Activity Coefficients in Aqueous Mixtures of Phosphates with Sodium Chloride, Sodium Bromide, and Sodium Iodide, and the pH of Phosphate Buffer Solutions

By Roger G. Bates

The electromotive force of cells with hydrogen electrodes and silver-silver bromide or silver-silver iodide electrodes was measured at 25° C. The electrolyte in each cell consisted of an aqueous mixture of (a) potassium dihydrogen phosphate, (b) disodium hydrogen phosphate, and (c) sodium bromide or sodium iodide. The molalities of (a) and (b) were always equal, whereas the ratio of the molality of (c) to that of (a) or (b) was 1, 0.5, or 0.2. The ionic strengths ranged from 0.04 to 0.25. The data are compared with similar measurements for phosphate-chloride mixtures reported in an earlier paper. At a given ionic strength, the activity-coefficient term, $f_{H_2PO_4}f_X/f_{HPO_4}$ where X represents halide, increases when bromide at a given concentration is substituted for chloride at the same concentration, or when iodide replaces bromide. Accurate values for the pH of phosphate buffer solutions with and without added salt can be obtained only at low ionic strengths.

I. Introduction

During the past several years, methods for determining activity pH ($-\log a_H$) for standard buffer solutions from electromotive-force measurements of cells without liquid junction have been developed. These methods have been used to assign pH values to certain phosphate, phthalate, and borate solutions prepared from Standard Samples certified by the National Bureau of Standards [1, 2, 3].[1] Cells with hydrogen and silver-silver chloride electrodes were employed in each instance. The electromotive-force data for aqueous mixtures of the buffers with sodium or potassium chloride afford an unequivocal determination of $-\log a_H f_{Cl}$, where f_{Cl} is the activity coefficient of chloride ion [2] for each solution studied. Furthermore, the value of this quantity in a buffer solution without chloride can be ascertained by a suitable extrapolation from a series of determinations in which the molal ratio of chloride to buffer is varied. It is impossible to derive $-\log a_H$ from these measurable quantities without an estimate of f_{Cl}, and the evaluation of this ionic activity coefficient must rest partly upon arbitrary considerations. It must be realized that paH computed from the emf of cells without liquid junction is primarily a unit on an arbitrary scale, as is that determined by the usual pH assembly with a liquid junction [5, 6]. Its significance in terms of thermodynamic constants may be limited to a small number of standard solutions of assigned paH and may not be imparted to mixtures of unknown composition whose paH it is desired to determine.

The chloride ion plays a unique and important role in the derivation of paH from the emf of the hydrogen-silver chloride cell without junction. However reasonable the assumptions involved in the computation may appear, their validity can usually not be affirmed. Hence, it is important to demonstrate the extent to which the properties of chloride ion, and of the silver-silver chloride electrode, influence the paH of the buffer solution without chloride obtained by these means. For this purpose, equimolal mixtures of potassium

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

[2] The molal scale of activity is used throughout this paper. The so-called "activity pH", $-\log a_H$, will be designated paH, in accordance with the suggestion of Sørensen and Linderstrøm-Lang [4]. Concentrations will be given in molality (m). The symbol μ is used for ionic strength.

dihydrogen phosphate and disodium hydrogen phosphate were chosen. The paH of these solutions has already been calculated from measurements of $-\log \mathbf{a}_H f_{Cl}$ in mixtures of the phosphate buffer with varying amounts of sodium chloride [1]. Sodium bromide and sodium iodide were added to equimolal phosphate buffers in such amounts that the ratios of the molality of halide to that of each phosphate had the three values 1, 0.5, and 0.2. Measurements of the emf of hydrogen-silver bromide and hydrogen-silver iodide cells, with these phosphate-halide mixtures as cell solutions, were made at 25° C. The assumptions were tested by computing the paH of the phosphate buffer, in the absence of added salt, from the three series of emf data.

