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THE SECOND DISSOCIATION CONSTANT OF *p*-PHENOLSULFONIC ACID AND pH VALUES OF PHENOLSULFONATE-CHLORIDE BUFFERS FROM 0° TO 60° C.

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ABSTRACT

The thermodynamic dissociation constant of the phenol group of *p*-phenolsulfonic acid was calculated from electromotive-force measurements of hydrogen–silver-chloride cells without liquid junction. Thirty-nine buffer mixtures of potassium *p*-phenolsulfonate, sodium hydroxide, and sodium chloride were studied in five series of experiments from 0° to 60° C at intervals of 5 degrees. In three series, the molal ratio of phenolsulfonate ion to phenolate-sulfonate ion was unity, and in two series the buffer ratio was 2:3. For two series of experiments, one at each buffer ratio, the molality of sodium chloride was maintained constant near 0.05 for all dilutions of the buffer. In the other experiments, the molality of each component of the solution varied between 0.0037 and 0.1.

The values of pK_2, the negative of the common logarithm of the second dissociation constant, between 0° and 60° C are given by the equation

$$pK_2 = 1961.2/T - 1.1436 + 0.012139T,$$

where T is in degrees Kelvin.

Equations were formulated to give the changes of free energy, heat content, entropy, and heat capacity that accompany the dissociation, at infinite dilution, of a mole of phenolsulfonate ion at any temperature between 0° and 60° C. For the dissociation of the phenol group at 25° C, $\Delta F°$ is 12,351 cal, $\Delta H°$ is 4,036 cal, $\Delta S°$ is -27.9 cal deg^{-1}, and $\Delta C°p$ is -33 cal deg^{-1}.

The pH value of each buffer-chloride mixture was calculated from the experimental data and the activity coefficients that were found to characterize each series of solutions. The pH values of other phenolsulfonate buffers which have molal ratios, m_1/m_2, of phenolsulfonate ion to bivalent phenolate-sulfonate ion between 2/3 and 1 can be computed for temperatures between 0° and 60° C with an accuracy of ± 0.002 unit from their compositions and from the dissociation constants and ionic parameters given in this paper. The equation used is

$$pH = pK_2 - \log(m_1/m_2) - 3A\sqrt{\mu}/(1+8B\sqrt{\mu}),$$

where μ is the ionic strength. Buffer solutions of this type are suitable pH standards in the range 8.6 to 9.0.

CONTENTS

I. ALKALINE BUFFER STANDARDS

Few acids are known whose dissociation constants fall in the region 10^{-7} to 10^{-9}. Consequently, few buffer standards with pH values between 7.0 and 9.0 are available for the calibration of pH equipment and for the control of acidity. Regulation of pH in this slightly alkaline region is, however, of great importance in studies of biological processes and of the body fluids, in the treatment of water, and in the processing of foods and medicines.

Among the buffer solutions that have been employed in this range are mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate, mixtures of boric acid and borax, and solutions of glycine and sodium hydroxide [1].[1] At a pH of 7.5, however, the second acid hydrogen of phosphoric acid is 85 percent neutralized [2]. The pH values of phosphate buffers above pH 7.5 are, therefore, considerably influenced by contamination of the solution with carbon dioxide and by accidental errors in composition. The same objection applies to the use of mixtures of glycine and sodium hydroxide below pH 9.

Borax solutions have pH values of about 9.2, and a buffer composed of borax and boric acid must contain considerable amounts of free boric acid if a pH of 8.2 is to be achieved. Furthermore, such solutions may contain appreciable concentrations of associated polyboric acids [3, 4]. Until boric acid solutions have been further investigated, their pH values between pH 8 and pH 9 will be subject to some uncertainty.

The substituted phenols are acids, and the acid strength varies widely with the number and kinds of substituents. In the search for a useful buffer standard for the slightly alkaline region, several phenols were found that had suitable dissociation constants. Many of these substances, like phenol itself, are liquids or low-melting solids. Some are hygroscopic, unstable to heat or to light, or otherwise unsuitable as standard materials.

The sodium and potassium hydroxybenzoates and hydroxybenzenesulfonates (phenolsulfonates), however, are typical salts and are free from most of these objections. They are crystalline materials, stable at 110° C, and may be recrystallized readily from water. Acree, Mellon, Avery, and Slagle [5] have suggested the use of phenolsulfonates in the preparation of solutions of known acidity. Furthermore, the pH values of buffer systems composed of bivalent and univalent anions can be determined with less difficulty than can those of buffers of a weak monobasic acid and its alkali-metal salt. A dibasic-acid buffer, a mixture of potassium phenolsulfonate and sodium hydroxide for example, covers a much larger range of pH on dilution than does a monobasic-acid system, without sacrifice of considerable buffer capacity.

An electrometric titration of sodium *p*-phenolsulfonate with sodium hydroxide solution showed that the phenol group of *p*-phenolsulfonic acid, one of the simplest dibasic acids of this type, was half neutralized at about pH 8.7. Further substitution of hydrogen in the benzene ring with halogen increases the dissociation of the phenol. Potassium *p*-phenolsulfonate is anhydrous at room temperature, and is therefore more satisfactory than the hydrated sodium salt for the preparation of standard buffers.

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

It is the purpose of this paper to report the measurement of the dissociation constant of the phenol group of *p*-phenolsulfonic acid at 5-degree intervals from 0° to 60° C. The pH values of certain mixtures of potassium *p*-phenolsulfonate, sodium hydroxide, and sodium chloride have been determined. These solutions are proposed as pH standards in the range 8.6 to 9.0.

II. DISCUSSION OF THE ELECTROMOTIVE-FORCE METHOD

The calculation of the second dissociation constant, K_2, of a weak acid and the pH values of solutions of the acid mixed with its salts from emf measurements of hydrogen–silver-chloride cells has been outlined in earlier publications from this Bureau [2, 6, 7]. Mention should be made, however, of the assumptions upon which these calculations are based.

In the absence of side reactions, a cell that contains hydrogen and silver–silver-chloride electrodes is reversible to hydrogen and chloride ions, and its potential depends upon the product of the activities of these ions alone. If the molalities, *m*, of these ions are known, the cell potential then gives the activity coefficient product, $f_{\mathrm{H}}f_{\mathrm{Cl}}$. The square root of this product, $\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$, is the mean activity coefficient of hydrochloric acid, $f_{\pm}$. It is related to the partial molal free energy, or "chemical potential," of hydrochloric acid in the solution, and may be evaluated by several methods which include measurements of freezing point and vapor pressure as well as of emf.

The activity or activity coefficient of a single ion species cannot be evaluated by the methods of thermodynamics alone. Hence to obtain a pH value, or negative of the common logarithm of the activity of the hydrogen ion, an extra-thermodynamic assumption must be made to relate ionic activity to measurable quantities. The dissociation constant, however, is obtained by extrapolation of an appropriate function of emf to the limit at infinite dilution, where all of the activity coefficients are equal. Its value is free from assumptions which interrelate activity coefficients of the ions in the mixture.

For a starting point in the calculation of ionic activity coefficients from emf measurements of cells of the type used here, it is customary to consider that the activity coefficients of hydrogen and chloride ions in the mixture are equal to the mean activity coefficient of hydrochloric acid. This assumption was proposed by Guggenheim [8] and has been used widely. It is further assumed that all ions of the same numerical charge have identical activity coefficients. In this case, then,

$$f_i = \sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}, \tag{1}$$

when *i* represents a singly charged ion.

