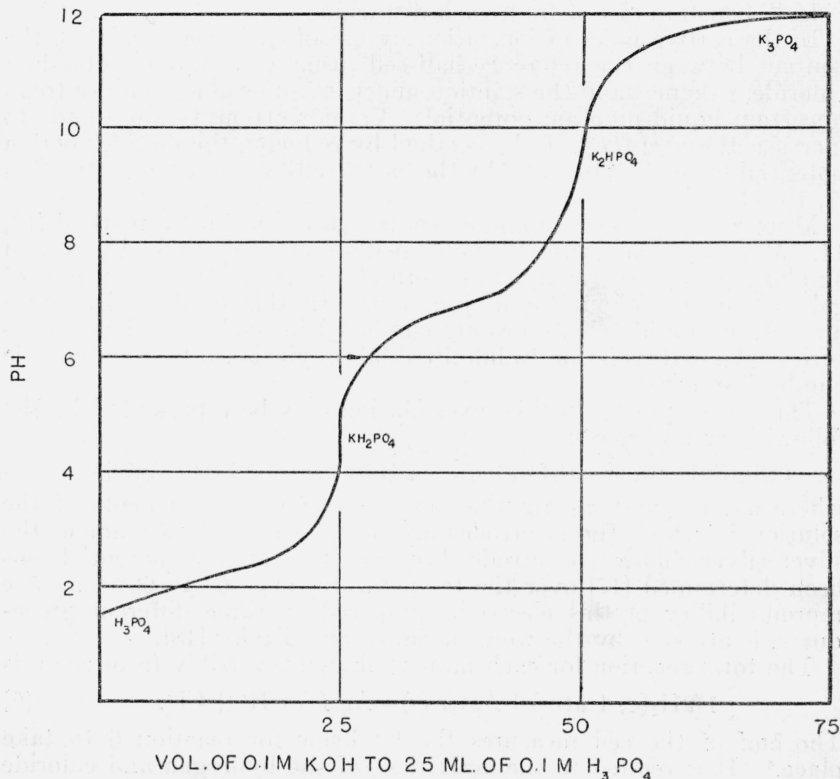
FIGURE 1.—pH *changes in the titration of a solution of phosphoric acid with strong alkali.*

region of the curve corresponding to the addition of 25 to 50 ml of the alkali to 25 ml of the acid, equilibrium 2 is the only one of significance. The solutions studied in determining the second dissociation constant have pH values which lie near the center of this region of the titration curve.

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[2] This term may be applied correctly to any specified equilibrium. For equilibria of types 1 and 4, the term "ionization constant" may be employed. The use of this term for reactions 2 and 3, where ions are both reactants and products, is not as fortunate. The term "dissociation constant" will be applied here to all four of these equilibria. It is understood that each equilibrium should include water as a reactant:

$$HA + H_2O = H_3O^+ + A^-.$$
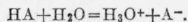
Water has been omitted for simplicity, and hydronium ion (H_3O^+) will be referred to as hydrogen ion (H^+).

2. DISSOCIATION CONSTANTS FROM CELLS WITHOUT LIQUID JUNCTION

If the dissociation of a weak acid mixed with one of its salts conformed to the simple law of mass action at useful concentrations, the dissociation constant of the acid could be obtained from electromotive force (emf, E) measurements of a single mixture. As a consequence of association, interionic or salt effects and other factors, such solutions depart from ideality as the concentration increases. It is therefore necessary to extrapolate the data to zero concentration to secure "ideal" constants freed from such disturbing effects [7, 8].
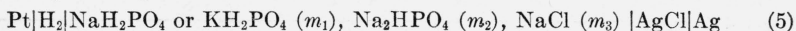
In the early studies of ionization by use of emf measurements, the contact between the reference half-cell (usually saturated potassium chloride, calomel) and the solution under investigation gave rise to an uncertain liquid-junction potential. Various attempts were made to increase the accuracy of the method by reducing the liquid-junction potential to small values and by the use of cells without liquid junction [9, 10, 11, 12].

More recently, Harned and coworkers have outlined a method [13, 14, 15] for obtaining dissociation constants of weak acids, bases, and ampholytes by thermodynamic procedure from measurements of galvanic cells without liquid junction.[3] In this method, hydrogen and silver-chloride electrodes are employed in buffered chloride mixtures. An extrapolation to infinite dilution yields the thermodynamic equilibrium constant.

The cell employed in this investigation may be represented by the following arrangement:

$$\text{Pt}|\text{H}_2|\text{NaH}_2\text{PO}_4 \text{ or } \text{KH}_2\text{PO}_4 \ (m_1), \ \text{Na}_2\text{HPO}_4 \ (m_2), \ \text{NaCl} \ (m_3) \ |\text{AgCl}|\text{Ag} \qquad (5)$$

where m_1, m_2, and m_3 are the molalities of the components of the solution in which the electrodes are immersed. Use is made of the silver–silver-chloride electrode because its standard potential has been determined [17] over the temperature range 0° to 60° C. The reproducibility of this electrode, prepared by three different procedures, is attested by the work of Smith and Taylor [18].

The total reaction for each faraday drawn reversibly from cell 5 is

$$1/2\text{H}_2(\text{g, 1 atm}) + \text{AgCl (s)} = \text{Ag (s)} + \text{H}^+ + \text{Cl}^-. \qquad (6)$$
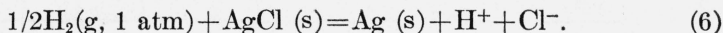
The emf of the cell measures the tendency for reaction 6 to take place.[4] It is related to the activities [5] of the hydrogen and chloride ions by the Nernst equation in the form

$$E - E° = -\frac{RT}{F}(2.3026) \log (a_\text{H} a_\text{Cl}) = -\frac{RT}{F}(2.3026) \log (a_\text{H} m_\text{Cl} f_\text{Cl}) \quad (7)$$

[3] For the application of the method in this Bureau to the determination of the second dissociation constant of malonic acid, see the paper by Hamer, Burton, and Acree [16]. The results of a recalculation of the standard potential of the silver-silver chloride electrode from recent values of the natural constants and the electromotive-force data of Harned and Ehlers [17] are also listed.

[4] The presence of unrecognized "side reactions" is responsible for a frequent error in emf measurements. In such cases, irreversible chemical reactions at either electrode effect a lowering of the measured emf or an elevation above the value which measures the tendency for the principal reaction of the cell to proceed. This type of polarization is known to be absent from hydrogen–silver-chloride cells when reasonable precautions are taken to prevent silver ion from diffusing to the hydrogen electrode, when substances reduced in solution by hydrogen are absent, and when oxygen is excluded. The residual liquid-junction potential caused by the solubility of silver chloride in the solutions is small at finite concentrations and disappears in the determination of the dissociation constant, since both $E°$ and K are obtained by an extrapolation to pure solvent.

[5] The activities of ions and molecules are usually represented by a_i and a_m. By definition, $a_i = f_i m_i$, where f_i is the activity coefficient of the ions of species i, the concentration, m_i, of which is expressed in moles (gram ions) per kilogram of water. The value of an activity coefficient depends on the scale of concentration used, and where it is necessary to make the distinction subscripts are added. Thus f_m, f_c, and f_x represent, respectively, activity coefficients on the molal, volume concentration, and mole fraction scales. In this paper the molal scale is employed exclusively, and the subscript is omitted. The symbol γ is often used for f_m.

where R is the gas constant (8.3127 Int. j deg $^{-1}$ mole $^{-1}$ [19], T is the absolute temperature $(t+273.16)$ [20], F is the faraday (96,500 Int. coulombs [20]), and $E°$ is the standard potential of cell 5.

The equilibrium expression for the second dissociation of phosphoric acid (eq 2) is formulated as follows:

$$K_2 a_{H_2PO_4} = a_H a_{HPO_4} \tag{8}$$

or

$$K_2 m_{H_2PO_4} f_{H_2PO_4} = a_H m_{HPO_4} f_{HPO_4}, \tag{8a}$$

in which K_2 is the second dissociation constant. The symbol a_H represents the activity of the hydrogen ion and all of its solvates to which the hydrogen electrode is reversible. The negative common logarithm of this activity is the pH value. In contrast with the inadequacy of the simple mass-law expression, eq 8 and 8a are exact.

Since the hydrogen-ion activity in mixtures of primary and secondary phosphate ions in the pH range 5 to 9 is governed principally by eq 8a, combination of this expression with eq 7 gives a relation involving electromotive force, the second dissociation constant, activity coefficients, and the molalities of the buffer solutions used in the cells:

$$pK_2 = (E-E°)/k + \log(m_{H_2PO_4} m_{Cl}/m_{HPO_4}) + \log(f_{H_2PO_4} f_{Cl}/f_{HPO_4}), \tag{9}$$

where pK_2 is the negative logarithm of K_2 and k is written for $2.3026RT/F$.

If the activity coefficient of each ion species in the phosphate-chloride mixtures were known accurately, a single measurement of emf would suffice to determine the value of pK_2 at a particular temperature. Unfortunately, activity coefficients for mixtures such as these are not known with precision, and the solution of eq 9 is impossible. Likewise, the extremely dilute region in which the last term of the equation becomes negligibly small is experimentally inaccessible. Recourse may be had, however, to extrapolation formulas such as the Debye-Hückel limiting-law expression, $-\log f_i = A z_i^2 \sqrt{\mu}$ [21], or one of its semiempirical extensions, for the activity coefficient. These formulas, which relate $\log f_i$ to the ionic strength, μ,[6] become more accurate representations of f_i as the solution becomes more dilute. Most important, however, is the fact that the plot of pK_2' [7] with respect to ionic strength is often nearly linear over much of the experimental range, and an extrapolation to zero ionic strength, yielding the true value of pK_2, is made without difficulty. The value of pK_2 is independent of any assumptions regarding the validity of the expressions for f_i that were chosen as an aid to extrapolation [1].

Substitution of the Debye-Hückel limiting-law expression for each activity coefficient in eq 9 gives for pK_2'

$$pK_2' = (E-E°)/k + \log(m_{H_2PO_4} m_{Cl}/m_{HPO_4}) + 2A\sqrt{\mu}, \tag{10}$$

where A is a constant for aqueous solutions at a particular temperature. Values of pK_2' from eq 10 approach the true value of pK_2 in dilute solutions.