II. Determination of the Activity Coefficients

The cells used in this study can all be represented by the following scheme,

$$Pt; H_2(g, 1 \text{ atm}), KH_2PO_4(m_1), Na_2HPO_4(m_1),$$
$$NaX(m_2), AgX(s); Ag,$$
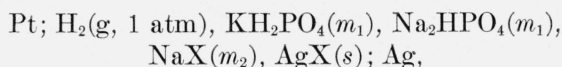
where X is chloride, bromide, or iodide, and m is molality. When the standard potential, E°, of the cell is known, $-\log \mathbf{a}_H f_X$ is readily obtained from the emf, E, and natural constants:

$$-\log \mathbf{a}_H f_X = -\log (f_H f_X m_H) = \frac{(E-E^\circ)\mathbf{F}}{2.3026RT} + \log m_X. \tag{1}$$

In eq 1, $\mathbf{F}$ is the faraday, R the gas constant, and T the absolute temperature. By substitution of the equilibrium constant for the second dissociation of phosphoric acid in eq 1, we obtain an equation for the activity-coefficient term, designated $\log f_r$,

$$\log f_r \equiv \log \frac{f_{H_2PO_4} f_X}{f_{HPO_4}} = pK - \frac{(E-E^\circ)\mathbf{F}}{2.3026RT} - \log m_X$$
$$-\log \frac{m_{H_2PO_4}}{m_{HPO_4}}, \tag{2}$$

where pK is the common logarithm of the reciprocal of K, the second dissociation constant [1, 7]. In all of the phosphate buffers to be discussed, the last term of eq 2 is zero.

1. Experimental Procedures

Preparation of the equimolal mixture of solid potassium dihydrogen phosphate and disodium hydrogen phosphate was described by Bates and Acree [1]. Sodium bromide was recrystallized three times from water and was dried at 200° to 300° C. The dry product was found to be neutral. Sodium iodide was recrystallized twice from water and dried in vacuum at 50° C for 1 to 2 days. Filters of sintered glass were used in each instance for separating the crystals from the saturated solution.

Silver-silver bromide electrodes were made as described by Keston [8]. However, the paste of silver oxide and silver bromate was decomposed at 550° C instead of at 650° C. Silver bromate was prepared from sodium bromate and silver nitrate. It was recrystallized from hot water. Silver-silver iodide electrodes were formed on platinum spirals by thermal decomposition, at 450° C, of a paste composed of 90 percent of silver oxide and 10 percent of silver iodide by weight [9]. Silver iodide, prepared from silver nitrate and recrystallized potassium iodide, was washed 40 times with water and digested at 70° C under water for 2 days. Hydrogen electrodes were made by deposition of platinum black on platinum foils sealed in glass. A 3-percent solution of chloroplatinic acid that contained a small amount of lead acetate was used, and the electrolysis was continued for 3 minutes at a current of 250 to 300 ma. Electrodes were always used in pairs and were freshly made for each cell.

The solutions were prepared by weight methods, and nitrogen was passed through them to remove air. Details of the cells and of a part of the equipment are given in an earlier publication [7]. Some of the temperature measurements were made with a platinum resistance thermometer and the rest with a calibrated mercury thermometer. The temperature was regulated within ±0.03 deg C.

The titration cell already described [10] was used for a part of the measurements made with hydrogen and silver-silver bromide electrodes. For this purpose, "semimicro" silver-silver bromide electrodes were prepared. The mixture of silver and silver bromide on each electrode weighed 15 to 20 mg. The cell was immersed in the constant-temperature bath and a known

amount of buffer-bromide mixture added. When the emf had become constant, usually in about 2 hours, a measured portion of air-free water was introduced from the burette. Occasionally a second dilution was made. The emf data for the seven solutions prepared by dilution within the cell are not considered to be as accurate as the rest. These measurements are therefore marked for identification in the table of results given in the next section.

The measuring equipment was checked in two ways. The potentiometer was connected with another similar instrument in the same laboratory, and the emf of a cell was occasionally measured by both instruments. The two values always agreed within 0.02 mv. The potentiometers and standard cells had been calibrated by this Bureau. The second method offered a comparison of the silver-silver chloride electrodes with those of Harned and Ehlers [11], for which the standard potential of this electrode was derived. It furnished, as well, an additional check upon the temperature control and on the accuracy of the potentiometer. The emf of three hydrogen-silver chloride cells that contained $0.09931m$ of hydrochloric acid was measured and found to be 0.35272 ± 0.00002 v at $25°$ C. This value is identical with that obtained by interpolation in the data of Harned and Ehlers.

2. Results and Calculations

The experimental data are summarized in tables 1 and 2. Values of $-\log (f_H f_X m_H)$, where X represents either bromide or iodide, are given in the last columns. They were calculated from the emf by eq 1.