It has been found that the measured stoichiometrical activity coefficients of many electrolytes in very dilute aqueous solution approach the theoretical values calculated from the Debye-Hückel limiting-law expressions for each of their component ions:

$$-\log f_i = Az_i^2\sqrt{\mu}, \tag{2}$$

where μ is the ionic strength and z_i is the valence of the ion i. The Hückel equation [9],

$$-\log f_i = \frac{Az_i^2\sqrt{\mu}}{1+Ba_i\sqrt{\mu}} - \beta\mu, \tag{3}$$

has been shown to represent the activity coefficient with considerable success at higher concentrations, as well. The constants A and B of eq 2 and 3 vary with temperature and dielectric constant. The symbols a_i and β represent adjustable parameters. The dimensions of a_i are cm$\times 10^{-8}$. The term $\beta\mu$ can be considered as the resultant of several effects which contribute to $-\log f_i$. These contributions, which vary linearly with ionic strength, undoubtedly include the change of dielectric constant with concentration of ionized solutes as well as interactions among resonant dipolar ions and nonpolar ions.

For the calculation of pH values, therefore, the mean activity coefficients of hydrochloric acid in the mixtures are represented by eq 3 (with $z_i^2=2$), and the activity coefficients of all ions in the mixture are expressed in terms of $\sqrt{f_\mathrm{H}f_\mathrm{Cl}}$. The activity coefficients of all univalent ions are set equal to $\sqrt{f_\mathrm{H}f_\mathrm{Cl}}$ (eq 1). The relationship between the activity coefficients of univalent and bivalent ions is given by eq 3. The activity coefficient of a bivalent anion, $\mathrm{A}^=$, in the mixture is then given in terms of the mean activity coefficient of hydrochloric acid by

$$-\log f_{\mathrm{A}^=} = -4\log\sqrt{f_\mathrm{H}f_\mathrm{Cl}} + 3\ \beta\mu. \tag{4}$$

The same values of a_i and β are assumed to apply to all ions of a particular mixture at a particular temperature. The values of these parameters are considered to be weighted averages for all the types of ions in the solution.

Although the value of pK_2 is independent of the validity of any expression for activity coefficients, the extrapolation to zero ionic strength is considerably facilitated when a fairly close approximation to each activity coefficient can be made. When eq 2 is combined with the fundamental emf equation for the hydrogen–silver-chloride cell and with the equilibrium expression for the second step in the dissociation of p-phenolsulfonic acid,

$$\mathrm{HOC_6H_4SO_3^-}\ \text{(phenolsulfonate)} = \mathrm{H^+} + \mathrm{C_6H_4(SO_3^-)\ (O^-)}\ \text{(phenolate-sulfonate)}, \tag{5}$$

the following equation[2] is obtained:

$$\mathrm{p}K_2' = (E-E^\circ)/k + \log(m_\mathrm{HPs}m_\mathrm{Cl}/m_\mathrm{Ps}) + 2A\sqrt{\mu}, \tag{6}$$

where pK_2' is the negative logarithm of the "apparent dissociation constant." Upon extrapolation to infinite dilution. pK_2' becomes pK_2. The symbols E and E° represent, respectively, the emf and standard potential of the cell, and k is $2.3026RT/\boldsymbol{F}$. The gas constant, R, has the value 8.3127 int. j deg^{-1} mole^{-1} [10]; T is the absolute temperature (t+273.16, where t is in degrees centigrade [11]; and $\boldsymbol{F}$ is the

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[2] In this equation, and elsewhere in this paper, Ps represents the phenolsulfonate ion and Ps represents the phenolate-sulfonate ion.

faraday (9.650×10^4 int. coulombs [11]). The standard potential, $E°$, has been measured at 5-degree intervals from 0° to 60° C by Harned and Ehlers [12]. Its value was recalculated by Hamer, Burton, and Acree [6], and is listed in their paper, together with the constants A and B of eq 2 and 3. The values of k in international units are also given in an earlier publication from this Bureau [2].

When eq 3 is used for each activity coefficient, the dissociation constant is represented by an equation similar to eq 6 in form:

$$\mathrm{p}K_2' = \mathrm{p}K_2 - \beta\mu = (E-E°)/k + \log\,(m_{\mathrm{HPs}}m_{\mathrm{Cl}}/m_{\mathrm{Ps}}) + 2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}). \tag{7}$$

It is usually possible to choose a value of a_i that will make $\mathrm{p}K_2'$ a linear function of μ. The slope of the plot of $\mathrm{p}K_2'$ with respect to μ is $-\beta$, and the intercept at zero ionic strength is $\mathrm{p}K_2$, the thermodynamic dissociation constant.

In this way the values of a_i and β that fit a particular series of mixtures are established. When these values of the parameters are employed, eq 3 (with $z_i^2=1$) represents the negative of the logarithm of the mean activity coefficient of hydrochloric acid, $-\log\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$. Equation 3 also represents, as we have assumed, the negative logarithm of the activity coefficient of each ion species in the mixture, when the appropriate value of z_i is used. It is then a simple matter to compute pH values from eq 8 for the emf of the cell, with the substitution of the right side of eq 3 for $-\log f_{\mathrm{Cl}}$ [13]:

$$\mathrm{pH} = (E-E°)/k + \log m_{\mathrm{Cl}} - A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}) + \beta\mu. \tag{8}$$

In the use of eq 6 and 7 it should be realized that hydrolysis of some of the phenolate-sulfonate ion lowers the molality of that ion and increases the molality of phenolsulfonate ion by the same margin. It was found that at 25° C not more than 0.3 percent of the phenolate-sulfonate ion in any of the buffers used in this investigation was hydrolyzed. If the effect of this hydrolysis had not been considered in the calculations, however, a maximum error of 0.01 unit would have been included in the $\mathrm{p}K_2'$ values for the most dilute buffer at the highest temperature measured. Hydrolysis affects the calculation of pH by eq 8 only through changes in a_i, β, and μ. At room temperature these errors are negligible. At higher temperatures, however, hydrolysis is considerably enhanced. Corrections for hydrolysis therefore were made at each temperature.

If m_1 is the stoichiometrical molality of phenolsulfonate salt, m_2 that of the phenolate-sulfonate, and m_3 that of sodium chloride, the ratio $m_{\mathrm{HPs}}/m_{\mathrm{Ps}}$ is given by

$$m_{\mathrm{HPs}}/m_{\mathrm{Ps}} = (m_1+m_{\mathrm{OH}})/(m_2-m_{\mathrm{OH}}). \tag{9}$$

When m_{OH} is known, the ionic strength may also be calculated:

$$\mu = m_1+3m_2+m_3-m_{\mathrm{OH}}. \tag{10}$$

The molality of hydroxyl ion, m_{OH}, can be computed directly from the emf data by the equation

$$(E-E°)/k = \mathrm{p}K_{\mathrm{w}} + \log(m_{\mathrm{OH}}/m_{\mathrm{Cl}}) + \log(f_{\mathrm{OH}}/f_{\mathrm{Cl}}), \tag{11}$$

or

$$-\log m_{\mathrm{OH}} = \mathrm{p}K_{\mathrm{W}} - (E-E°)/k - \log m_{\mathrm{Cl}}, \tag{11a}$$

where pK_w is the negative of the common logarithm of the thermodynamic dissociation constant (ion product) of water at the stated temperature [14]. Equations 11 and 11a were derived by the substitution of the equilibrium expression for the dissociation of water into the equation that relates the emf of the hydrogen–silver-chloride cell to the activities of hydrogen and chloride ions. The last term of eq 11 is zero, as a result of the assumed equality of the activity coefficients of the two univalent ions. The computation of hydrolysis corrections is accordingly a simple matter.

III. EXPERIMENTAL PROCEDURE AND RESULTS

1. MATERIALS

A commercial preparation of potassium *p*-phenolsulfonate was recrystallized four times from water at temperatures below the boiling point of the saturated solution. Only the first crops of crystals were retained. A slightly pink color observed when the commercial material was dissolved in water was discharged by the use of an activated vegetable carbon furnished by the Polarimetry Section of this Bureau. The mother liquors from subsequent recrystallizations were colorless. Tests showed the presence of sulfate in the original material, but this impurity was removed by the first recrystallization.