An approximation much closer to the experimental activity coefficients than is given by the limiting law may be obtained from the

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[6] The ionic strength is defined by $\mu = \Sigma m_i z_i^2/2$, where z_i is the valence of an ion species of molality m_i. For the solutions used here, where $m_1 = m_3$, $\mu = 2m_1 + 3m_2$.

[7] pK_2' is the negative logarithm of the "apparent" dissociation constant obtained in eq 9 by use of any approximate values for f_i (cf. eq 10).

equation of Guggenheim [22] or from the Debye-Hückel formula, based theoretically on recognition of a finite mean lower limit for the distance of approach of the ions, represented by the parameter a_i; Hückel [23] extended the usefulness of the latter equation still higher in the range of ionic strengths by adding a term linear in μ. The change of the activity coefficient of any ion species i as a function of ionic strength is thus best represented in terms of two general constants, A and B, and two adjustable parameters, a_i and β, in the equation

$$-\log f_i = \frac{A z_i^2 \sqrt{\mu}}{1 + B a_i \sqrt{\mu}} - \beta \mu. \tag{11}$$

The values of a_i and β are averages characteristic of the mixture, depending upon the specific properties of the ions that compose the mixture and upon the relative ionic concentrations. The constants A and B vary only with the dielectric constant and temperature.[8]

When each activity coefficient of eq 9 is expressed in the form of eq 11, the dissociation constant becomes

$$pK_2 = [(E - E^\circ)/k + \log(m_{H_2PO_4} m_{Cl}/m_{HPO_4}) + 2A\sqrt{\mu}/(1 + B a_i \sqrt{\mu})] + \beta \mu. \tag{12}$$

All quantities on the right side of eq 12 are known, with the exception of the parameters a_i and β. Further, provided eq 11 is adequate to express the change of activity coefficient with ionic strength, it is evident that there will be a particular value of a_i for which pK_2, the expression in brackets (eq 12), will be a linear function of μ, that is,

$$pK_2 = pK_2' + \beta \mu. \tag{13}$$

Computations of pK_2' were therefore made at each temperature for several values of a_i until the most satisfactory straight line was established. The slope of this plot of pK_2' with respect to μ gives the value of the parameter β; the intercept at zero ionic strength is pK_2, the negative common logarithm of the true, or "thermodynamic," dissociation constant.

3. pH VALUES OF THE PHOSPHATE-CHLORIDE MIXTURES

It is implied in the foregoing discussion that the activity coefficient of chloride ion, f_{Cl}, in each of the solutions studied can be computed from eq 11 with the use of the numerical values of the average parameters a_i and β for the 13 temperatures. Hence, combination of eq 7 and 11 gives an expression which makes possible the calculation of the pH values at any temperature directly from the emf and the composition of the solution:

$$pH = (E - E^\circ)/k + \log m_{Cl} - A\sqrt{\mu}/(1 + B a_i \sqrt{\mu}) + \beta \mu. \tag{14}$$

III. ERRORS OF METHOD AND SIMPLIFICATIONS

1. BUFFER RATIO

The successful application of eq 12 to a determination of pK_2 requires an accurate knowledge of the ratio of primary phosphate ion to secondary phosphate ion. This quantity, $m_{H_2PO_4}/m_{HPO_4}$, is the

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[8] The dielectric constant is assumed to be constant with changing ionic strength and to be the same as the gross dielectric constant of pure water.

"buffer ratio", and its value is derived from the known molalities of the primary and secondary alkali metal phosphates of which the cell solutions are composed. As a result of dissociation and hydrolysis, however, the true ratio of the ions is not always the same as the ratio of the stoichiometrical molalities of the buffer salts.

From the equilibrium constants for eq 1 and 3 [9] it may be shown that the quantity of H_3PO_4 is less than 0.01 percent of the $H_2PO_4^-$ in solutions whose pH values lie between 6 and 8, whereas the amount of $PO_4^{\equiv}$ is less than 0.05 percent of the total HPO_4^-. The maximum error of 0.05 percent in the buffer ratio caused by neglect of the phosphoric acid and trivalent phosphate ion corresponds to about 0.0002 pH unit, or somewhat less than 0.02 mv in the emf. This error is slightly less than the experimental uncertainty inherent in the measurement.

The possibility of the formation of $HPO_4^{\equiv}$ by the dissociation of $H_2PO_4^-$, or of the combination of $HPO_4^{\equiv}$ with hydrogen ion to form $H_2PO_4^-$, upon solution of the phosphate salts in water demands particular attention, for such changes in composition alter the numerator and denominator of the buffer ratio in opposite directions.

Since the influence of the first and third dissociation equilibria (eq 1 and 3) has been shown to be negligible, any deviation of the pH of the mixture from that of pure water may be ascribed to eq 2 and 4. For the most dilute solution of the smallest buffer ratio (solution C9), these reactions cause a maximum change in buffer ratio which corresponds to 0.0005 in pH and pK_2, or about 0.03 mv in the emf. The stoichiometrical ratio, then, may be used as the buffer ratio in solutions having pH values between 6 and 8 without dissociation or hydrolysis corrections.

2. EFFECT OF CARBONATE

The titration of the first acid group of carbonic acid is complete at a pH value near 8.5, in a 0.1 M solution. Any carbonate impurity in these phosphate buffer solutions would be present, then, chiefly as dissolved carbon dioxide (or carbonic acid) and bicarbonate ion and would be removed only slowly by the bubbling hydrogen. Likewise, the reaction of carbon dioxide with the disodium salt during recrystallization would yield bicarbonate. The technique to be described later for making weight dilutions with carbon-dioxide-free water in an inert atmosphere precludes the possibility of contamination of the solutions at the time of their preparation.

A calculation of the effect of carbonate impurity on the pH value of a buffer solution may be performed readily with the use of approximate values for the dissociation constants of phosphoric acid, carbonic acid, and water.

Carbonate ion, as well as phosphoric acid and trivalent phosphate ion, is present in negligible quantity at pH values between 6 and 8. For a mixture of sodium bicarbonate, sodium dihydrogen phosphate, and disodium hydrogen phosphate, in which the total molality of phosphate in all forms is designated by X and the total carbonate by Y, the hydrogen-ion activity may be expressed in terms of X; Y; the second dissociation constant of phosphoric acid, K_2; the first dissociation constant of carbonic acid, K_4 [25, 26]; the ionization constant

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[9] pK_1 (25°)=2.124 (Nims [24]); pK_3 (25°)=12.325 (Bjerrum and Unmack [4]).

of water, K_w [27]; the sodium-ion molality; and activity coefficients, as follows:

$$\frac{YK_4}{K_4+a_{\mathrm{H}}f_{\mathrm{HCO_3}}}=\frac{a_{\mathrm{H}}}{f_{\mathrm{H}}}-\frac{K_w}{a_{\mathrm{H}}f_{\mathrm{OH}}}+m_{\mathrm{Na}}-X\left[\frac{2K_2f_{\mathrm{H_2PO_4}}+a_{\mathrm{H}}f_{\mathrm{HPO_4}}}{K_2f_{\mathrm{H_2PO_4}}+a_{\mathrm{H}}f_{\mathrm{HPO_4}}}\right]. \quad (15)$$

Consider a solution 0.05 m with respect to sodium dihydrogen phosphate and to disodium hydrogen phosphate. When appropriate values for the activity coefficients (calculated from eq 11 with $a_i = 4.0$ and $\beta = 0.0993$) are substituted in eq 15, the pH of this solution in the absence of carbonate is found to be 6.775. For a solution in which each of the phosphate salts is present at a molality of 0.005, the pH will be 7.024.

Absorption of carbon dioxide by the first solution in amount corresponding to 0.1 mole percent of the total phosphate, X, would yield a mixture having the composition: 0.0501 m sodium dihydrogen phosphate, 0.0499 m disodium hydrogen phosphate, and 0.0001 m sodium bicarbonate. The pH value computed for this mixture is 6.773. The same relative amount of carbonate in the 0.005 m solution changes the value of that solution to 7.022. The lowering of pH which attends the absorption of 0.1 mole percent carbonate is 0.002 pH unit in each case. As the salts used contained no detectable carbonate and utmost precautions were used to exclude atmospheric carbon dioxide during the preparation of the solutions, it is believed that errors from the possible presence of carbonates are less than 0.001 pH.

IV. EXPERIMENTAL METHODS

The design of the equipment and the experimental procedure differed principally from those described by Hamer and Acree [28] in the following respects. The cells were mounted individually and connected to the hydrogen-supply manifold by standard joints. It was thus possible to clean, dry, and fill the cells outside the bath. The use of solutions having pH values of 7 or above necessitated special precautions in the exclusion of carbon dioxide, and led to a technique for making weight dilutions while keeping the solutions in an atmosphere of purified nitrogen.

1. EQUIPMENT

Figure 2 is a side view of a brass rack holding 5 of the cells, and figure 3 shows the 55-gallon water thermostat with the 10 cells in position and connected to the hydrogen-supply manifold.

The thermostat was equipped with 2 heating units which provided 12 stages of intermittent or constant heat ranging in power consumption from 200 to 4,000 watts. At the highest rate of heating, 20 to 30 minutes was ordinarily required to raise the water temperature 5 degrees. A refrigerator compressor unit served to lower the temperature. It was also used in conjunction with the heaters to control the temperature between 0° and 25° C.