The standard potential, $E°$, of the hydrogen-silver bromide cell was taken to be 0.07128 v at $25°$ C [12]. For the hydrogen-silver iodide cell, the emf data of table 2, together with $pK = 7.198$ [1, 7], yield, by the method of Owen [13], -0.15201 v for $E°$. This potential was used in the subsequent computations. Owen [13] found -0.15225 for the same cell with silver-silver iodide electrodes formed by the thermal decomposition of a mixture of silver oxide and silver iodate. Gould and Vosburgh [14], however, obtained -0.1519. Their electrodes were of the same type as those used in this investigation.

Values of $-\log (f_H f_X m_H)$ for solutions that contained sodium bromide and sodium iodide at a

TABLE 1. *Emf of the cell*, Pt; H_2 (1 atm), KH_2PO_4 (xm_1), Na_2HPO_4 (xm_1), NaBr (xm_2), AgBr (s); Ag, at $25°$ C; *values of* $-\log (f_H f_{Br} m_H)$

x	E_{25}	$-\log (f_H f_{Br} m_H)$
SERIES A: $m_1 = m_2 = 0.05$		
	Volt	
1	0.55418	6.864
0.9438	.55601	6.870
0.5666	.57237	6.924
0.4172 [a]	.58211	6.957
0.3800	.58487	6.963
0.1882	.60625	7.019
SERIES B: $m_1 = 2m_2 = 0.05$		
1	[b] 0.57322	6.885
0.8486	.57815	6.897
0.6544	.58666	6.928
0.5218 [a]	.59343	6.945
0.4984 [a]	.59523	6.955
0.3506	.60570	6.979
0.2468 [a]	.61647	7.009
SERIES C: $m_1 = 5m_2 = 0.05$		
1	[c] 0.59731	6.895
0.8070	.60417	6.918
0.6600 [a]	.61051	6.937
0.5240	.61754	6.956
0.4922 [a]	.61966	6.965
0.4316 [a]	.62338	6.971

[a] Dilution made in a titration cell.
[b] Average of two cells. Mean deviation, 0.09 mv.
[c] Average of three cells. Mean deviation, 0.04 mv.

TABLE 2. *Emf of the cell*, Pt; H_2 (1 atm), KH_2PO_4 (xm_1), Na_2HPO_4 (xm_1), NaI (xm_2), AgI (s); Ag, at $25°$ C; *values of* $-\log (f_H f_I m_H)$

x	E_{25}	$-\log (f_H f_I m_H)$
SERIES D: $m_1 = m_2 = 0.05$		
	Volt	
1	[a] 0.33036	6.856
0.5616	[a] .34898	6.920
0.3228	[a] .36620	6.971
0.1606	[a] .38753	7.028
SERIES E: $m_1 = 2m_2 = 0.05$		
1	0.34925	6.874
0.4594	.37387	6.952
0.3314	.38402	6.982
SERIES F: $m_1 = 5m_2 = 0.05$		
1	0.37355	6.887
0.6462	.38749	6.933
0.4090	.40183	6.977
0.3006	.41116	7.001

[a] Average emf of two cells. The differences between duplicate cells made from these four solutions were 0.07, 0.17, 0.07, and 0.04 mv.

molality equal to that of each phosphate salt are compared with similar data for phosphate-chloride mixtures [1] in figure 1. When the three curves, plotted from measurements at sufficiently high concentrations that the buffer ratio was always unity, are extended to zero ionic strength, they meet at 7.198, the value of pK at 25° C. The separation of these three curves at a given ionic strength decreases as the ratio of halide to phosphate decreases, but the curves fail to meet, if the ionic strength exceeds 0.05, even at zero concentration of halide.
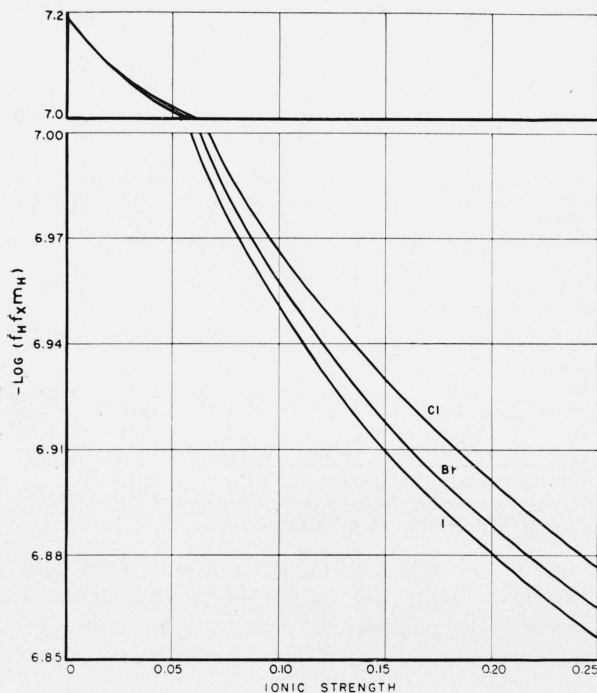