The potassium *p*-phenolsulfonate was assayed by measurement of the amount of bromine consumed under conditions such that two atoms of bromine were readily substituted and further substitution was negligible.[3] The sample (0.001 mole of the salt in 200 ml of 1 *M* hydrochloric acid) was brought to a temperature of 0° to 0.4° C and allowed to react with bromine (formed by the addition of a slight excess of a standard solution of potassium bromate and potassium bromide) for 15 minutes. The excess bromine was then determined by the addition of potassium iodide and titration of the iodine with thiosulfate solution. Potassium bromate was used as a primary standard, and the thiosulfate solution was compared frequently with the bromate-bromide solution by means of blank analyses from which the potassium phenolsulfonate was omitted.

Three bromometric analyses gave 100.03 ±0.1 percent for the purity of the first preparation (employed for solutions A1 to A9). The second preparation, from which the remaining buffer solutions were prepared, gave 100.09 ±0.1 percent for the mean of three analyses. Three differential electrometric titrations of the first sample gave a mean of 100.08 percent, with an average departure from the mean of 0.2 percent. The blank correction was determined with Nile Blue A sulfate.[4] The electrometric end point was readily estimated to within 0.2 percent by graphical means, but a further uncertainty of nearly the same magnitude was introduced with the use of a blank correction. The results of the titrations of the phenol group with alkali must, therefore, be considered as only corroborative evidence of the purity of the salt. An error of 0.1 percent in the purity of the potassium phenolsulfonate introduces an error of 0.0009 unit in pK_2.

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[3] This method of analysis was adapted by E. E. Sager, of this Bureau, from the experimental conditions for the bromometric determination of furfural [15]. The authors are indebted to Mrs. Sager for the purification and analysis by this method of the sample of potassium phenolsulfonate from which buffer solutions A1 to A9 were prepared.

[4] The color range of this indicator (10.3 to 12.0) includes the pH at which the neutralization of the phenol is complete. The pH-titration curve of *p*-phenolsulfonic acid, determined electrometrically, indicates that a 0.04-*M* solution of disodium phenolate sulfonate has a pH of about 10.7.

The first preparation of phenolsulfonate was analyzed by the Metal and Ore Analysis Section of this Bureau with the following results: carbon—34.02, 34.03 percent; hydrogen—2.40, 2.57 percent; sulfur—14.98 percent. The theoretical percentages of these elements are, respectively, 33.95, 2.37, and 15.10.

Anhydrous potassium *p*-phenolsulfonate is the form of the salt stable at room temperature. When exposed to laboratory air of about 20- to 30-percent humidity, a dry sample absorbed 0.03 to 0.05 percent of moisture. This water was readily lost at 110° C, and the salt was always dried at this temperature before the buffer solutions were prepared. The use of temperatures higher than 110° C should be avoided. One sample was heated overnight at 170° C, and was found thereafter to give a positive test for sulfate. When the salt is heated in air at temperatures of 150° C and above, the odor of phenol is apparent.

Sodium chloride was precipitated from its saturated aqueous solution with dry hydrogen chloride. The salt was then fused in platinum to remove occluded acid. It was fractured and bottled without grinding.

A solution of sodium hydroxide was prepared by dilution of a 50-percent alkali solution that had been centrifuged to remove the insoluble sodium carbonate. The diluted solution was kept in a bottle lined with paraffin and was protected from the air by a guard tube of soda-lime. The solution was standardized frequently against acid potassium phthalate. The average deviation of the analyses was about 0.03 percent.

2. PREPARATION OF THE BUFFER SOLUTIONS AND ELECTRODES

All the solutions were prepared by weight methods. For each series of experiments, a stock solution was prepared from weighed amounts of sodium chloride, potassium *p*-phenolsulfonate, and sodium hydroxide solution. Ten dilutions of this stock solution were made in the manner described earlier by Bates and Acree [2]. The specific conductance of the water was usually less than 0.6×10^{-6} mho. For two series of experiments, the dilutions were made with a sodium chloride solution that had the same molality of salt as the stock solution. It was found that the cells attained equilibrium somewhat more rapidly when the solutions were saturated with hydrogen instead of with nitrogen. In the preparation of the phenolsulfonate buffers, carbon-dioxide-free air was passed through each solution flask while the dilution was being made. The solutions were then freed of air by passing hydrogen through them for about 2 hours before the final weighings were made. The weights were corrected to a vacuum basis.

The hydrogen electrodes were prepared by a modification of the method of Popoff, Kunz, and Snow [16]. The platinum foils were plated lightly with gold and then electrolyzed for 90 seconds in a 3-percent solution of chloroplatinic acid. The electrodes were cleaned by electrolysis in concentrated hydrochloric acid solution. The silver-silver-chloride electrodes were considerably smaller than those described by Hamer and Acree [13] but were larger than the "semimicro" type used by Bates, Siegel, and Acree [17] for electrometric titrations in a cell without liquid junction. About 65 mg of silver was formed by heating a paste of silver oxide at 540° C on a spiral of platinum

3 mm in diameter and 5 mm long. Approximately 20 percent of the silver was converted to silver chloride by electrolysis in 1-*M* hydrochloric acid solution for 45 minutes with a current of 5 ma.

Hydrogen and silver chloride electrodes were always freshly prepared for each series of experiments. The cells contained two electrodes of each kind. The silver chloride electrodes were checked for agreement in a 0.05-*m* solution of hydrochloric acid, and only those electrodes that agreed in potential within 0.06 mv were used. The "aging effect" of silver chloride electrodes, or change of potential during the first few hours after preparation, has been shown by Smith and Taylor [18] to result from the slow diffusion of electrolyte into the pores of the electrode. Thick, adherent layers of silver chloride retard the diffusion and prolong the period of aging. To obviate errors due to concentration-polarization, all the cells were prepared at least 18 hours before measurements were made.

3. RESULTS OF THE ELECTROMOTIVE-FORCE MEASUREMENTS

The cells were usually filled in the late afternoon, kept at 25° C overnight, and measured throughout the following day before the temperature of the water bath was lowered for the measurements at temperatures below 25° C on the third day. The measurements in the range 25° to 60° C were made on the fourth day, and the temperature brought back to 25° C for a final check. The zero point of the thermometer was usually redetermined before each series of experiments was begun. Other experimental details are given in an earlier publication [2].

The electromotive forces, corrected to a hydrogen partial pressure of 760 mm, are given in tables 1 and 2, together with the molalities of potassium *p*-phenolsulfonate (m_1), potassium sodium *p*-phenolate sulfonate (m_2), and sodium chloride (m_3) in each of the buffer solutions. The accuracy of the emf values is probably about ±0.1 mv (±0.0017 pH unit). It may be seen that the "buffer ratio", m_1/m_2, is approximately unity for solutions of series A and series C, whereas the solutions of series B and D have a buffer ratio of about 2:3. In all the buffers that make up series C and D, the chloride molality (m_3) was kept constant near 0.05. This device was advantageous in assuring reproducibility and rapid attainment of equilibrium of the silver chloride electrodes at low concentrations of the buffer salts.

