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CONSISTENCY OF pH STANDARD VALUES WITH THE CORRESPONDING THERMODYNAMIC ACID DISSOCIATION CONSTANTS

(Technical Report)

Prepared for publication by

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Consistency of pH standard values with the corresponding thermodynamic acid dissociation constants (Technical Report)

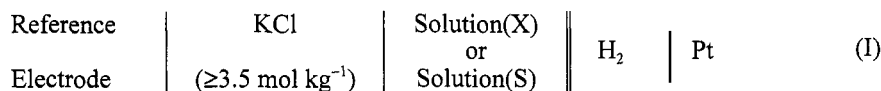
Abstract: With the simplest possible assumptions on the ion activity coefficients, namely a Debye-Hückel approach, pH values of eleven standard buffer solutions have been calculated from the corresponding thermodynamic acidity constants, $K_{(I \rightarrow 0)}$, and compared to the electrometrically assigned pH(S) values (by Harned cell method). Agreement is within ± 0.01 in the temperature range 10–40°C for all standards, except carbonate. The results for the phthalate, acetate, phosphate and carbonate systems at 25°C indicate that this consistency is improved if specific ion interactions are taken into account, according to the Pitzer theory.

INTRODUCTION

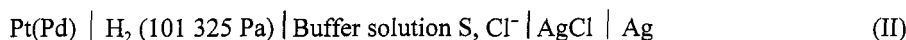
It is universally accepted [1] that pH of an unknown solution X, pH(X), is defined in relative terms through the OPERATIONAL DEFINITION derived from the Nernst equation

$$\text{pH(X)} - \text{pH(S)} = [E(\text{S}) - E(\text{X})]F / (RT \ln 10) \quad (1)$$

in which comparison is made with a reference solution S of assigned pH(S). $E(\text{S})$ and $E(\text{X})$ are emf values [2] of the OPERATIONAL CELL



when the hydrogen gas electrode, or its substitute, is transferred from solution X, $E(\text{X})$, to solution S, $E(\text{S})$, each of them establishing a liquid-junction with the electrolyte of the reference half-cell. pH(S) values are CONVENTIONALLY ASSIGNED through a methodology [3] based on the emf of Harned type cells [4] without liquid-junction. These values are evaluated for standard buffer solutions (of ionic strength, I , not exceeding 0.1 mol kg⁻¹, to which Cl⁻ has been added in various concentrations) by measuring emf values of the cell:



$$E = E^0 - (RT \ln 10 / F) \lg [m_{\text{H}} m_{\text{Cl}} \gamma_{\text{H}} \gamma_{\text{Cl}} / (m^0)^2] \quad (2)$$

where $m^0 = 1 \text{ mol kg}^{-1}$ represents the standard state condition.

$$\text{p}(a_{\text{H}} \gamma_{\text{Cl}}) \equiv -\lg (m_{\text{H}} \gamma_{\text{H}} \gamma_{\text{Cl}} / m^0) = (E - E^0) F / (RT \ln 10) + \lg (m_{\text{Cl}} / m^0) \quad (3)$$

A quantity, $\text{p}(a_{\text{H}} \gamma_{\text{Cl}})$, is expressed in terms of known and experimentally determined quantities, m_{Cl} , E and E^0 . E^0 is derived from the emf, E , of the cell



and calculated from eq. 2, with $\gamma_{\text{H}} \gamma_{\text{Cl}} = \gamma_{\pm}^2$ where γ_{\pm} is the mean ionic activity coefficient of HCl in 0.01 mol kg⁻¹ solution [3].

Extrapolation of $\text{p}(a_{\text{H}} \gamma_{\text{Cl}})$ values to $m_{\text{Cl}} = 0$, with the use of equation (3) [5], leads to $\text{p}(a_{\text{H}} \gamma_{\text{Cl}})^0$ from which $\text{p}a_{\text{H}}$ can be calculated

$$\text{p}a_{\text{H}} = \text{p}(a_{\text{H}} \gamma_{\text{Cl}})^0 + \lg \gamma_{\text{Cl}} \quad (4)$$

$\lg \gamma_{\text{Cl}}$ is approximated by the Debye-Hückel model

$$\lg \gamma_i = - \frac{Az_i^2 (I / \text{mol kg}^{-1})^{1/2}}{1 + Ba (I / \text{mol kg}^{-1})^{1/2}} \quad (5)$$

in which the Bates-Guggenheim convention for the ion size parameter [2] has been introduced, $Ba = 1.5$. A is the Debye-Hückel limiting slope and z_i is the ion electric charge

$$\lg \gamma_{\text{Cl}} = - \frac{A (I / \text{mol kg}^{-1})^{1/2}}{1 + 1.5 (I / \text{mol kg}^{-1})^{1/2}} \quad (6)$$

The $p a_{\text{H}}$ values thus obtained are conventionally adopted as reference values

$$p a_{\text{H}} = \text{pH(S)} \quad (7)$$

All measured pH(X) values depend on the material chosen for reference solution [6,7], as a result of

- (i) the validity of the Bates-Guggenheim convention for each standard solution
- (ii) different contribution of liquid junction potential for each standard solution, as a result of different composition and ionic mobility.