FIGURE 1. *Values of* $-log\ (f_H f_X m_H)$ *in equimolal phosphate buffers containing sodium halide* (NaX) *at a molality equal to that of each phosphate, plotted as a function of ionic strength.*

The activity-coefficient term, $\log\ (f_{H_2PO_4}f_X/f_{HPO_4})$, was computed by eq 2. The values obtained in this manner for each ratio of bromide and iodide to phosphate were smoothed with the aid of plots of P, defined by

$$P \equiv \log f_r - 1.017\sqrt{\mu}/(1+1.31\sqrt{\mu}), \qquad (3)$$

as a function of ionic strength, μ. These lines were drawn to the origin, inasmuch as P is zero at infinite dilution. Their curvatures were small. The average deviation, Δ, of the "observed" log f_r from the smooth curve is given in the next to

the last column of table 3. These deviations, expressed in millivolts, are designated Δ' and are listed in the last column. The value of log f_r in phosphate buffer solutions with varying amounts of sodium chloride, sodium bromide, or sodium iodide, and in buffer solutions without halide (log $f_r°$), is given in table 4. Log f_r in mixtures

TABLE 3. *Smoothing of log* f_r

Series	m_X/μ	Number of solutions	Δ	Δ'
PHOSPHATE-BROMIDE MIXTURES				
				mv
A	0.2	6	0.0009	0.05
B	.11	7	.0026	.15
C	.048	6	.0014	.08
PHOSPHATE-IODIDE MIXTURES				
D	0.2	4	0.0006	0.04
E	.11	3	.0002	.01
F	.048	4	.0014	08

TABLE 4. *Log* f_r, *log* $f_r°$, *and* $-log\ (f_H f_X m_H)°$ *for phosphate buffer solutions*

Ionic strength	log f_r when m_{NaX}/μ is—			log $f_r°$	$-\log (f_H f_X m_H)°$
	0.2	0.11	0.048		
X=Cl					
0.01				0.089	7.109
.05	0.1770	0.1760	ª0.1749	.1748	7.023
.07	.2018	.2004	.1989	.1983	7.000
.1	.2310	.2290	.2268	.2263	6.972
.15	.2679	.2649	.2616	.2610	6.937
.20	.2968	.2926	.2884	.2870	6.911
.25	.3209	.3156	.3103	.3084	6.890
X=Br					
0.01				0.090	7.108
.05	0.1818	0.1802	0.1782	.1772	7.021
.07	.2080	.2058	.2035	.2020	6.996
.1	.2391	.2360	.2330	.2310	6.967
.15	.2786	.2739	.2699	.2672	6.931
.20	.3091	.3032	.2986	.2952	6.903
.25	.3340	.3270	.3220	.3183	6.880
X=I					
0.01				0.091	7.107
.05	0.1859	0.1836	0.1808	.1790	7.019
.07	.2132	.2105	.2067	.2048	6.993
.1	.2453	.2421	.2372	.2350	6.963
.15	.2857	.2817	.2759	.2730	6.925
.20	.3170	.3116	.3058	.3028	6.895
.25	.3425	.3357	.3306	.3267	6.871

ª Values of log f_r in the phosphate-chloride mixtures are given for $m_{NaCl}/\mu =$ 0.03 instead of 0.048.

that contained bromide or iodide was read from the smoothed curves and for chloride-phosphate mixtures was taken from data given in the earlier paper [1]. The limiting values, $\log f_r^\circ$, were obtained from plots of $\log f_r$ with respect to m_X/μ, as shown in figure 2. Straight-line extrapolations were used.