TABLE 1.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenolsulfonate* (m_1), *potassium sodium p-phenolate sulfonate* (m_2), *and sodium chloride* (m_3): *series A and B*

Solution number	m_1	m_2	m_3	E_{0°	E_{5°	E_{10°	E_{15°	E_{20°
A1	0.09628	0.09744	0.09622	0.78744	0.79105	0.79460	0.79807	0.80156
A2	.05979	.06051	.05975	.79900	.80295	.80674	.81048	.81418
A3	.04130	.04180	.04127	.80826	.81235	.81636	.82030	.82419
A4	.03070	.03107	.03068	.81578	.82003	.82419	.82830	.83235
A5	.016220	.016416	.016210	.83202	.83667	.84118	.84567	.85004
A6	.009425	.009539	.009419	.84605	.85091	.85570	.86040	.86502
A7	.007710	.007803	.007705	.85125	.85633	.86118	.86604	.87077
A8	.005805	.005875	.005801	.85848	.86355	.86858	.87349	.87839
A9	.003703	.003748	.003701	.86994	.87525	.88048	.88565	.89073
A10	.09780	.09873	09761	.78720	.79081	.79425	.79766	.80120
A11	.06503	.06565	.06491	.79700	.80094	.80464	.80828	.81196
A12	.05321	.05371	.05311	.80197	.80595	.80975	.81351	.81731
A13	.03944	.03982	.03937	.80949	.81361	.81762	.82152	.82549
A14	.017758	.017927	.017724	.82977	.83433	.83874	.84308	.84744
A15	.016094	.016248	.016063	.83223	.83683	.84128	.84569	.85007
A16	.008621	.008703	.008604	.84818	.85308	.85785	.86256	.87628
A17	.003723	.003758	.003716	.86964	.87496	.88016	.88529	.89043

TABLE 1.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenolsulfonate (m_1), potassium sodium p-phenolate sulfonate (m_2), and sodium chloride (m_3): series A and B*—Continued

Solution number	m_1	m_2	m_3	E_{0°	E_{5°	E_{10°	E_{15°	E_{20°
B1	.07306	.09859	.10110	.79311	.79682	.80051	.80410	.80763
B2	.04951	.06682	.06851	.80264	.80642	.81030	.81413	.81784
B3	.04269	.05761	.05907	.80624	.81010	.81409	.81798	.82178
B4	.02465	.03326	.03411	.81995	.82425	.82847	.83265	.83676
B5	.012009	.016207	.016618	------	------	------	------	------
B6	.010339	.013953	.014307	.84216	.84694	.85162	.85621	.86075
B7	.006241	.008422	.008636	.85533	.86034	.86528	.87015	.87496
	E_{25°	E_{30°	E_{35°	E_{40°	E_{45°	E_{50°	E_{55°	E_{60°
A1	0.80500	0.80839	0.81169	0.81506	0.81833	0.82159	0.82482	0.82808
A2	.81793	.82157	.82517	.82878	.83229	.83583	.83930	.84278
A3	.82815	.83197	.83577	.83956	.84329	.84703	.85072	.85435
A4	.83644	.84046	.84441	.84839	.85224	.85613	.85993	.86376
A5	.85445	.85875	.86304	.86730	.87149	.87570	.87983	.88394
A6	.86979	.87434	.87888	.88343	.88789	.89234	.89664	.90104
A7	.87553	.88039	.88501	.88968	.89423	.89879	.90334	.90779
A8	.88332	.88813	.89294	.89771	.90246	.90715	.91152	.91617
A9	.89589	.90099	.90597	.91092	.91577	.92060	.92534	.93002
A10	.80467	.80807	.81137	.81461	.81794	.82118	.82435	.82760
A11	.81565	.81928	.82284	.82641	.82989	.83335	.83681	.84024
A12	.82109	.82485	.82852	.83219	.83578	.83937	.84292	.84651
A13	.82942	.83332	.83716	.84101	.84476	.84851	.85220	.85590
A14	.85184	.85611	.86036	.86461	.86876	.87290	.87697	.88105
A15	.85450	.85886	.86313	.86742	.87160	.87576	.87994	.88410
A16	.87212	.87657	.88114	.88571	.89022	.89469	.89909	.90363
A17	.89555	.90054	.90559	.91051	.91541	.92016	.92488	.92953
B1	.81120	.81462	.81811	.82153	.82491	.82830	.83163	.83498
B2	.82172	.82541	.82910	.83272	.83633	.83993	.84349	.84706
B3	.82579	.82963	.83335	.83702	.84068	.84438	.84801	.85165
B4	.84097	.84504	.84902	.85301	.85697	.86093	.86474	.86863
B5	.86120	------	------	------	------	------	------	------
B6	.86545	------	------	------	------	------	------	------
B7	.87982	.88470	.88942	.89386	.89845	.90310	.90759	.91205

TABLE 2.—*Electromotive forces of hydrogen–silver-chloride cells containing mixtures of potassium p-phenolsulfonate (m_1), potassium sodium p-phenolate sulfonate (m_2), and sodium chloride (m_3)· series C and D*

Solution number	m_1	m_2	m_3	E_{0°	E_{5°	E_{10°	E_{15°	E_{20°
C1	0.10283	0.09802	0.04977	0.80179	0.80573	0.80932	0.81277	0.81674
C2	.08011	.07636	.05003	.80191	.80579	.80951	.81318	.81698
C3	.06418	.06118	.05003	.80212	.80603	.80987	.81360	.81731
C4	.05087	.04849	.05003	.80223	.80617	.81003	.81382	.81757
C5	.03578	.03411	.05003	.80243	.80657	.81047	.81428	.81806
C6	.015343	.014625	.05003	.80331	.80733	.81124	.81508	.81884
C7	.009787	.009329	.05003	.80392	.80797	.81194	.81583	.81967
D1	.06582	.09822	.04822	.81342	.81752	.82151	.82544	.82936
D2	.04580	.06834	.04824	.81353	.81761	.82166	.82566	.82964
D3	.03314	.04945	.04824	.81384	.81800	.82208	.82609	.83006
D4	.02682	.04002	.04825	.81404	.81823	.82235	.82638	.83034
D5	.02193	.03272	.04826	.81423	.81849	.82263	.82663	.83060
D6	.012187	.018186	.04826	.81471	.81899	.82312	.82715	.83117
D7	.006540	.009760	.04827	.81542	.81967	.82383	.82793	.83198
D8	.006003	.008958	.04827	.81543	.81961	.82378	.82788	.83189
	E_{25°	E_{30°	E_{35°	E_{40°	E_{45°	E_{50°	E_{55°	E_{60°
C1	0.82040	0.82401	0.82769	0.83130	0.83489	0.83846	0.84198	0.84549
C2	.82075	.82435	.82800	.83161	.83518	.83876	.84229	.84583
C3	.82108	.82472	.82836	.83201	.83563	.83923	.84269	.84629
C4	.82132	.82501	.82867	.83234	.83598	.83962	.84313	.84673
C5	.82185	.82560	.82930	.83297	.83663	.84024	.84382	.84743
C6	.82274	.82646	.83023	.83395	.83767	.84130	.84491	.84852
C7	.82353	.82731	.83105	.83468	.83835	.84201	.84560	.84913
D1	.83331	.83718	.84097	.84484	.84859	.85235	.85611	.85981
D2	.83364	.83750	.84136	.84526	.84905	.85284	.85661	.86033
D3	.83407	.83797	.84185	.84577	.84958	.85339	.85718	.86088
D4	.83437	.83830	.84220	.84613	.84996	.85378	.85758	.86136
D5	.83465	.83860	.84252	.84644	.85022	.85407	.85790	.86169
D6	.83529	.83917	.84310	.84705	.85090	.85470	.85851	.86228
D7	.83606	.84003	.84398	.84795	.85180	.85563	.85946	.86319
D8	.83601	------	------	------	------	------	------	------

IV. CALCULATION OF THE SECOND DISSOCIATION CONSTANT AND RELATED THERMODYNAMIC QUANTITIES FROM 0° TO 60° C

In the search for the proper extrapolation function, the negative logarithm of the apparent dissociation constant, pK_2', was computed for solutions A1 to A9 from eq 6, which comprises the Debye-Hückel limiting law. Examination of curve *A* of figure 1 shows that it would be difficult to obtain an accurate pK_2 value by extrapolation to infinite dilution with the use of eq 6. Equation 7 gave values of pK_2' which, plotted as a function of ionic strength, lend themselves to an easy extrapolation. Curves *B*, *C*, and *D*, figure 1, were computed from eq 7 with a_i values of 4, 8, and 10 angstrom units, respectively. Corrections for hydrolysis by eq 9, 10, and 11a were made in all cases.