The thermoregulator contained about 160 ml of mercury. A small reservoir for excess mercury, separated by a stopcock from one arm of the regulator, permitted control of the temperature at any point between 0° and 60° C without undue change in the height of the mercury in the capillary tube which carried the platinum-wire contact.
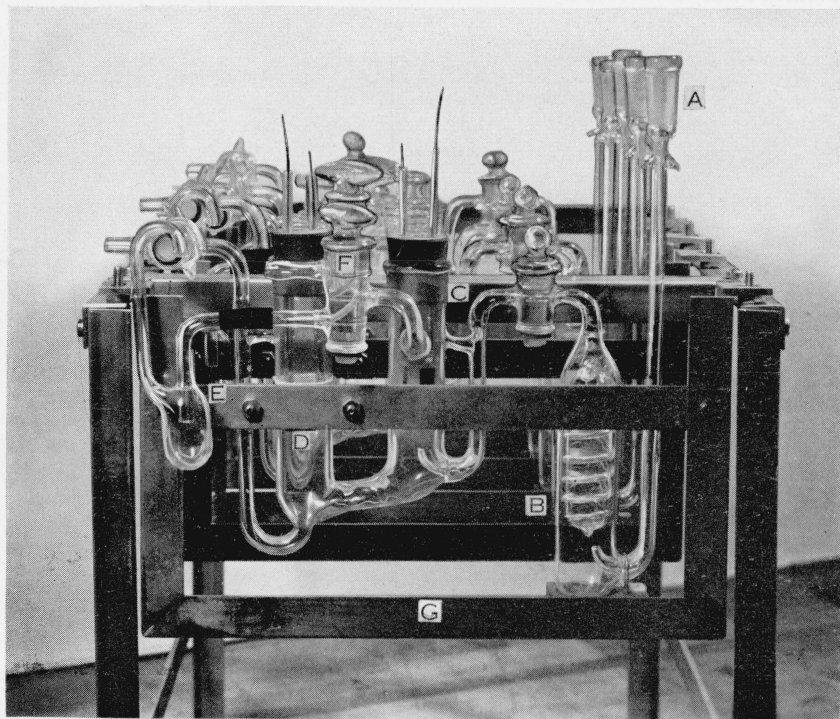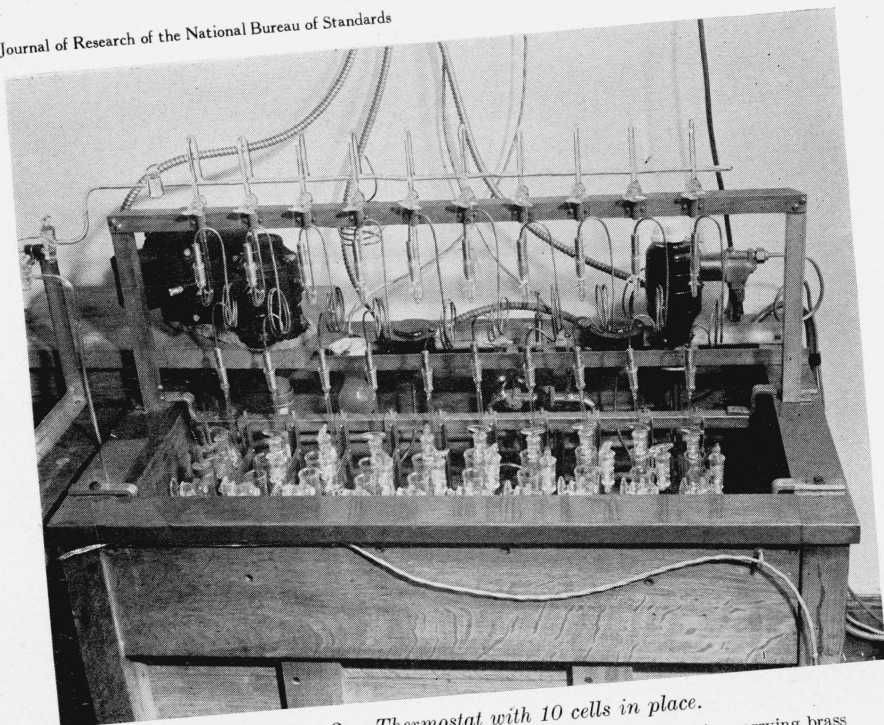
FIGURE 2.—*Side view of one of the cells.*

FIGURE 3.—*Thermostat with 10 cells in place.*

Each cell is connected with the hydrogen supply manifold by copper tubing carrying brass standard-taper joints.

The details of the cell are shown in figure 2. The cells were constructed of Pyrex glass and were supported individually on brass frames, shown at G. In operation, hydrogen enters at the standard-taper joint, A, having passed from the hydrogen manifold above the bath through the copper capillary tubing which leads to the cell. The copper was soldered at either end to tapered brass joints ground to fit the standard glass joints of the cells and manifold. In the equilibrator, B, the gas bubbles slowly through cell solution. This arrangement precludes the possibility of dilution or concentration of the solution in the hydrogen electrode compartment, C, through which the gas passes next. In the operation of the cell, compartment D houses two silver–silver-chloride electrodes.

Hydrogen escapes from the cell through the three-way stopcock, F, and the detachable trap, E, provided with a vertical exit tube which extends above the level of the water in the bath and is bent through 180° at the upper end to retard the entrance of air. The tube which conducts hydrogen from the cell into the trap terminates about 2 cm from the bottom of the trap. This construction ensured that the small quantity of solution that might be forced out of the hydrogen-electrode compartment by the flow of hydrogen would not block the bottom of the gas tube and cause an increase in the pressure of the gas within the system.

When the cells were immersed to the top of compartments C and D (fig. 2) the emf readings were identical with those obtained when they were completely immersed. Equilibrium conditions of temperature and vapor pressure were probably established in all cases.

Except at 0°, it was found convenient to adjust the bath within $\pm 0.02°$ of the desired temperature. For the cells of highest temperature coefficient, this range of temperature corresponds to slightly over 0.02 mv in emf, or about 0.0004 pH unit. The thermometer was graduated in tenths of a degree, and 0.01° could be estimated with the aid of a lens. It was checked by comparison with a thermometer calibrated by the Thermometry Section of this Bureau. Zero-point corrections were made from time to time.

The electromotive forces were measured with a Leeds & Northrup type K potentiometer. A cell which contained potassium dihydrogen phosphate, disodium hydrogen phosphate, and sodium chloride, each at a molality of approximately 0.01, was found to have a resistance of 750 ohms at 25° C. A Leeds & Northrup type R galvanometer with critical damping was employed in conjunction with the potentiometer as a null-point instrument. The galvanometer coil had a resistance of 550 ohms. The standard cell was a saturated cell of low temperature coefficient [29]. The potentiometer and standard cell were calibrated by the Resistance Measurements Section and the Electrochemistry Section, respectively, of this Bureau.

2. MATERIALS

Disodium hydrogen phosphate, potassium dihydrogen phosphate, and sodium chloride were obtained as reagent-grade salts which conformed with American Chemical Society specifications. In addition, qualitative tests on the phosphates showed aluminum to be absent. Disodium hydrogen phosphate dodecahydrate was found

to fuse when dehydration at 80° to 100° C was attempted. The salt, purified by three recrystallizations from redistilled water, was therefore dried in air at room temperature for 3 days. Drying the preparation in the oven at 110° to 130° C was then possible. Ignition of the anhydrous salt to pyrophosphate in a platinum crucible indicated the presence of from 0.02 to 0.04 percent of volatile impurity (assumed to be water). Quantitative tests for carbonate by evolution and absorption of carbon dioxide using 10-g samples of the phosphate, showed the absence of weighable amounts of this impurity. Weight titrations of three samples of the anhydrous disodium hydrogen phosphate with hydrochloric acid solution with the use of naphthyl red indicator gave 100.06, 100.04, and 100.06 percent, respectively, for the degree of neutralization of the second acid hydrogen. A standard comparison solution prepared from indicator, water, and the appropriate amount of potassium dihydrogen phosphate was used to facilitate the recognition of the endpoint.

Five analyses of the disodium hydrogen phosphate by weighing magnesium pyrophosphate were performed by the Reagents and Platinum Metals Section of this Bureau. The results gave 99.995 percent of Na_2HPO_4, with an average deviation of 0.030 percent.

The potassium dihydrogen phosphate was recrystallized three times; the first and last recrystallizations were made from redistilled water and the second from alcohol, which removes potassium bromide. Oven-drying at 130° C readily removed the last traces of water, as evidenced by the loss of weight on ignition of samples of the salt to form the metaphosphate. Four analyses of the potassium dihydrogen phosphate, which were made by the Reagents and Platinum Metals Section, gave 100.003 percent of KH_2PO_4, with an average deviation of 0.008 percent.

The sodium chloride was recrystallized twice from redistilled water.

Hydrochloric acid of reagent grade was diluted to a concentration near that of the azeotropic mixture and was distilled in an all-glass still. The middle third of the distillate was retained for use. About 18 liters of approximately 0.1 M acid was prepared by dilution of this fraction and was used in the preparation of the solutions for the determination of the second dissociation constant. This stock solution was standardized gravimetrically by the precipitation and weighing of silver chloride.

A correction for the solubility of silver chloride in the wash solution was applied. The mean deviation from the mean value of six analyses was 0.04 percent.

Nitrogen used in de-aerating the cell solutions was purified by a modification of the method of Van Brunt [30]. It was passed through two scrubbers containing a mixture of equal parts of ammonium hydroxide and saturated ammonium carbonate in contact with copper strips, then through two bottles of 1 M sulfuric acid, a tower of soda lime, and finally through a wash bottle of distilled water. Ammonia was shown to be absent from the nitrogen by passing a slow stream of the gas through a mixture of dilute hydrochloric acid, a few drops of methyl orange solution, and enough dilute alkali to cause partial conversion of the indicator. The color remained unaltered by prolonged bubbling of the gas.

Tank hydrogen was used in the cells. Traces of carbon dioxide and oxygen were removed as described by Hamer and Acree [28], except

that the gas which left the palladinized asbestos unit was further treated by contact with reduced copper oxide heated to about 450° C. It was then conducted through copper tubing of small diameter to the hydrogen-supply manifold above the bath.

The water used in making the cell solutions was distilled from alkaline permanganate and redistilled in a current of carbon-dioxide-free air. The conductance of the water was approximately 0.8×10^{-6} mho.