The estimated accuracy of the emf of the bromide and iodide cells is about 0.10 mv. The combined errors in emf, in choice of the proper standard potentials for these types of electrodes, and in smoothing and extrapolating $\log f_r$ require that the limiting quantity, $\log f_r^\circ$, be assigned uncertainties of ± 0.002 for the chloride series and ± 0.003 for the bromide and iodide series.
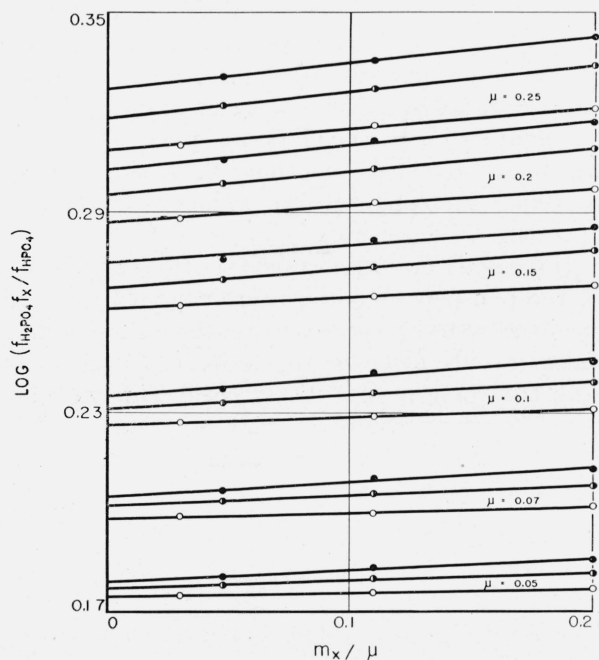
FIGURE 2. *Log* $(f_{H_2PO_4}f_X/f_{HPO_4})$ *plotted as a function of the fractional contribution of halide*, NaX, *to the total ionic strength.*

Lower curve of each group: X is Cl; middle curve: X is Br; upper curve: X is I

The last column of table 4 gives the limiting value of $-\log (f_H f_X m_H)$, when halide is absent, at each ionic strength. Inasmuch as the ratio of the molalities of the two phosphate anions remains unity, $-\log (f_H f_X m_H)^\circ$ is obtained simply by subtraction of $\log f_r^\circ$ from pK:

$$-\log (f_H f_X m_H)^\circ = pK - \log f_r^\circ \qquad (4)$$

Equation 4 is readily derived from the mass law and the definition of f_r (eq 2).

It is noteworthy that $-\log (f_H f_X m_H)^\circ$ decreases as X increases in atomic weight. This change is to be expected if the activity coefficients of the halogen acids at zero concentration in a phosphate solution are in the same order as the mean activity coefficients of the sodium and potassium halides and the halogen acids in their pure aqueous solutions. For the same reason, $\log f_r^\circ$ increases from chloride to iodide. The employment of these activity coefficients in the estimation of the paH of phosphate buffer solutions will be considered in the next section.

III. pH of Phosphate Buffer Solutions

Bates and Acree [1] found that the change of $\log f_r$ with ionic strength for each of the ratios of chloride to phosphate could be represented satisfactorily by an equation of the Hückel [15] type with two adjustable parameters, a^* and β^*. Log f_r° at 25° C can be expressed by the equation,

$$\log f_r^\circ = \frac{1.017 \sqrt{\mu}}{1 + 0.3281\, a^\circ \sqrt{\mu}} + \beta^\circ \mu. \qquad (5)$$

The values of a° and β° for the chloride, bromide, and iodide series were determined by fitting $\log f_r^\circ$, given in table 4, to eq 5. The parameters, obtained by least-square methods, are listed in table 5. The average difference, Δ, between the "observed" $\log f_r^\circ$ and that calculated by eq 5 is given in the last column.

TABLE 5. *Parameters of eq 5 for* $\log\ (f_{H_2PO_4}f_X/f_{HPO_4})$ *in phosphate buffers without halide*

	a°	β°	Δ
Cl	4.4	0.054	0.0002
Br	4.2	.069	.0000
I	4.0	.079	.0003

Up to this point, the treatment has remained thermodynamically rigorous. However, an evaluation of paH, or $-\log f_H m_H$, will involve an assumption that is partly arbitrary, as indicated earlier in this paper. The formal mass-law expression for the paH of a phosphate buffer solution, with substitution of the Hückel equation

for the activity coefficients of the two phosphate anions at 25° C, can be written as follows,

$$paH = pK - \log \frac{m_{H_2PO_4}}{m_{HPO_4}} - \frac{1.5255\sqrt{\mu}}{1+0.3281a\sqrt{\mu}} - \beta\mu. \quad (6)$$