The use of 8 A was found to yield a straight line for the 4 series of buffers at each of the 13 temperatures. The error in establishing a_i is estimated to be less than ±0.2 A. The slopes of these lines (β in eq 7) decreased with increasing temperature. The extrapolations of series A and B solutions followed a common course, in spite of the different buffer ratios involved. The β slopes for the two series (C and D), in which constant chloride molality was maintained, differed from each other, but β for series C was identical with the common slope of series A and B at all temperatures except 0° and 5° C.

TABLE 3.—*Numerical values of 3A, 8B, and β from 0° to 60° C*

t	$3A$	$8B$	$-\beta$		
			Series A and B	Series C	Series D
°*C*					
0	1.467	2.602	0.082	0.089	0.100
5	1.478	2.609	.075	.083	.093
10	1.490	2.616	.070	.070	.083
15	1.503	2.623	.066	.066	.081
20	1.516	2.631	.060	.060	.073
25	1.529	2.638	.057	.057	.069
30	1.544	2.647	.051	.051	.061
35	1.559	2.656	.049	.049	.060
40	1.575	2.664	.044	.044	.054
45	1.591	2.674	.041	.041	.053
50	1.607	2.682	.039	.039	.050
55	1.625	2.693	.041	.041	.055
60	1.643	2.702	.038	.038	.052

The values of β for all four series of solutions at the 13 temperatures are given in table 3, together with the values of $3A$ and $8B$. With the use of these constants and parameters, pK_2, the thermodynamic dissociation constant of the phenol group, was computed from eq 7. The mean value of pK_2 for each group of solutions is given in table 4. The seventh column of the table lists the average value for the five groups, weighted equally. Values of the dissociation constant, K_2, and of K_W/K_2 are given in the last two columns. The use of K_W/K_2 for approximate hydrolysis corrections will be described later. The uncertainty ascribed to pK_2 represents the mean departure of all 39 measurements from the average value. All the values at 0°, 25°, and 60° C are shown in figure 2, and the average pK_2 values are plotted as a junction of temperature in figure 3.

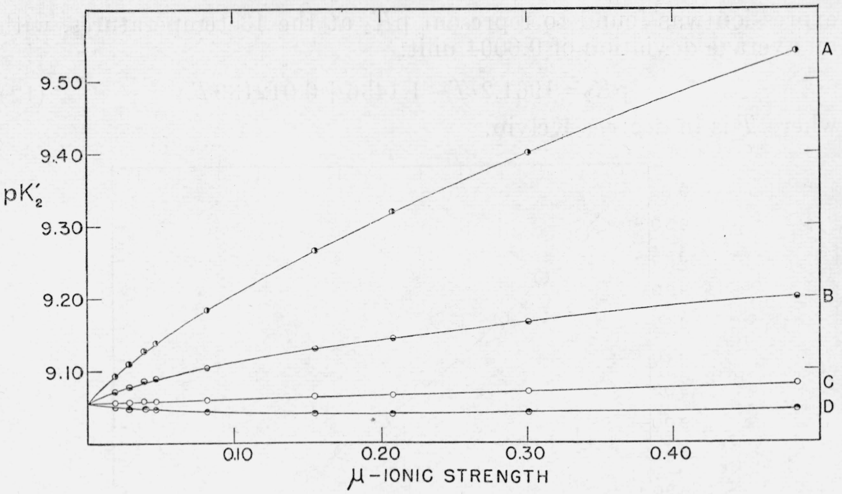

FIGURE 1.—*Extrapolation of the electromotive force data solutions A1 to A9.*

Curve *A* is calculated from eq 6; curves *B*, *C*, and *D* were computed from eq 7 with a_1 values of 4*A*, 8*A*, and 10*A*, respectively.

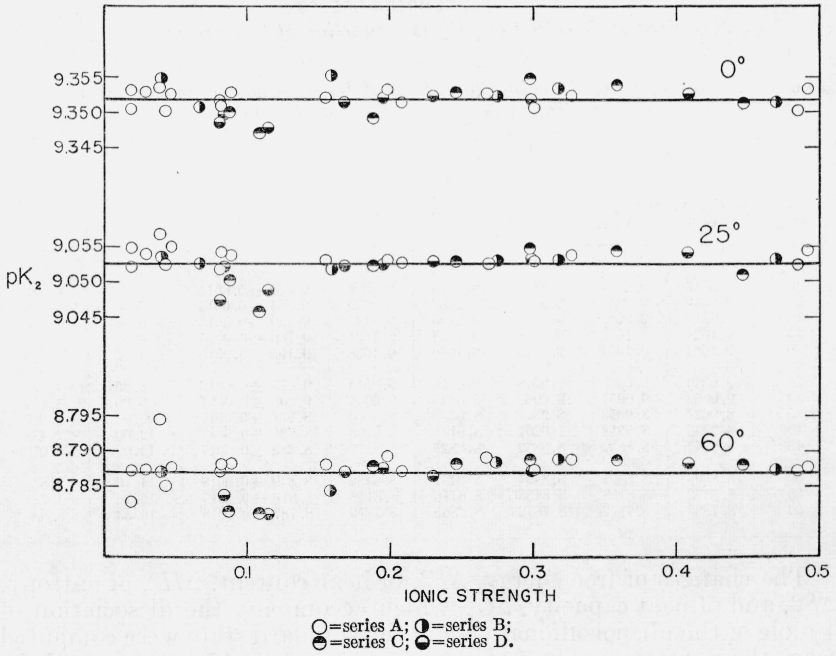

FIGURE 2.—*Negative logarithm of the second dissociation constant at 0°, 25°, and 60° plotted against ionic strength.*

The average values of pK_2 were fitted to the equation of Harned and Robinson [19] by the method of least squares. The following expression was found to represent pK_2 at the 13 temperatures, with an average deviation of 0.0004 unit:

$$\mathrm{p}K_2 = 1961.2/T - 1.1436 + 0.012139T, \qquad (12)$$

where T is in degrees Kelvin.

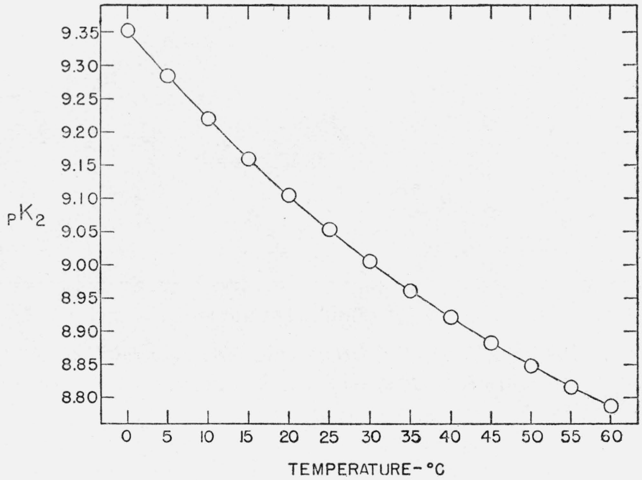

FIGURE 3.—*Plot of pK_2 as a function of temperature.*

TABLE 4.—*Summary of the values for pK_2 and K_2 from measurements of five groups of solutions at temperatures from 0° to 60° C*