3. SOLUTIONS

Figure 4 shows schematically the apparatus assembly employed in the transfer of portions of the stock solution to each of the 10 solution flasks out of contact with air.
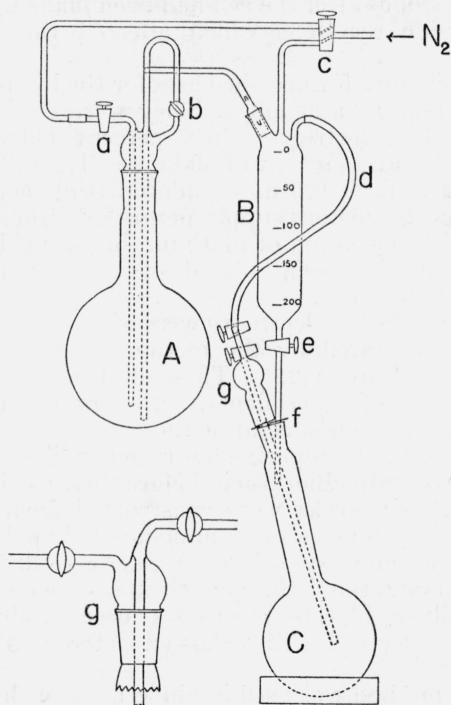
FIGURE 4.—*Schematic diagram of apparatus employed in transferring portions of the stock solution to solution flasks without the danger of contamination by carbon dioxide.*

The stock solution for each series of cells was prepared in the stock-solution flask, *A*, from weighed portions of powdered disodium hydrogen phosphate and of hydrochloric acid solution or, in the case of series B*, from weighed portions of sodium chloride, potassium dihydrogen phosphate, disodium hydrogen phosphate, and water. With stopcock *b* closed, nitrogen forced the stock solution into the 200-ml buret, *B*, which had been flushed previously with nitrogen. With the buret filled, stopcock *c* was rotated 180°, and the gas was passed through the rubber tube, *d*, to the solution flask, *C*, of 1-liter capacity, in which the dilution was made. The structure of the top

of a solution flask is shown at *g*. With the nitrogen flowing, the desired amount of stock solution was drawn through stopcock *e* into the flask, *C*. The flask was then weighed and the proper quantity of water added with the inert gas flowing through *C*. After the dilutions were completed, nitrogen was passed at the rate of about 2 bubbles per second through all 10 solution flasks for 1 to 2 hours before the final weighings were made. Vacuum corrections were made on all weighings.

4. ELECTRODES

Hydrogen and silver–silver-chloride electrodes were always used in pairs, two electrodes of the same kind being mounted in the same rubber stopper. In this way, it was possible to check the agreement of each pair of electrodes after the cell had been made up and to detect any changes or side reactions which affected the two electrodes unequally.

The platinum foils that formed the bases for the hydrogen electrodes were 8 mm wide and 15 mm long. They were coated lightly with spongy platinum by electrolysis in 3-percent chloroplatinic acid solution for 1 minute at a current of 300 ma. Ten milligrams of lead acetate was added to each 100 ml of chloroplatinic acid solution. A reversing switch on the current supply permitted either foil to be used as anode during the deposition of platinum black on the other. The electrodes were ordinarily freshly plated for each run and were soaked in distilled water before use.

The silver–silver-chloride electrodes were of the thermal-electrolytic type. They were prepared by the method described in an earlier publication from this Bureau [28]. These electrodes also were usually remade for each series of experiments. After preparation, they were soaked in distilled water for several hours.

For the purpose of intercomparing hydrogen or silver–silver-chloride electrodes in 0.05 *M* hydrochloric acid before their use in pH measurements, vessels with six necks were constructed from 1-liter round-bottomed flasks. These vessels accommodated six pairs of electrodes and hydrogen supply and exit tubes. Measurable differences (larger than 0.01 mv) among the hydrogen electrodes were rarely found, although silver–silver-chloride electrodes occasionally differed by 0.05 mv. Pairs of electrodes that showed differences of as much as 0.1 mv were rejected.

The evacuation method was used in filling most of the cells. Later, the danger of concentration polarization at the silver electrode was obviated by soaking each pair of electrodes overnight in a portion of the particular solution in which they were to be used.

5. PROCEDURE

With the cell in position for filling, the flask containing the solution was attached at *A* (fig. 2) by a standard joint of glass. The hydrogen supply was connected to the solution flask and to the three-way stopcock, *F*, of the cell in such fashion that the gas could be used to force solution from the flask through *A* into the cell or could be led in, through *F*, to expel solution through the tube attached to the base of *D*. The trap, *E*, was removed during the filling of the cell, and a thick-

walled rubber tube leading to an oil pump was attached to the cell in its place.

When the electrodes had not been soaked previously in the buffer solution but had been stored in distilled water, they were dried superficially, fixed in place, and the entire cell evacuated for 5 to 10 minutes. The stopcock of the solution flask was then opened and the cell filled with solution. This wash solution was expelled by hydrogen pressure and the cell refilled. When the silver–silver-chloride electrodes had been soaked in buffer solution, the cell was not evacuated but was flushed with hydrogen before the wash solution was admitted.

The initial emf measurements were made at 25° C. Two hours was ordinarily sufficient to attain equilibrium. After constant emf values had been maintained for at least 2 hours, the temperature of the bath was lowered to 0.2° to 0.5° C, the lowest temperature at which measurements were made; a short, unambiguous extrapolation with the aid of the temperature coefficient yielded the emf at 0° C. The bath was raised at 5-degree intervals to 60° C and was finally brought back to 25° C. Three sets of emf measurements at 25° C were thus obtained. The measurements usually required about 2 hours at each temperature. The entire series of experiments was ordinarily completed in 3 days. Cells whose final readings at 25° C differed from the initial equilibrium values by more than 0.18 mv (corresponding to 0.003 pH unit) were rejected as unsatisfactory.

V. CALCULATION OF THE DISSOCIATION CONSTANT

The electromotive forces recorded in five satisfactory series of experiments at three different buffer ratios were corrected to a pressure of 760 mm of hydrogen (unit activity) in the usual way [31]. The corrected values for the 13 temperatures are listed in tables 1, 2, and 3. Series A solutions contained $H_2PO_4^-$ and $HPO_4^=$ in the ratio 1.0132. The buffer ratios for series B and C solutions were 1.5684 and 0.6540, respectively. Series B* differed from series B in that potassium dihydrogen phosphate was used in place of sodium dihydrogen phosphate. The buffer ratio was the same in both series.

When pK_2', the expression in square brackets in eq 12, was computed for various values of a_i, the average ion-size parameter, it was found that a value of approximately 4 A would give the desired linear change of pK_2' with ionic strength. It was evident, however, that a slope of zero would not be obtained.

The adjustment of a_i was made to the nearest 0.1 A to yield the best extrapolation at each temperature. Within the error of the experiments, the same value of a_i was found to apply to the three buffer ratios at any particular temperature. There was a small variation of a_i with temperature. The slope of the plot of pK_2' with respect to μ is numerically equal to β, as may be seen from eq 13. The values of k, a_i, $3A$, Ba_i, and β for each temperature and series of solutions are given in table 4.[10]

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[10] Numerical values of A, B, and k at 5-degree intervals from 0° to 60° C have been recalculated by Hamer, Burton, and Acree [16, table 2] from reliable values of the faraday, the electronic charge, the Boltzmann constant, and the dielectric constant. Their values of k are given in absolute volts. Conversion to International volts has been made by dividing by 1.00034 [20].

TABLE 1.—*Electromotive forces of hydrogen–silver-chloride cells containing phosphate-chloride mixtures*

SERIES A

Solution number	$m_1 = m_3$	m_2	$E_0°$	$E_5°$	$E_{10}°$	$E_{15}°$	$E_{20}°$
A1	0.09079	0.08961	0.66626	0.67011	0.67382	0.67754	0.68131
A2	.07340	.07245	.67289	.67680	.68059	.68436	.68823
A3	.05507	.05435	.68185	.68593	.68987	.69379	.69780
A4	.03726	.03678	.69361	.69761	.70190	.70612	.71009
A5	.03017	.02977	.69960	.70399	.70822	.71244	.71676
A6	.010491	.010354	.72970	.73447	.73923	.74398	.74884
A7	.09079	.08915	.66635	.67007	.67380	.67751	.68133
A8	.07475	.07340	.67240	.67624	.68005	.68381	.68775
A9	.05199	.05105	.68328	.68758	.69156	.69552	.69954
A10	.03592	.03527	.69457	.69871	.70289	.70705	.71133
A11	.018456	.018122	.71387	.71832	.72279	.72725	.73185
A12	.015090	.014818	.71954	.72411	.72871	.73326	.73795
A13	.010151	.009968	.73058	.73536	.74013	.74489	.74982
A14	.008598	.008442	.73518	.73996	.74482	.74967	.75472
A15	.005978	.005870	.74507	.75000	.75503	.76004	.76525
A16	.004213	.004137	.75434	.75952	.76467	.76984	.77525

Solution number	$E_{25}°$	$E_{30}°$	$E_{35}°$	$E_{40}°$	$E_{45}°$	$E_{50}°$	$E_{55}°$	$E_{60}°$
A1	0.68515	0.68900	0.69281	0.69672	0.70058	0.70445	0.70834	0.71222
A2	.69228	.69616	.70012	.70399	.70793	.71198	.71595	.71999
A3	.70191	.70606	.71016	.71420	.71836	.72243	.72657	.73075
A4	.71455	.71872	.72303	.72738	.73166	.73596	.74030	.74468
A5	.72119	.72564	.73014	.73451	.73900	.74355	.74808	.75263
A6	.75382	.75879	.76383	.76882	.77380	.77880	.78385	.78893
A7	.68510	.68904	.69281	.69670	.70049	.70443	.70830	.71211
A8	.69160	.69562	.69933	.70343	.70737	.71124	.71521	.71920
A9	.70370	.70813	.71219	.71640	.72045	.72457	.72885	.73306
A10	.71560	.72008	.72443	.72880	.73308	.73746	.74175	.74610
A11	.73653	.74138	.74604	.75082	.75551	.76028	.76494	.76975
A12	.74268	.74752	.75228	.75713	.76189	.76670	.77154	.77641
A13	.75471	.75980	.76475	.76981	.77483	.77993	.78494	.79014
A14	.75972	.76495	.77005	.77518	.78028	.78539	.79052	.79573
A15	.77045	.77592	.78118	.78652	.79178	.79714	.80240	.80782
A16	.78059	.78626	.79168	.79716	.80265	.80817	.81354	.81912