Bates and Acree assumed that $a°$ and $\beta°$, the parameters of eq 5 for phosphate buffers without added chloride, could be identified with a and β of eq 6, for the same buffer solutions.[3] The validity of this assumption is not subject to experimental proof, but a partial test can be obtained through a comparison of the paH derived in this manner from emf measurements made with the three different halide electrodes. The results of these calculations are given in the first half of table 6. At 0.25, the highest ionic strength studied, the paH values derived from measurements of the chloride and iodide cells differ by 0.025 unit.

It is evident from a comparison of paH with $-\log (f_H f_X m_H)°$ given in table 4 that the normal

TABLE 6. paH *of phosphate buffer mixtures:* $KH_2PO_4(m_1)$, $Na_2HPO_4(m_1)$, $NaX(m_2=0)$, *from the emf of cells without liquid junction at 25° C*

m_1	Ionic strength	paH when X is—		
		Chloride	Bromide	Iodide
Equation 6				
0.0025	0.01	7.065	7.063	7.062
.005	.02	7.017	7.016	7.014
.01	.04	6.959	6.956	6.953
.0125	.05	6.937	6.934	6.931
.025	.10	6.862	6.855	6.849
.0375	.15	6.811	6.803	6.794
.05	.20	6.773	6.762	6.752
.0625	.25	6.742	6.729	6.717
Equation 7				
.0025	0.01	7.066	7.065	-----
.005	.02	7.019	7.020	-----
.01	.04	6.962	-----	-----
.0125	.05	6.942	6.944	-----
.025	.10	6.873	6.873	6.876
.0375	.15	6.830	6.829	6.834
.05	.20	6.796	6.796	6.802
.0625	.25	6.774	6.774	6.781

[3] The last two terms of eq 6 represent $-\log (f_{H_2PO_4}/f_{HPO_4})°$. It is evident by comparison with eq 5 that this method of evaluating paH sets $\log f_X°$ equal to $-0.5085\sqrt{\mu}/(1+0.3281a°\sqrt{\mu})$, without a term linear in ionic strength.

decrease of the latter quantity with increasing atomic weight of the halogen has not been compensated; indeed paH shows a slightly larger decrease than does $-\log (f_H f_X m_H)°$ at the same ionic strength. A part of the difficulty is associated with the two-parameter form of eq 5. If a small systematic change, within experimental error, were made in $\log f_r°$, significant changes in $a°$ and $\beta°$ of a compensatory nature might be necessary to afford the best fit of the data to eq 5. For example, $a°=4.0$ and $\beta°=0.079$ reproduce $\log f_r°$ for the iodide series with a mean deviation of 0.0003. Yet the deviation would be only 0.0008, or still considerably less than the uncertainty assigned to $\log f_r°$, if 4.4 and 0.135 were chosen as the correct set of parameters. If the latter values gave the best fit, however, the paH computed from the iodide series would be 0.006 unit higher at an ionic strength of 0.25. In other words, these changes in the two parameters do not offset one another in the calculation of paH. Measurements at ionic strengths above 0.25, which are of most use in fixing accurate values of the parameters, are lacking here.

If the activity-coefficients of the three halide ions in the phosphate solution were assumed to equal the mean activity coefficients of the corresponding halogen acids, after the suggestion of Guggenheim [16], and these mean activity coefficients were set equal to their values in pure solutions of HX [11, 17, 18] at the appropriate ionic strengths, paH could be evaluated:

$$paH = -\log (f_H f_X m_H)° + \log f_X° \equiv \\ -\log (f_H f_X m_H)° + \log f_{HCl} \quad (7)$$

The results of this calculation are given in the second half of table 6. The agreement among the three sets of values is improved, but the paH is higher than before. The activity coefficient of hydrochloric acid is lowered by potassium ions [19] and sodium ions [20]. Hence, paH computed in this manner is understandably too high.

The paH calculated from pK or from $-\log (f_H f_X m_H)°$ will approach $-\log \mathbf{a}_H$ in dilute solutions, where all reasonable assumptions relating the ionic activity coefficients yield substantially equivalent results. In the region of higher ionic strengths, the paH value must be considered a unit on an arbitrary scale.

IV. References

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