t	pK_2						$K_2 \times 10^{10}$	$K_w/K_2 \times 10^5$
	Series A, 1 to 9	Series A, 10 to 17	Series B	Series C	Series D	Average		
°C								
0	9.3519	9.3521	9.3530	9.3513	9.3508	9.352 ±0.0014	4.45	0.258
5	9.2849	9.2846	9.2836	9.2837	9.2829	9.284 ±0.0014	5.20	.358
10	9.2210	9.2202	9.2198	9.2205	9.2195	9.220 ±0.0015	6.03	.485
15	9.1621	9.1603	9.1608	9.1594	9.1591	9.160 ±0.0015	6.92	.652
20	9.1064	9.1054	9.1048	9.1046	9.1038	9.105 ±0.0015	7.85	.868
25	9.0540	9.0530	9.0528	9.0516	9.0514	9.053 ±0.0013	8.85	1.138
30	9.0062	9.0054	9.0063	9.0035	9.0044	9.005 ±0.0017	9.89	1.489
35	8.9627	8.9613	8.9622	8.9596	8.9600	8.961 ±0.0017	10.94	1.910
40	8.9225	8.9212	8.9207	8.9191	8.9205	8.921 ±0.0017	12.00	2.43
45	8.8847	8.8837	8.8832	8.8825	8.8822	8.883 ±0.0017	13.09	3.07
50	8.8507	8.8491	8.8494	8.8481	8.8482	8.849 ±0.0018	14.16	3.87
55	8.8172	8.8158	8.8158	8.8146	8.8148	8.816 ±0.0017	15.28	4.77
60	8.7883	8.7872	8.7872	8.7863	8.7859	8.787 ±0.0018	16.33	5.89

The changes of free energy, $\Delta F°$, of heat content, $\Delta H°$, of entropy, $\Delta S°$, and of heat capacity, $\Delta C_p°$, which accompany the dissociation of 1 mole of the phenolsulfonate ion in the standard state were computed from the numerical values of the constants of eq 12 by means of the equations given in the paper of Bates and Acree [2]. These quantities are listed in table 5. For convenience, they are given both in calories and in international joules. One calorie has been taken as 4.1833 international joules [20].

The pK_2 values are thought to be correct within ±0.002 unit. The uncertainty in $\Delta F°$ introduced by the uncertainties in pK_2 is about

±3 cal. The value of ΔS° may be in error by 0.3 cal deg^{-1}. A combination of these errors in entropy and free energy gives an estimated uncertainty of about 70 cal for ΔH° and 4 cal deg^{-1} for ΔC_p°.

TABLE 5.—*Thermodynamic data for the second dissociation of p-phenolsulfonic acid from 0° to 60° C*

t	ΔF°		ΔH°		ΔS°		ΔC_p°	
°C	*int.j*	*cal*	*int. j*	*cal*	*int.j deg*$^{-1}$	*cal deg*$^{-1}$	*int.j deg*$^{-1}$	*cal deg*$^{-1}$
0	48,896	11,688	20,202	4,829	−105.0	−25.1	−127	−30
5	49,428	11,815	19,561	4,676	−107.4	−25.7	−129	−31
10	49,970	11,945	18,909	4,520	−109.7	−26.2	−132	−31
15	50,525	12,078	18,245	4,361	−112.0	−26.8	−134	−32
20	51,091	12,213	17,570	4,200	−114.4	−27.3	−136	−33
25	51,668	12,351	16,883	4,036	−116.7	−27.9	−139	−33
30	52,257	12,492	16,185	3,869	−119.0	−28.4	−141	−34
35	52,858	12,635	15,474	3,699	−121.3	−29.0	−143	−34
40	53,471	12,782	14,752	3,526	−123.7	−29.6	−146	−35
45	54,094	12,931	14,019	3,351	−126.0	−30.1	−148	−35
50	54.730	13,083	13,274	3,173	−128.3	−30.7	−150	−36
55	55,377	13,238	12,517	2,992	−130.6	−31.2	−152	−36
60	56,036	13.395	11,749	2,809	−132.9	−31.8	−155	−37

Unfortunately, there has been no direct calorimetric determination of the heat of dissociation of phenolsulfonate ion for comparison with that calculated by differentiation of the emf data. The change in heat capacity, ΔC_p°, is smaller than the corresponding value for the second dissociation of phosphoric acid (−33 cal as compared with −54 cal). ΔC_p° is the difference between the sum of the heat capacities of the products and that of the reactants when the dissociation takes place at infinite dilution. Since the hydrogen ion is common to the dissociation of both acids, this difference of 21 cal in ΔC_p° must mean that the specific heats of the univalent and bivalent phosphate anions differ by a larger amount than do the specific heats of univalent phenolsulfonate and bivalent phenolate-sulfonate anions. This requirement is entirely reasonable, in view of the relatively large concentration of negative charge on the $HPO_4^=$ ion and the probability that the phenolate-sulfonate ion exists in two electromeric forms.

The changes in heat capacity and entropy that accompany the second dissociation of six dibasic or polybasic acids at infinite dilution are given in table 6. The acids are listed in order of increasing pK_2. The entropy changes for the second dissociation of all six of these acids are 30 ±5 cal at 25° C. Any theoretical interpretation of these quantities must, however, await the time when accurate data for a large number of acids are available.

The ΔC_p° value for sulfuric acid given in table 6 was computed from calorimetric data. The measurements by Randall and Taylor [23] of the heat capacities of solutions of sulfuric acid at concentrations high enough to avoid appreciable influence of the second dissociation of the acid were plotted as a function of the square root of the molality and were extrapolated to zero concentration. In this way, 6 cal was found for the sum of the heat capacities of hydrogen and bisulfate ions at infinite dilution. Combination of this value with the heat capacities at infinite dilution of potassium sulfate [24] and of hydrochloric acid and potassium chloride [25] gave ΔC_p° for the second dissociation of sulfuric acid.

TABLE 6.—*Entropy and heat-capacity changes for the second dissociation of certain acids at 25° C*

Acid	$\Delta S°$ cal deg $^{-1}$	$\Delta C_p°$ cal deg $^{-1}$	Reference
Sulfuric	−26.3	[a]−73	Pitzer [21].[d]
Oxalic	[b]−24.8	−59	Harned and Fallon [22].
Malonic	−30.0	−61	Hamer, Burton, and Acree [6].
Phosphoric	[c]−29.6	[c]−45	Bates and Acree [2].
p-Phenolsulfonic	−27.9	−33	Bates, Siegel, and Acree.
Carbonic	−35.2		Pitzer [21].[d]

[a] Calculated by the authors from the data on the heat capacities of sulfuric acid solutions given by Randall and Taylor [23], together with the heat capacities at infinite solution of potassium sulfate (Randall and Rossini [24]) and of hydrochloric acid and potassium chloride (Rossini [25]).

[b] Calculated by the authors from the data of Harned and Fallon [22].

[c] The values of Nims [26], recalculated by Bates and Acree [2], are, respectively, −30.2 and −45. Pitzer [21] gives −30.3 as the standard entropy change for the second dissociation of phosphoric acid.

[d] Pitzer [21] measured the heat of ionization and computed the entropy from the thermodynamic relation $\Delta S° = (\Delta H° - \Delta F°)/T$. For the dissociation of bisulfate and bicarbonate ions, $\Delta F°$ at 25° C was taken from the emf measurements of Hamer [27] and of MacInnes and Belcher [28], respectively.