TABLE 2.—*Electromotive forces of hydrogen–silver-chloride cells containing phosphate-chloride mixtures*

SERIES B

Solution number	$m_1 = m_3$	m_2	$E_0°$	$E_5°$	$E_{10}°$	$E_{15}°$	$E_{20}°$
B1	0.09079	0.05789	0.65677	0.66023	0.66365	0.66701	0.67077
B2	.07410	.04725	.66341	.66712	.67076	.67440	.67809
B3	.05294	.03375	.67355	.67740	.68123	.68499	.68884
B4	.03459	.02205	.68629	.69027	.69431	.69826	.70237
B5	.02343	.014937	.69757	.70190	.70608	.71028	.71456
B6	.014911	.009507	.71039	.71480	.71923	.72362	.72812
B7	.009764	.006226	.72237	.72696	.73159	.73625	.74101
B8	.007546	.004811	.72924	.73388	.73857	.74328	.74812
B9	.005365	.003420	.73851	.74335	.74825	.75319	.75819

SERIES B*

Solution number	$m_1 = m_3$	m_2	$E_0°$	$E_5°$	$E_{10}°$	$E_{15}°$	$E_{20}°$
B*1	0.09077	0.05787	0.65774	0.66132	0.66493	0.66850	0.67211
B*2	.05151	.03284	.67499	.67884	.68271	.68652	.69040
B*3	.04604	.02935	.67831	.68226	.68622	.69002	.69394
B*4	.02877	.018341	.69206	.69619	.70032	.70434	.70850
B*5	.009373	.005976	.72335	.72806	.73277	.73739	.74216
B*6	.006059	.003863	.73499	.73990	.74481	.74969	.75468
B*7	.004099	.002614	.74543	.75056	.75565	.76071	.76590
B*8	.002835	.0018073	.75509	.76034	.76561	.77080	.77612

TABLE 2.—*Electromotive forces of hydrogen–silver-chloride cells containing phosphate-chloride mixtures*—Continued

SERIES B—Continued

Solution number	$E_{25}°$	$E_{30}°$	$E_{35}°$	$E_{40}°$	$E_{45}°$	$E_{50}°$	$E_{55}°$	$E_{60}°$
B1	0. 67466	0. 67840	0. 68217	0. 68583	0. 68947	0. 69309	0. 69684	0. 70052
B2	. 68183	. 68560	. 68948	. 69278	. 69665	. 70053	. 70456	. 70823
B3	. 69276	. 69662	. 70069	. 70470	. 70863	. 71261	. 71656	. 72041
B4	. 70659	. 71068	. 71494	. 71915	. 72328	. 72750	. 73170	. 73592
B5	. 71897	. 72334	. 72799	. 73241	. 73674	. 74133	. 74580	. 75027
B6	. 73276	. 73730	. 74182	. 74650	. 75111	. 75584	. 76053	. 76520
B7	. 74583							
B8	. 75316							
B9	. 76338	. 76843	. 77369	. 77893	. 78415	. 78935	. 79470	. 79984

SERIES B*—Continued

Solution number	$E_{25}°$	$E_{30}°$	$E_{35}°$	$E_{40}°$	$E_{45}°$	$E_{50}°$	$E_{55}°$	$E_{60}°$
B*1	0. 67567	0. 67938	0. 68317	0. 68684	0. 69053	0. 69419	0. 69790	0. 70166
B*2	. 69430	. 69825	. 70235	. 70646	. 71045	. 71445	. 71850	. 72257
B*3	. 69787	. 70191	. 70607	. 70992	. 71413	. 71825	. 72227	. 72638
B*4	. 71271	. 71709	. 72149	. 72579	. 73012	. 73441	. 73875	. 74315
B*5	. 74694	. 75183	. 75684	. 76177	. 76671	. 77168	. 77667	. 78175
B*6	. 75965	. 76482	. 77010	. 77530	. 78051	. 78574	. 79101	. 79633
B*7	. 77097	. 77643						
B*8	. 78151	. 78698	. 79257	. 79806	. 80353	. 80912	. 81467	. 82030

TABLE 3.—*Electromotive forces of hydrogen–silver-chloride cells containing phosphate-chloride mixtures*

SERIES C

Solution number	$m_1 = m_3$	m_2	$E_0°$	$E_5°$	$E_{10}°$	$E_{15}°$	$E_{20}°$
C1	0. 09079	0. 13882	0. 67584	0. 67976	0. 68365	0. 68755	0. 69145
C2	. 06661	. 10185	. 68536	. 68943	. 69346	. 69750	. 70157
C3	. 04820	. 07371	. 69514	. 69936	. 70356	. 70776	. 71195
C4	. 02578	. 03943	. 71353	. 71803	. 72250	. 72701	. 73156
C5	. 011957	. 018283	. 73534	. 74018	. 74506	. 74996	. 75490
C6	. 007914	. 012102	. 74679	. 75183	. 75691	. 76198	. 76715
C7	. 004944	. 007560		. 76467	. 77006	. 77545	. 78087
C8	. 002943	. 004501	. 77347	. 77900	. 78455	. 79015	. 79577
C9	. 0019314	. 002953	. 78435	. 79009	. 79587	. 80167	. 80758

SERIES C—Continued

Solution number	$E_{25}°$	$E_{30}°$	$E_{35}°$	$E_{40}°$	$E_{45}°$	$E_{50}°$	$E_{55}°$	$E_{60}°$
C1	0. 69533	0. 69950	0. 70322	0. 70744	0. 71148	0. 71520	0. 71932	0. 72339
C2	. 70575	. 71001	. 71404	. 71818	. 72248	. 72651	. 73080	. 73502
C3	. 71622	. 72065	. 72474	. 72909	. 73358	. 73774	. 74220	. 74675
C4	. 73612	. 74098	. 74550	. 75017	. 75507	. 75979	. 76455	. 76935
C5	. 75993	. 76513	. 77017	. 77530	. 78042	. 78556	. 79080	. 79619
C6	. 77240							
C7	. 78622	. 79205	. 79767					
C8	. 80152	. 80755	. 81329	. 81914	. 82501	. 83089	. 83682	. 84277
C9	. 81338	. 81973	. 82573	. 83184	. 83793	. 84403	. 85007	. 85613

TABLE 4.—*Numerical values of k, $3A$, a_i, Ba_i, and β at temperatures from 0° to 60° C for series A, B, B*, and C solutions*

t	k	$3A$	a_i	Ba_i	β (series A)	β (series B)	β (series B*)	β (series C)
° C	Int. v	A						
0	0.05418	1.4670	3.5	1.1386	0.098	0.160	0.103	0.046
5	.05517	1.4784	3.6	1.1740	.091	.153	.104	.043
10	.05616	1.4901	3.7	1.2099	.095	.157	.101	.046
15	.05715	1.5027	3.8	1.2460	.091	.158	.097	.046
20	.05814	1.5159	3.8	1.2498	.087	.149	.096	.044
25	.05914	1.5294	3.8	1.2532	.081	.140	.093	.040
30	.06013	1.5441	3.8	1.2574	.077	.137	.093	.036
35	.06112	1.5591	3.8	1.2616	.081	.136	.081	.043
40	.06211	1.5750	3.8	1.2654	.073	.131	.079	.037
45	.06311	1.5909	4.0	1.3368	.093	.152	.098	.050
50	.06410	1.6074	4.0	1.3412	.087	.150	.095	.056
55	.06509	1.6251	4.0	1.3464	.081	.137	.091	.049
60	.06608	1.6434	4.0	1.3512	.084	.144	.094	.051

The effect of various a_i values on the course of the extrapolation is evident in figure 5, where pK_2' from the measurements of solutions A7 to A16 is plotted as a function of ionic strength. Curve A was computed with the use of the Debye-Hückel limiting-law expression for the activity coefficients of the phosphate and chloride ions (eq 10). The four lower curves were derived from eq 12; pK_2' represents the quantity in brackets.[11] An a_i parameter of 3.04 A was used for curve B, 3.5 A for curve C, 4.0 A for curve D, and 4.5 A for curve E. Careful examination shows that curves A, B, and C are concave downward, D is very nearly straight, and E is concave upward. Actually,
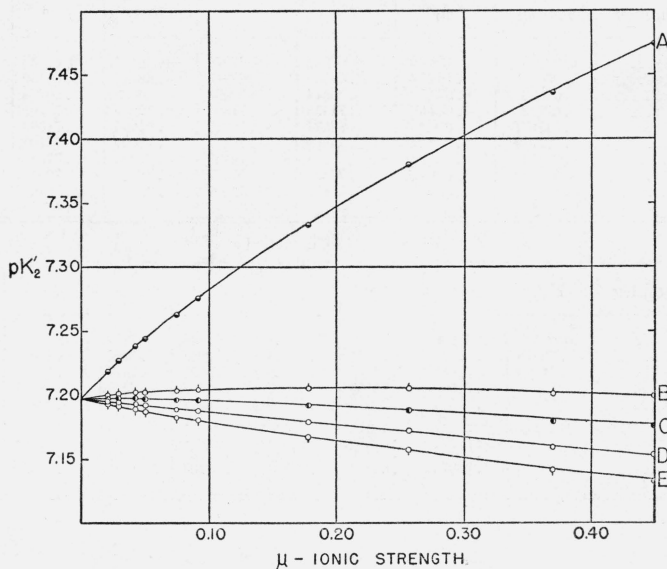

FIGURE 5.—*Extrapolation plots for the second dissociation constant.*

Curve A was computed from eq 10; curves B, C, D, and E were obtained with the use of eq 12 with a_i values of 3.04, 3.5, 4.0, and 4.5, respectively.

[11] Curve A likewise may be considered to be calculated from eq 12 with $a_i=0$, as is easily seen from comparison of eq 10 and 12.

pK_2' is most nearly a linear function of μ when an a_i value of 3.8 A is employed.