Definition	$\text{pH} = -\lg a_{\text{H}}$
Standard electrode potential	E^0 / V
Cell for determination of standard potential and equation describing its emf	Pt H ₂ HCl (0.01 mol kg ⁻¹) AgCl Ag $E = E^0 - (RT \ln 10 / F) \lg (m_{\text{H}} m_{\text{Cl}} \gamma_{\text{H}} \gamma_{\text{Cl}})$
Harned cell for assignment of pH(S) values and equation describing pH(S)	Pt H ₂ S, Cl ⁻ AgCl Ag $\text{pH(S)} = -\lg(a_{\text{H}} \gamma_{\text{Cl}})^0 + \lg \gamma_{\text{Cl}}$
Operational cell for measurement of pH(X) from pH(S) and equation describing pH(X)	Ref. Electrode KCl ($\geq 3.5 \text{ mol kg}^{-1}$) X or S H ₂ Pt $\text{pH(X)} = \text{pH(S)} + (E_{\text{S}} - E_{\text{X}}) F / RT \ln 10$

Fig. 1. Conventionally procedures for the assignment of standard pH(S) values to standard buffers (RVS, PS and S) and measurement of pH(X) of solution under test.

Figure 1 summarises the conventional procedures for estimating the thermodynamically unattainable quantity pH. Outstanding research problems are

- (i) Evaluation or correction of the residual liquid junction contribution included in the $E(\text{S}) - E(\text{X})$ term, so that pH(X) values are calculated independently of liquid junction potentials.
- (ii) Validity of the conventional assignment of pH(S) values and consistency with pH(S) values evaluated through other models of electrolyte solutions in order to recommend a broader and more realistic basis.

pH(S) values are conventionally assigned to chosen reference buffer solutions which are variously referred to as RVS (potassium hydrogen phthalate), PS (NBS/NIST reference buffers $2 < \text{pH} < 10$) and S (other recommended buffer standards) [1].

An alternative method of assignment of pH to reference buffers, has been proposed based on the thermodynamic ($I = 0$) acid dissociation constants of the weak acids involved. With the use of computational techniques, the method has initially been developed for triacids, H₃A [8], and is redrawn (Fig.2) for diacids, H₂A.

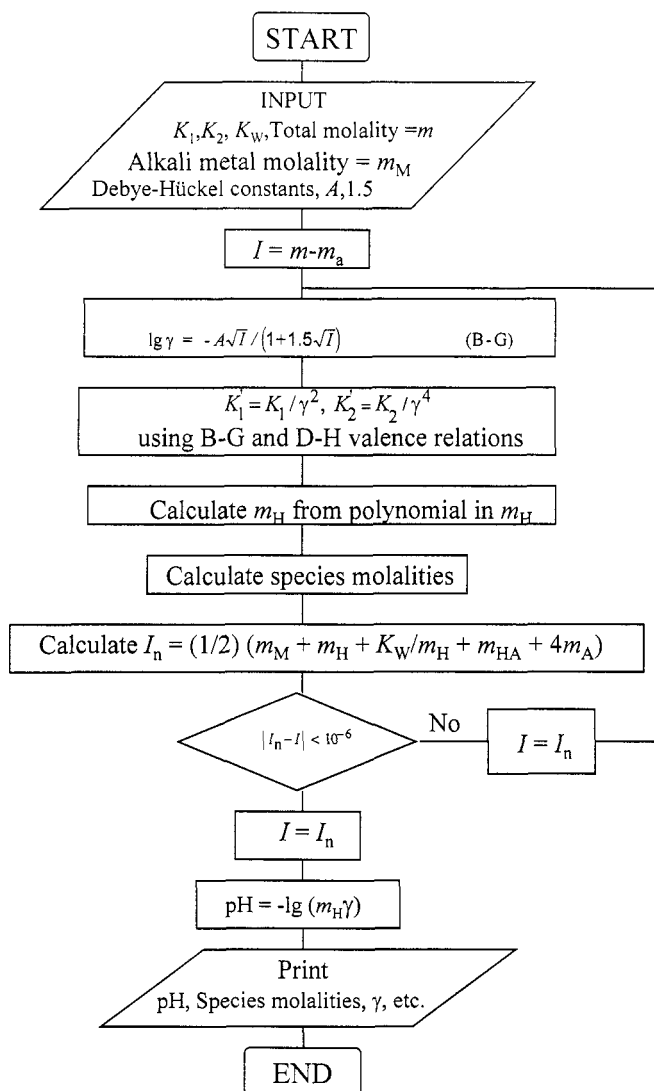


Fig. 2. Flow chart for iterative computer program based on the Debye-Hückel model