V. pH VALUES OF PHENOLSULFONATE SOLUTIONS

1. CALCULATION OF THE pH VALUES FROM ELECTROMOTIVE-FORCE MEASUREMENTS

The pH value of each buffer solution was computed directly from the emf by eq 8, with the use of an a_i value of 8 A the β values given in table 3. The pH values are listed in tables 7 and 8. The change of pH with temperature of four buffers of series A is shown in figure

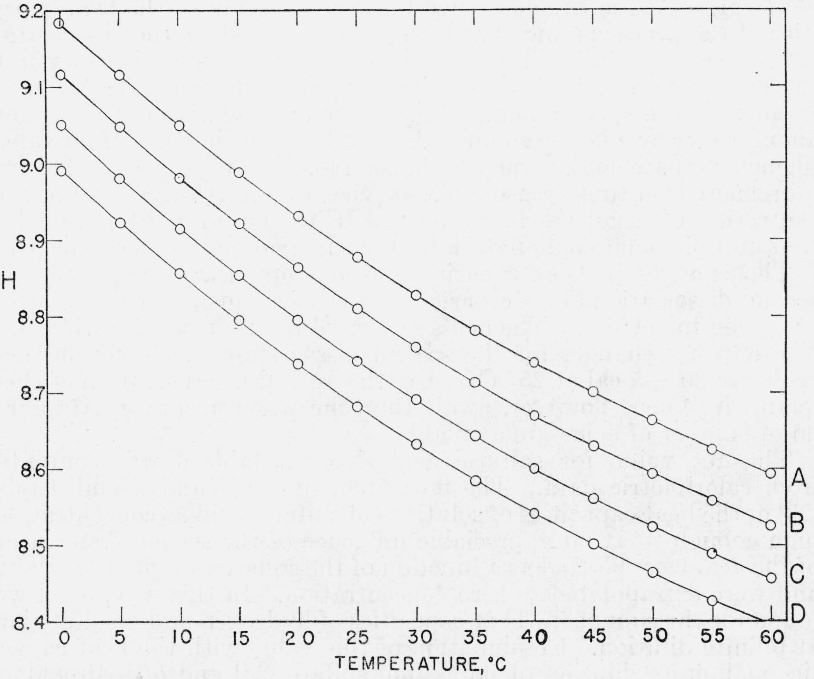

FIGURE 4.—pH *values of four phenolsulfonate-chloride solutions plotted as a function of temperature.*

Curves *A*, *B*, *C*, and *D* represent, respectively, solutions A8, A5, A3, and A1.

4. Curves *A*, *B*, *C*, and *D* represent respectively solutions A8, A5, A3, and A1.

Each of these solutions is a suitable standard for pH. The buffer capacity of the most dilute buffers, however, is fairly low. These solutions are more susceptible to errors in pH caused by the absorption of carbon dioxide from the air, by alkali from glass bottles in which they may be stored, and by dilution than are the buffers whose component salts are at least 0.01 *m*.

TABLE 7.—pH *values of mixtures of potassium p-phenolsulfonate* (m_1), *potassium sodium p-phenolate sulfonate* (m_2), *and sodium chloride* (m_3): *series A and B*

Solution number	m_1	m_2	m_3	pH				
				0°	5°	10°	15°	20°
A1	0.09628	0.09744	0.09622	8.992	8.923	8.857	8.795	8.738
A2	.05979	.06051	.05975	9.024	8.956	8.889	8.828	8.770
A3	.04130	.04180	.04127	9.051	8.981	8.915	8.854	8.796
A4	.03070	.03107	.03068	9.072	9.003	8.937	8.876	8.818
A5	.016220	.016416	.016210	9.116	9.048	8.982	8.922	8.865
A6	.009425	.009539	.009419	9.154	9.085	9.025	8.959	8.901
A7	.007710	.007803	.007705	9.168	9.101	9.035	8.975	8.918
A8	.005805	.005875	.005801	9.184	9.115	9.050	8.989	8.932
A9	.003703	.003748	.003701	9.210	9.141	9.076	9.016	8.958
A10	.09780	.09873	.09761	8.993	8.924	8.856	8.793	8.738
A11	.06503	.06565	.06491	9.019	8.952	8.884	8.822	8.764
A12	.05321	.05371	.05311	9.033	8.964	8.897	8.835	8.777
A13	.03944	.03982	.03937	9.055	8.985	8.919	8.856	8.799
A14	.017758	.017927	.017724	9.110	9.041	8.975	8.913	8.856
A15	.016094	.016248	.016063	9.116	9.047	8.980	8.919	8.861
A16	.008621	.008703	.008604	9.156	9.087	9.021	8.960	8.903
A17	.003723	.003758	.003716	9.206	9.138	9.072	9.012	8.955
B1	.07306	.09859	.10110	9.120	9.051	8.985	8.923	8.866
B2	.04951	.06682	.06851	9.148	9.076	9.010	8.949	8.890
B3	.04269	.05761	.05907	9.157	9.085	9.019	8.958	8.899
B4	.02465	.03326	.03411	9.199	9.124	9.058	8.997	8.939
B5	.012009	.016207	.016618	----------	----------	----------	----------	----------
B6	.010339	.013953	.014307	9.254	9.185	9.120	9.058	9.000
B7	.006241	.008422	.008636	9.292	9.222	9.157	9.096	9.038

	pH							
	25°	30°	35°	40°	45°	50°	55°	60°
A1	8.682	8.633	8.585	8.542	8.502	8.464	8.427	8.395
A2	8.715	8.665	8.618	8.575	8.535	8.498	8.461	8.429
A3	8.741	8.691	8.644	8.601	8.561	8.524	8.489	8.456
A4	8.763	8.713	8.667	8.624	8.584	8.547	8.511	8.479
A5	8.810	8.760	8.714	8.671	8.630	8.594	8.558	8.526
A6	8.848	8.797	8.751	8.709	8.669	8.632	8.595	8.564
A7	8.863	8.816	8.769	8.727	8.687	8.651	8.616	8.584
A8	8.878	8.828	8.783	8.740	8.701	8.664	8.625	8.594
A9	8.904	8.856	8.810	8.767	8.726	8.689	8.652	8.618
A10	8.682	8.633	8.585	8.541	8.501	8.463	8.425	8.393
A11	8.709	8.660	8.613	8.570	8.530	8.492	8.455	8.423
A12	8.722	8.673	8.626	8.583	8.543	8.506	8.469	8.438
A13	8.744	8.695	8.648	8.606	8.565	8.529	8.492	8.460
A14	8.802	8.752	8.706	8.664	8.623	8.587	8.551	8.519
A15	8.807	8.758	8.711	8.669	8.628	8.591	8.556	8.525
A16	8.850	8.797	8.751	8.708	8.669	8.632	8.596	8.566
A17	8.900	8.850	8.806	8.762	8.722	8.683	8.647	8.613
B1	8.810	8.759	8.713	8.668	8.629	8.592	8.554	8.522
B2	8.836	8.786	8.740	8.696	8.656	8.619	8.583	8.551
B3	8.847	8.798	8.750	8.706	8.666	8.629	8.593	8.561
B4	8.885	8.835	8.787	8.744	8.704	8.667	8.630	8.598
B5	8.936	----------	----------	----------	----------	----------	----------	----------
B6	8.947	----------	----------	----------	----------	----------	----------	----------
B7	8.984	8.936	8.890	8.843	8.802	8.766	8.730	8.697

TABLE 8.—pH *values of mixtures of potassium p-phenolsulfonate* (m_1), *potassium sodium p-phenolate sulfonate* (m_2), *and sodium chloride* (m_3): *series C and D*