With the use of the β values for each series of solutions at the 13 temperatures, values of pK_2 were computed from eq 13 for each solution measured. Figure 6 is a graph of all values of pK_2 for the three buffer ratios at 0°, 25°, and 60° C. The average value of
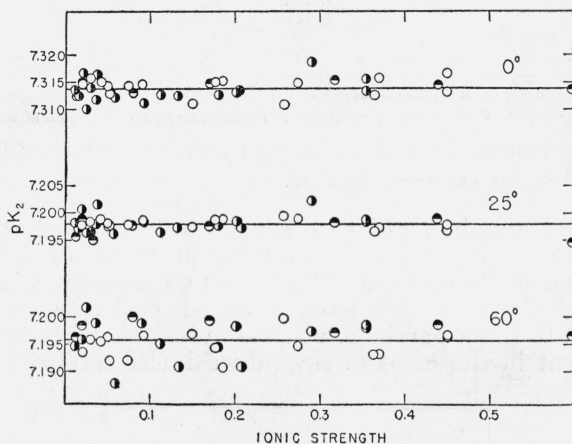

FIGURE 6.—*Plots of all values of pK_2 (eq 12) at 0°, 25°, and 60° C as a function of ionic strength.*

○ = series A; ◑ = series B and B*; ◕ = series C

pK_2 for each series is given in table 5. The mean value for the five series, weighting each one equally, is given in the next to the last column of the table, together with the mean departure from the mean. The largest uncertainty is inherent in the value at 60° and corresponds to 0.12 mv, or 0.002 in pK_2..

TABLE 5.—*Summary of the values for pK_2 and K_2, calculated from measurements of five groups of solutions at temperatures from 0° to 60° C*

t	Series A 1 to 6	Series A 7 to 16	Series B	Series B*	Series C	pK_2 (average)	$K_2 \times 10^8$
°C							
0	7.3133	7.3147	7.3145	7.3125	7.3139	7.314 ±.0012	4.85
5	7.2806	7.2818	7.2815	7.2817	7.2806	7.281 ±.0010	5.24
10	7.2538	7.2545	7.2540	7.2544	7.2533	7.254 ±.0010	5.57
15	7.2295	7.2303	7.2307	7.2308	7.2305	7.230 ±.0012	5.89
20	7.2114	7.2136	7.2127	7.2134	7.2129	7.213 ±.0010	6.12
25	7.1978	7.1983	7.1988	7.1977	7.1972	7.198 ±.0010	6.34
30	7.1880	7.1913	7.1888	7.1895	7.1909	7.190 ±.0013	6.46
35	7.1847	7.1862	7.1854	7.1853	7.1856	7.185 ±.0015	6.53
40	7.1798	7.1830	7.1811	7.1819	7.1822	7.182 ±.0015	6.58
45	7.1796	7.1818	7.1803	7.1816	7.1818	7.181 ±.0015	6.59
50	7.1817	7.1841	7.1835	7.1844	7.1851	7.184 ±.0017	6.55
55	7.1853	7.1873	7.1869	7.1888	7.1893	7.188 ±.0020	6.49
60	7.1940	7.1954	7.1943	7.1973	7.1981	7.196 ±.0022	6.37

The pK_2 values found in 10 different investigations by conductance and emf methods are compared in table 6. The temperature is 25° C in each case.

TABLE 6.—*Comparison of measurements of* pK_2 *at* 25° *C*

Reference	Year	Method	pK_2
Abbott and Bray [32]	1909	Conductance	[a] 6.69
Michaelis and Garmendia [33]	1914	emf (with liquid junction)	[ab] 7.07
Michaelis and Krüger [34]	1921	___do___	[ab] 7.11
Prideaux and Ward [35]	1924	___do___	[ab] 7.17
Cohn [36]	1927	___do___	[abc] 7.17
Bjerrum and Unmack [4]	1929	___do___	7.207
Nims [5]	1933	emf (without liquid junction)	7.206
Guggenheim and Schindler [37]	1934	emf (with liquid junction)	7.228
Sima [38]	1939	___do___	7.02
This investigation		emf (without liquid junction)	7.198

[a] Value at 18° corrected to 25° by use of temperature coefficient of pK_2 from data of this investigation. $pK_{18}-pK_{25}=0.02$.

[b] Recalculated by Bjerrum and Unmack [4] by the use of 0.3360 v for the potential of the 0.1 N calomel reference electrode.

[c] Calculated by Cohn from earlier results [33, 34, 39].

A large-scale graph of pK_2 with respect to t (fig. 7) shows that the dissociation constant reaches a maximum value of 6.593×10^{-8} (pK_2 reaches a minimum value of 7.1809) at a temperature of 43.75° C. Harned and Embree [40] have assumed that the plot of pK with respect to t is a parabola, an assumption that has been verified by experiment in the cases of several weak electrolytes, particularly
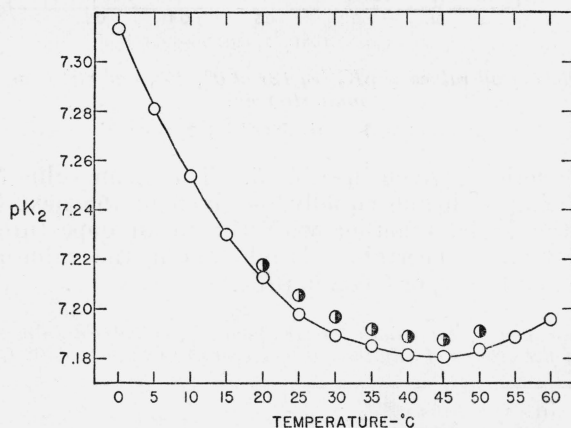

FIGURE 7.—*Plot of the second dissociation constant as a function of temperature.*
The values given by Nims [5] are included as half-shaded circles.

for temperatures close to that for the minimum, θ. Their empirical equation for the variation of pK with temperature in this range is

$$pK_t = pK_{min} + 5 \times 10^{-5}(t-\theta)^2. \tag{16}$$

Later, Owen [41] generalized eq 16 as follows:

$$pK_t = pK_{min} + p(t-\theta)^2. \tag{17}$$

The experimental pK_2 values are given by eq 16 with an average deviation of 0.008. When a value of 6.2×10^{-5} is assigned to p, pK_2 is represented by eq 17 with a mean deviation of 0.003. In both cases the values from 20° to 60° C fit acceptably, but below 20° these equations leave much to be desired.

Recently, Harned and Robinson [42] suggested an equation for the variation of pK with absolute temperature, T, which is based upon the observation that electromotive forces of the hydrogen–silver-chloride cell (and consequently ΔF, the change of free energy in the cell)[12] are quadratic functions of temperature, within the error of the experiments. This assumption requires that $\Delta F°$, the free-energy change for the dissociation of 1 mole of $H_2PO_4^-$ in the standard state, shall also be a quadratic function of temperature and leads to an empirical equation for the variation of pK_2 with T:

$$pK_2 = \frac{A}{T} + B + CT. \qquad (18)$$

The average values of pK_2 given in table 5 were used to obtain the numerical values of the constants of eq 18 by the method of least squares. With a mean deviation of 0.0013 at the 13 temperatures, pK_2 is given by the equation

$$pK_2 = \frac{1979.5}{T} - 5.3541 + 0.019840T. \qquad (19)$$

VI. THERMODYNAMIC QUANTITIES

Thermodynamic quantities for the second dissociation equilibrium of phosphoric acid can be computed from the parameters A, B, and C of the Harned and Robinson equation.

Values of the standard change of free energy, $\Delta F°$, for the process, $H_2PO_4^- = H^+ + HPO_4^-$; the standard change in heat content, $\Delta H°$; the standard entropy change, $\Delta S°$; and the change in heat capacity, $\Delta C_p°$, accompanying the dissociation of 1 mole of $H_2PO_4^-$ are given in table 7. These numerical values were computed from the equations

$$\Delta F° = -RT \ln K_2 = 2.3026R(A + BT + CT^2) \qquad (20)$$
$$= 9057 - 24.50T + 0.09078T^2$$

$$\Delta S° = -(d\Delta F°/dT) = 2.3026R(-B - 2CT) \qquad (21)$$
$$= 24.5 - 0.1816T$$

$$\Delta H° = \Delta F° + T\Delta S° = 2.3026R(A - CT^2) \qquad (22)$$
$$= 9057 - 0.09078T^2$$

$$\Delta C_p° = d\Delta H°/dT = 2.3026R(-2CT) \qquad (23)$$
$$= -0.1816T$$

TABLE 7.—*Thermodynamic quantities for the process:* $H_2PO_4^- = H^+ + HPO_4^-$

t	$\Delta F°$		$\Delta H°$		$\Delta S°$		$\Delta C_p°$	
	Int. j	cal	Int. j	cal	Int. j deg⁻¹	cal deg⁻¹	Int. j deg⁻¹	cal deg⁻¹
0	38,231	9,139	9,555	2,284	−105.0	−25.1	−207.5	−49.6
5	38,763	9,266	8,509	2,034	−108.8	−26.0	−211.3	−50.5
10	39,319	9,399	7,442	1,779	−112.5	−26.9	−215.0	−51.4
15	39,892	9,536	6,359	1,520	−116.3	−27.8	−218.8	−52.3
20	40,482	9,677	5,254	1,256	−120.1	−28.7	−222.6	−53.2
25	41,093	9,823	4,129	987	−123.8	−29.6	−226.3	−54.1
30	41,720	9,973	2,987	714	−127.6	−30.5	−230.1	−55.0
35	42,369	10,128	1,828	437	−131.4	−31.4	−234.3	−56.0
40	43,038	10,288	648	155	−135.5	−32.4	−238.0	−56.9
45	43,724	10,452	−552	−132	−139.3	−33.3	−241.8	−57.8
50	44,427	10,620	−1,770	−432	−143.1	−34.2	−245.6	−58.7
55	45,155	10,794	−3,004	−718	−146.8	−35.1	−249.3	−59.6
60	45,895	10,971	−4,263	−1,019	−150.6	−36.0	−253.1	−60.5

[12] For this cell, $(d\Delta F/dt) = -F(dE/dt)$.

A value of R of 8.3127 Int. j deg^{-1} mole^{-1} [19] was used to obtain the thermodynamic quantities in International joules. For comparison with data in the literature, which are often listed in calories, values of the thermodynamic quantities are also given in terms of that unit, 1 calorie being taken as 4.1833 Int. j, as recommended by the International Union of Chemistry [43].

Figure 8 is a graph of $\Delta H°$, the heat of dissociation, as a function of temperature in the range 0° to 60° C.

The pK_2 values found by Nims [5] from measurements of the hydrogen–silver-chloride cell from 20° to 50° C have been fitted to an equation of the Harned-Robinson form and the thermodynamic quantities calculated for comparison with those of table 7. At 25° C, Nims found $pK_2=7.206$, a value higher by 0.008 than the value found in this investigation. At this temperature, -30.2 cal deg^{-1} was found for $\Delta S°$; 817 cal for $\Delta H°$; and -45.2 cal deg^{-1} for $\Delta C_p°$.
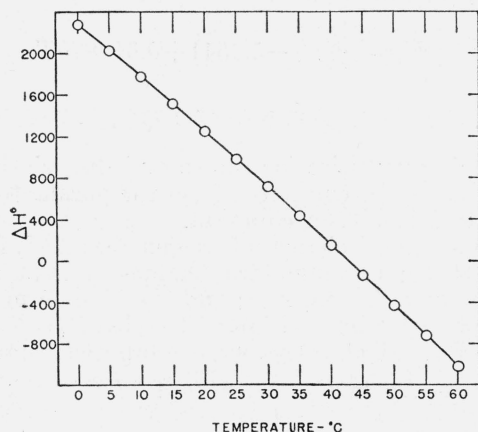

FIGURE 8.—*Heat of dissociation of dihydrogen phosphate ion, in calories, as a function of temperature.*

Figure 7, in which the pK_2 values of Nims are included as half-shaded circles, shows that the change of pK_2 with respect to temperature is substantially the same, between 20° and 50° C, for the two independent determinations. The values of Nims are 0.005 to 0.008 unit higher at each temperature than the present results.

Measurements of the dissociation constant should be made over as wide a range of temperatures as possible if the thermodynamic quantities derived from the temperature coefficient are to be obtained with the highest precision. It is furthermore particularly desirable that measurements be made at temperatures as far as possible from that of the minimum in pK, both above and below the temperature of the minimum.

The numerical values of table 7, for example, would have been quite different if they had been derived from measurements at only seven temperatures. For a comparison of $\Delta H°$, $\Delta S°$, and $\Delta C_p°$ calculated from the two independent determinations of pK_2 between 20° and 50° C, the pK_2 values found in this investigation for these temperatures were fitted to eq 18, and the derived thermodynamic quantities

were computed from A, B, and C, as before. Neglect of the measurements below 20° and above 50° C resulted in significant changes, and the values of the thermodynamic quantities were in each case closer to those derived from the measurements of Nims than are those of table 7. Thus $\Delta S°$ becomes -30.0 cal deg^{-1} at 25° C, $\Delta H°$ is 878 cal, and $\Delta C_p°$ becomes -48.4 cal deg^{-1} when the data at the lowest and highest temperatures are not used.

VII. pH VALUES OF PHOSPHATE SOLUTIONS

Equation 14 was used to calculate the pH number for each of the solutions used in the cells. The values for series A are given in table 8, for series B and B* in table 9, and for series C solutions in table 10. It is noteworthy that each of these solutions is a suitable standard for pH.

TABLE 8.—pH *values of mixtures of sodium dihydrogen phosphate* (m_1), *disodium hydrogen phosphate* (m_2), *and sodium chloride* (m_3): *series A*

Solution number	$m_1 = m_3$	m_2	pH				
			0°	5°	10°	15°	20°
A1	0.09079	0.08961	6.749	6.720	6.696	6.674	6.653
A2	.07340	.07245	6.782	6.751	6.727	6.703	6.683
A3	.05507	.05435	6.828	6.798	6.773	6.749	6.729
A4	.03726	.03678	6.886	6.851	6.828	6.806	6.781
A5	.03017	.02977	6.911	6.882	6.855	6.831	6.810
A6	.010491	.010354	7.041	7.009	6.981	6.957	6.937
A7	.09079	.08915	6.751	6.719	6.696	6.673	6.653
A8	.07475	.07340	6.781	6.749	6.725	6.701	6.682
A9	.05199	.05105	6.831	6.805	6.779	6.756	6.735
A10	.03592	.03527	6.889	6.857	6.831	6.807	6.788
A11	.018456	.018122	6.977	6.944	6.916	6.892	6.873
A12	.015090	.014818	7.001	6.968	6.940	6.916	6.896
A13	.010151	.009968	7.044	7.012	6.984	6.960	6.941
A14	.008598	.008442	7.062	7.028	7.000	6.976	6.958
A15	.005978	.005870	7.097	7.062	7.034	7.010	6.991
A16	.004213	.004137	7.125	7.092	7.063	7.038	7.020

Solution number	pH							
	25°	30°	35°	40°	45°	50°	55°	60°
A1	6.634	6.620	6.613	6.603	6.614	6.610	6.608	6.612
A2	6.666	6.651	6.644	6.633	6.640	6.639	6.637	6.641
A3	6.711	6.698	6.690	6.680	6.686	6.683	6.682	6.686
A4	6.766	6.751	6.743	6.735	6.738	6.735	6.734	6.738
A5	6.793	6.781	6.774	6.766	6.769	6.768	6.769	6.774
A6	6.921	6.909	6.902	6.808	6.808	6.895	6.894	6.900
A7	6.633	6.621	6.613	6.603	6.612	6.610	6.608	6.611
A8	6.662	6.650	6.638	6.631	6.639	6.635	6.633	6.637
A9	6.717	6.709	6.700	6.692	6.696	6.693	6.693	6.697
A10	6.769	6.759	6.751	6.744	6.745	6.744	6.742	6.745
A11	6.854	6.846	6.838	6.832	6.832	6.832	6.831	6.836
A12	6.879	6.868	6.859	6.853	6.853	6.852	6.852	6.856
A13	6.923	6.912	6.904	6.898	6.898	6.898	6.899	6.906
A14	6.940	6.931	6.924	6.918	6.917	6.917	6.918	6.923
A15	6.974	6.966	6.958	6.953	6.952	6.953	6.953	6.959
A16	7.003	6.995	6.987	6.982	6.981	6.982	6.982	6.987

TABLE 9.—pH *values of mixtures of sodium dihydrogen phosphate* (m_1), *disodium hydrogen phosphate* (m_2), *and sodium chloride* (m_3): *series B; and the* pH *values of mixtures of potassium dihydrogen phosphate* (m_1), *disodium hydrogen phosphate* (m_2), *and sodium chloride* (m_3); *series B**

SERIES B

Solution number	$m_1=m_3$	m_2	pH				
			0°	5°	10°	15°	20°
B1	0.09079	0.05789	6.599	6.566	6.540	6.516	6.497
B2	.07410	.04725	6.634	6.603	6.578	6.557	6.535
B3	.05294	.03375	6.678	6.647	6.622	6.599	6.578
B4	.03459	.02205	6.737	6.704	6.678	6.654	6.634
B5	.02343	.014937	6.785	6.755	6.728	6.705	6.684
B6	.014911	.009507	6.839	6.805	6.778	6.754	6.733
B7	.009764	.006226	6.886	6.853	6.825	6.802	6.783
B8	.007546	.004811	6.908	6.873	6.844	6.820	6.800
B9	.005365	.003420	6.939	6.905	6.876	6.853	6.833

SERIES B*

Solution number	$m_1=m_3$	m_2	pH				
			0°	5°	10°	15°	20°
B*1	0.09077	0.05787	6.597	6.568	6.543	6.521	6.501
B*2	.05151	.03284	6.682	6.652	6.625	6.602	6.582
B*3	.04604	.02935	6.697	6.668	6.642	6.618	6.597
B*4	.02877	.018341	6.766	6.730	6.703	6.678	6.658
B*5	.009373	.005976	6.886	6.855	6.827	6.803	6.784
B*6	.006059	.003863	6.922	6.891	6.864	6.840	6.821
B*7	.004099	.002614	6.955	6.924	6.896	6.873	6.854
B*8	.002835	.0018073	6.980	6.949	6.921	6.897	6.877

SERIES B—Continued

Solution number	pH							
	25°	30°	35°	40°	45°	50°	55°	60°
B1	6.481	6.470	6.462	6.454	6.462	6.459	6.456	6.460
B2	6.515	6.502	6.495	6.479	6.487	6.487	6.487	6.490
B3	6.559	6.545	6.538	6.531	6.534	6.533	6.530	6.532
B4	6.617	6.603	6.596	6.589	6.590	6.589	6.588	6.592
B5	6.667	6.655	6.651	6.645	6.644	6.646	6.646	6.650
B6	6.717	6.704	6.694	6.696	6.688	6.689	6.689	6.693
B7	6.766							
B8	6.785							
B9	6.818	6.805	6.799	6.795	6.794	6.794	6.798	6.801

SERIES B*—Continued

Solution number	pH							
	25°	30°	35°	40°	45°	50°	55°	60°
B*1	6.482	6.470	6.460	6.452	6.459	6.456	6.455	6.460
B*2	6.564	6.551	6.543	6.537	6.541	6.539	6.539	6.544
B*3	6.579	6.567	6.558	6.548	6.554	6.553	6.552	6.556
B*4	6.640	6.630	6.622	6.615	6.617	6.615	6.616	6.620
B*5	6.766	6.755	6.750	6.744	6.744	6.745	6.747	6.753
B*6	6.803	6.794	6.789	6.785	6.785	6.787	6.790	6.797
B*7	6.835	6.827						
B*8	6.860	6.850	6.845	6.839	6.837	6.839	6.842	6.848

TABLE 10.—pH *values of mixtures of sodium dihydrogen phosphate* (m_1), *disodium hydrogen phosphate* (m_2), *and sodium chloride* (m_3): *series C*