Solution number	m_1	m_2	m_3	pH				
				0°	5°	10°	15°	20°
C1	0.10283	0.09802	0.04977	8.973	8.904	8.837	8.770	8.717
C2	.08011	.07636	.05003	8.990	8.919	8.854	8.790	8.734
C3	.06418	.06118	.05003	9.003	8.933	8.869	8.806	8.747
C4	.05087	.04849	.05003	9.014	8.944	8.879	8.818	8.759
C5	.03578	.03411	.05003	9.029	8.962	8.898	8.836	8.778
C6	.015343	.014625	.05003	9.065	8.995	8.930	8.868	8.809
C7	.009787	.009329	.05003	9.084	9.014	8.949	8.888	8.829
D1	.06582	.09822	.04822	9.174	9.105	9.040	8.976	8.919
D2	.04580	.06834	.04824	9.194	9.124	9.059	8.996	8.939
D3	.03314	.04945	.04824	9.213	9.143	9.078	9.016	8.958
D4	.02682	.04002	.04825	9.224	9.155	9.090	9.028	8.969
D5	.02193	.03272	.04826	9.234	9.165	9.100	9.038	8.979
D6	.012187	.018186	.04826	9.257	9.188	9.123	9.060	9.002
D7	.006540	.009760	.04827	9.281	9.211	9.145	9.084	9.026
D8	.006003	.008958	.04827	9.282	9.211	9.145	9.084	9.025

	pH							
	25°	30°	35°	40°	45°	50°	55°	60°
C1	8.660	8.610	8.564	8.521	8.481	8.444	8.407	8.376
C2	8.678	8.627	8.578	8.537	8.497	8.460	8.423	8.391
C3	8.692	8.641	8.594	8.551	8.511	8.474	8.436	8.405
C4	8.703	8.653	8.606	8.563	8.526	8.487	8.450	8.418
C5	8.722	8.672	8.626	8.582	8.542	8.505	8.469	8.438
C6	8.755	8.709	8.658	8.615	8.576	8.538	8.503	8.471
C7	8.774	8.724	8.678	8.633	8.593	8.556	8.520	8.487
D1	8.864	8.815	8.767	8.725	8.683	8.646	8.609	8.576
D2	8.887	8.834	8.787	8.745	8.704	8.667	8.630	8.598
D3	8.903	8.853	8.806	8.763	8.722	8.686	8.649	8.616
D4	8.914	8.864	8.818	8.775	8.734	8.697	8.661	8.629
D5	8.924	8.875	8.828	8.785	8.744	8.707	8.671	8.640
D6	8.948	8.897	8.850	8.807	8.767	8.729	8.693	8.661
D7	8.971	8.921	8.874	8.831	8.790	8.753	8.717	8.684
D8	8.971	---------	---------	---------	---------	---------	---------	---------

The reproducibility of the pH values in the tables is about ±0.002 unit, an amount which corresponds with an uncertainty of 0.12 mv in emf. This uncertainty may be divided between experimental error in emf (±0.001 unit, or 0.06 mv) and errors in the molalities of the solutions, resulting from accidental errors in the preparation of the solutions and from unrecognized impurities (±0.001 unit). A further uncertainty of 0.001 unit is introduced with $E°$ and k. The estimated uncertainty of 0.2 A in a_i corresponds to about 0.002 unit in pH for the most concentrated solution studied, but this error diminishes rapidly as the ionic strength is lowered. It is impossible at present to estimate the absolute accuracy of a pH value. The validity of the assumption upon which the calculation of the activity coefficient of chloride ion rests has not been established.

2. STANDARD BUFFER SOLUTIONS

For the computation of the pH values of phenolsulfonate-chloride solutions other than those actually studied in this investigation, it is convenient to employ the equilibrium expression for the second dissociation in the logarithmic form, with the substitution of eq 3 for each activity coefficient:

$$\mathrm{pH} = \mathrm{p}K_2 - \log\,(m_{\mathrm{HPs}}/m_{\mathrm{Ps}}) - 3A\sqrt{\mu}/(1+8B\sqrt{\mu}). \qquad (13)$$

The correction for hydrolysis is made quite readily by means of eq 9; m_{OH} for use in this equation is obtained from the stoichiometrical ratio, m_1/m_2, of potassium *p*-phenolsulfonate to potassium sodium *p*-phenolate sulfonate by means of the approximation:

$$m_{\mathrm{OH}} \approx (K_{\mathrm{W}}K_2)/(m_1/m_2). \qquad (14)$$

This expression can be used with an error of less than 0.001 pH unit for all solutions in which the molality of each of the buffer salts exceeds 0.01. The values of $\mathrm{p}K_2$, $3A$, $8B$, and K_{W}/K_2 are found in tables 3 and 4, and μ is computed from eq 11.

The pH values computed from eq 13 will be consistent within ±0.002 unit with the emf measurements, if the buffer solutions meet the following requirements: (a) the ratio m_1/m_2 is between 2/3 and 1, (b) the molality of sodium chloride, m_3, is either approximately equal to the molality of potassium sodium *p*-phenolate sulfonate, m_2, or is 0.05, and (c) the temperature is between 0° and 60° C. The change of pH with temperature is larger, in general, for alkaline buffers than for acid buffers. For a change of 5 degrees, the last term on the right of eq 13 changes less than 0.003, whereas the molality term remains practically unaltered. The change in pH is, then, substantially the same as the change of $\mathrm{p}K_2$ with temperature, or about 0.01 pH unit per degree.

The pH values at 25° C of the 17 buffer solutions of series A have been calculated by eq 13 and are compared in table 9 with those computed by eq 8 from the individual emf values. The average difference between the two sets of pH values is less than 0.001 unit. It should be emphasized that this agreement does not establish the validity of the assumptions discussed earlier in this paper. It demonstrates, however, the applicability of eq 3 to the experimental data.

TABLE 9.—*Comparision of* pH *values for series A buffers at 25° C calculated from* $\mathrm{p}K_2$ *(eq 13) with those derived from the emf by eq 8*

Solution number	pH (eq 13)	pH (eq 8)	Solution number	pH (eq 13)	pH (eq 8)
A1	8.683	8.682	A10	8.681	8.682
A2	8.715	8.715	A11	8.709	8.709
A3	8.741	8.741	A12	8.722	8.722
A4	8.763	8.763	A13	8.744	8.744
A5	8.809	8.810	A14	8.802	8.802
A6	8.846	8.848	A15	8.808	8.807
A7	8.859	8.863	A16	8.850	8.850
A8	8.877	8.878	A17	8.902	8.900
A9	8.903	8.904			

In the practical determination of pH by electrometric methods, the electrode system is usually standardized by means of buffer solutions of known acidity. Phenolsulfonate solutions are most satisfactory as pH standards when the molality of each constituent of the buffer is between 0.01 and 0.05. With the use of eq 13, the pH values of a phenolsulfonate buffer in which the molalities of the phenolsulfonate, phenolate sulfonate, and chloride ions are each 0.025 have been computed and are given in table 10. This solution is prepared most conveniently by dissolving 0.05 mole (10.613 g) of potassium *p*-phenolsulfonate and 0.025 mole (1.461 g) of sodium chloride in sufficient carbonate-free sodium hydroxide solution to contain 0.025 mole of alkali. The solution is then diluted with freshly boiled water to a volume of 1,000 ml. These directions yield a buffer solution in which the component salts are each 0.025 molar, instead of 0.025 molal. This difference of about 1 percent in concentration of each constituent is entirely permissible for, as table 7 shows, a dilution of 1 percent changes the pH value of such a buffer by less than 0.001 unit.

Table 10.—pH *values of the buffer solution composed of potassium p-phenolsulfonate, potassium sodium p-phenolate sulfonate, and sodium chloride, each at a molality of 0.025*

t	pH	*t*	pH
°*C*		°*C*	
0	9.082	35	8.676
5	9.012	40	8.633
10	8.946	45	8.593
15	8.884	50	8.556
20	8.827	55	8.520
25	8.773	60	8.488
30	8.723		

If a precision of ±0.002 pH unit is desired, the purity of the phenolsulfonate must be assured either by analysis and recrystallization, if necessary, or by the use of a certified sample. Whereas an inert impurity present in amounts less than 0.6 percent will alter the pH by less than 0.002 unit, the presence of half that amount of free phenolsulfonic acid, for example, is sufficient to change it by the same margin. It is unlikely that the small amounts of phenol and potassium bisulfate formed by the hydrolytic breakdown of the salt at 110°, or in solution at the higher temperatures (40° to 60° C), would have a large effect on the pH value.

These standard buffer solutions should be protected carefully from contamination with carbon dioxide. They are best preserved in bottles of alkali-resistant glass. Until the stability of phenolsulfonate solutions has been thoroughly investigated, these buffers should be protected from direct sunlight and should be renewed frequently.

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