Solution number	$m_1=m_3$	m_2	pH				
			0°	5°	10°	15°	20°
C1	0.09079	0.13882	6.895	6.864	6.841	6.821	6.800
C2	.06661	.10185	6.945	6.915	6.890	6.869	6.848
C3	.04820	.07371	6.996	6.965	6.940	6.918	6.897
C4	.02578	.03943	7.088	7.056	7.029	7.006	6.986
C5	.011957	.018283	7.185	7.153	7.125	7.102	7.082
C6	.007914	.012102	7.232	7.199	7.171	7.147	7.127
C7	.004944	.007560	_____	7.242	7.215	7.193	7.173
C8	.002943	.004501	7.323	7.290	7.261	7.239	7.218
C9	.0019314	.002953	7.350	7.318	7.290	7.267	7.248

Solution number	pH							
	25°	30°	35°	40°	45°	50°	55°	60°
C1	6.779	6.767	6.757	6.751	6.760	6.758	6.756	6.759
C2	6.830	6.817	6.809	6.799	6.808	6.807	6.805	6.809
C3	6.878	6.866	6.855	6.846	6.853	6.851	6.850	6.856
C4	6.966	6.957	6.947	6.939	6.944	6.944	6.944	6.949
C5	7.064	7.054	7.046	7.040	7.040	7.040	7.043	7.050
C6	7.110	_____	_____	_____	_____	_____	_____	_____
C7	7.154	7.148	7.142	_____	_____	_____	_____	_____
C8	7.202	7.195	7.186	7.182	7.181	7.181	7.185	7.190
C9	7.229	7.224	7.217	7.213	7.212	7.214	7.216	7.220

The change of pH of 18 representative solutions with change in temperature is shown graphically in figures 9, 10, and 11.
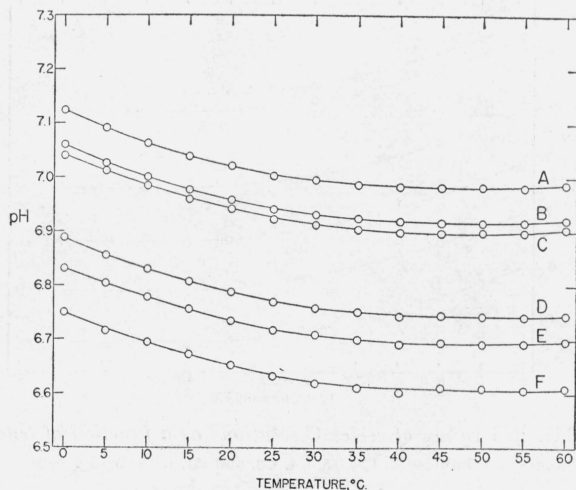

FIGURE 9.—pH *values of series A solutions as a function of temperature.*
Curves *A* to *F* represent pH values of solutions A16, A14, A13, A10, A9, and A7, respectively.

Writing the mass-action constant for the second dissociation (eq 8a) in the logarithmic form and combining it with eq 11, we have

$$pH = pK_2 - \log(m_{H_2PO_4}/m_{HPO_4}) - 3A\sqrt{\mu}/(1 + Ba_i\sqrt{\mu}). \qquad (24)$$

With the use of eq 24, pK_2 from table 5, and the values of $3A$ and Ba_i from table 4, it is possible to compute pH values at $0°$ to $60°$ C
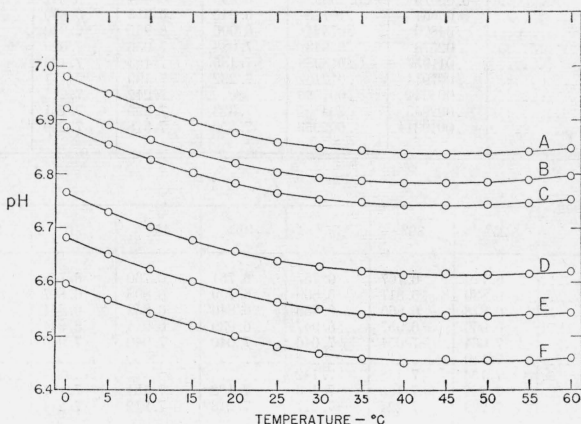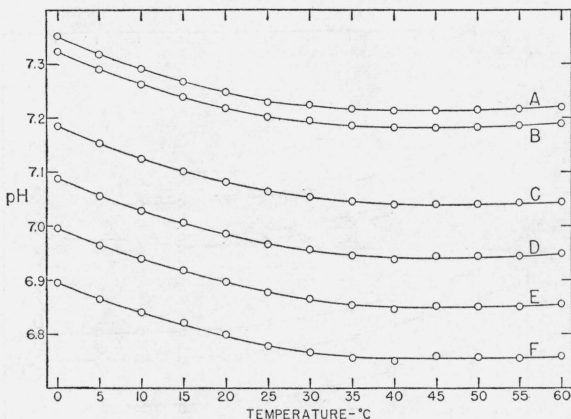

FIGURE 10.—pH *values of series B* solutions as a function of temperature.*
Curves A to F represent pH values of solutions B*8, B*6, B*5, B*4, B*2, and B*1, respectively.

FIGURE 11.—pH *values of series C solutions as a function of temperature.*
Curves A to F represent solutions C9, C8, C5, C4, C3, and C1, respectively.

for phosphate-chloride mixtures in which $m_{Cl} = m_{H_2PO_4}$. Values of the pH computed from eq 24 for series A solutions 11 to 20 are in accord to 0.001 unit with those derived from eq 14.

When the ionic strength is less than 0.5 and the ratio of the molality of primary phosphate ion to that of secondary phosphate ion lies between 0.5 and 2, an error of less than ±0.003 unit may be ascribed to the pH values calculated from eq 24, as also to those listed in tables 8, 9, and 10.

It is evident (table 4) that substitution of potassium dihydrogen phosphate (series B*) for the corresponding sodium salt (series B) affects only the β value. The fact that a $\beta\mu$ term does not appear in eq 24 suggests that solutions which differ only by the substitution of the potassium salt for the sodium salt should have identical pH values, provided the same a_i value applies to both types of mixtures.[13] This conclusion is supported by the agreement between the pH values for solutions B1 and B*1, which show a mean difference of only 0.002 unit for the 13 temperatures (see table 9).

A mixture of 0.02 m potassium dihydrogen phosphate, 0.03 m disodium hydrogen phosphate, and 0.02 m sodium chloride has a pH value very nearly 7 at room temperature. This solution may be used at temperatures between 20° and 30° C for the calibration of glass electrodes at a pH of 7, with an accuracy of ±0.02 unit. If a tolerance of ±0.032 unit is allowable, it may be used at all temperatures between 15° and 60° C. Table 11 gives pH values of this solution at 13 temperatures between 0° and 60° C. The buffer is prepared by dissolving 2.722 g of potassium dihydrogen phosphate, 4.260 g of anhydrous disodium hydrogen phosphate, and 1.169 g of sodium chloride in 1,000 g of freshly boiled distilled water (1002.94 ml at 25° C).

The change of pH at 25° C with molality of disodium hydrogen phosphate for four solutions in which the molalities of sodium dihydrogen phosphate and sodium chloride are both 0.03 is shown in table 12.

TABLE 11.—pH *values of the mixture* KH_2PO_4 *(0.02 m)*, Na_2HPO_4 *(0.03 m)*, NaCl *(0.02 m) from 0° to 60° C*

t	pH	t	pH
°C		°C	
0	7.115	35	6.975
5	7.083	40	6.968
10	7.056	45	6.970
15	7.032	50	6.970
20	7.012	55	6.970
25	6.994	60	6.974
30	6.983		

TABLE 12.—pH *values at 25° C for phosphate-chloride mixtures having the same molalities of* NaH_2PO_4 *and* $NaCl$ *(m₁=m₃) but different molalities of* Na_2HPO_4 *(m₂)*

$m_1=m_3$	m_2	pH
0.03	0.02	6.652
.03	.03	6.799
.03	.04	6.899
.03	.05	6.975

In order that a precision of ±0.003 unit in the pH value may be attained, the buffer solutions should be carefully prepared from tested samples of phosphates, pure sodium chloride, and carbon-dioxide-free water. Potassium dihydrogen phosphate, sodium dihydrogen phosphate, and disodium hydrogen phosphate should be recrystallized from freshly boiled distilled water, or preferably water of conductivity

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[13] For the mixtures composed entirely of sodium salts, the β value appears to be a linear function of the buffer ratio. A further investigation of specific salt effects on a_i and β values will be of importance.

grade. Careful ignition of samples of potassium dihydrogen phosphate to constant weight should give a loss in weight of 13.22 to 13.30 percent. The loss in weight on ignition of sodium dihydrogen phosphate and disodium hydrogen phosphate should be 15.00 to 15.08 percent and 6.34 to 6.42 percent, respectively. It is desirable that the absence of carbonate from the secondary phosphate be affirmed by analysis. Disodium hydrogen phosphate should be kept in a desiccator or dried at 110° to 120° C before use.

Precipitation of sodium chloride from its saturated aqueous solution with dry hydrogen chloride has been found to be a more satisfactory means of purification than recrystallization from water. The salt must then be fused in platinum to remove occluded acid. Traces of bromide must be absent from all buffer solutions in which the silver-chloride electrode is to be employed.

For routine work, buffer solutions whose pH values were correct to ± 0.01 unit have been prepared from reagent-grade chemicals and freshly boiled distilled water. Electromotive-force measurements of hydrogen–silver-chloride cells containing 16 phosphate-chloride mixtures prepared in this way were made at 25° C. The "experimental" pH values, computed from the emf by eq 14 with the use of the ionic parameters given in table 4, agreed on the average to 0.005 unit with those calculated by eq 24. The pH values of these solutions ranged from 7.2 to 7.8.

It should be emphasized, however, that a practical pH assembly with liquid junction, properly calibrated with a buffer of accurate pH value, cannot be relied upon to yield the correct values for the pH of unknown solutions that may have compositions, activities, and ion mobilities quite different from those of the standard [1].

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