METHODOLOGY

Expressing the thermodynamic acid dissociation constants, K_1 and K_2 in terms of the stoichiometric equilibrium constants, K_1' and K_2' , assuming the activity coefficient $\gamma_{\text{H}_2\text{A}} = 1$ and designating the activity coefficients of singly and doubly charged species by γ_1 and γ_2 , gives

$$K_1 = \frac{a_{\text{HA}} a_{\text{H}}}{a_{\text{H}_2\text{A}}} = \frac{m_{\text{HA}} m_{\text{H}}}{m_{\text{H}_2\text{A}}} \frac{\gamma_{\text{HA}} \gamma_{\text{H}}}{\gamma_{\text{H}_2\text{A}}} = K_1' \gamma_1^2 \quad (8)$$

$$K_2 = \frac{a_{\text{A}} a_{\text{H}}}{a_{\text{HA}}} = \frac{m_{\text{A}} m_{\text{H}}}{m_{\text{HA}}} \frac{\gamma_{\text{A}} \gamma_{\text{H}}}{\gamma_{\text{HA}}} = K_2' \gamma_2 \quad (9)$$

All concentrations may be evaluated by combining equilibrium, mass balance and electroneutrality equations

$$m = m_{\text{H}_2\text{A}} + m_{\text{HA}} + m_{\text{A}} \quad (10)$$

$$m_{\text{H}} + m_{\text{M}} = m_{\text{OH}} + m_{\text{HA}} + 2m_{\text{A}} \quad (11)$$

where a , m and γ represent the activity, molality and activity coefficient, respectively, of the species

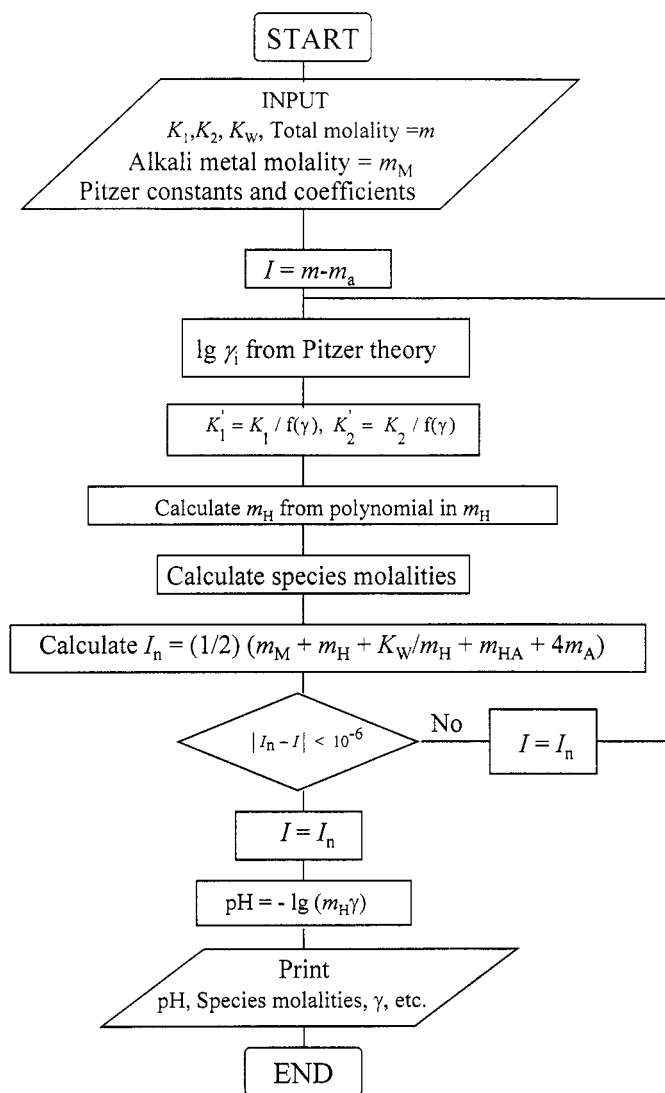


Fig. 3. Flow chart for iterative computer program based on the Pitzer model.

indicated as subscripts; ionic charges have been omitted for simplicity, m is the total molality of acid and salt in the buffer mixture and m_M is the alkali metal molality relevant for the buffer system under consideration.

From equations (8–11), one obtains

$$m_H^3 + m_H^2 (m_M + K_1') + m_H (m_M K_1' + K_1' K_2' - m K_1' - K_w) + m_M K_1' K_2' - 2m K_1' K_2' - K_1' K_w = 0 \quad (12)$$

where the term $K_w K_1' K_2'$, where K_w is the ionic product of water, has been neglected.

The activity coefficients are calculated separately, assuming that

$$\gamma_1 = \gamma_{Cl} = \gamma \quad (13)$$

$$\gamma_2 = \gamma^4 \quad (14)$$

whose calculation requires the knowledge of the ionic strength I .

Starting with a reasonably estimated value of $I / \text{mol kg}^{-1}$ ($I = m - m_a$, where m_a is the analytical molality of the acid in the buffer mixture) one can iterate all the parameters until agreement to within 10^{-6} is reached. The Bates-Guggenheim convention is adopted for γ_{Cl} , $Ba = 1.5$, but calculations were also

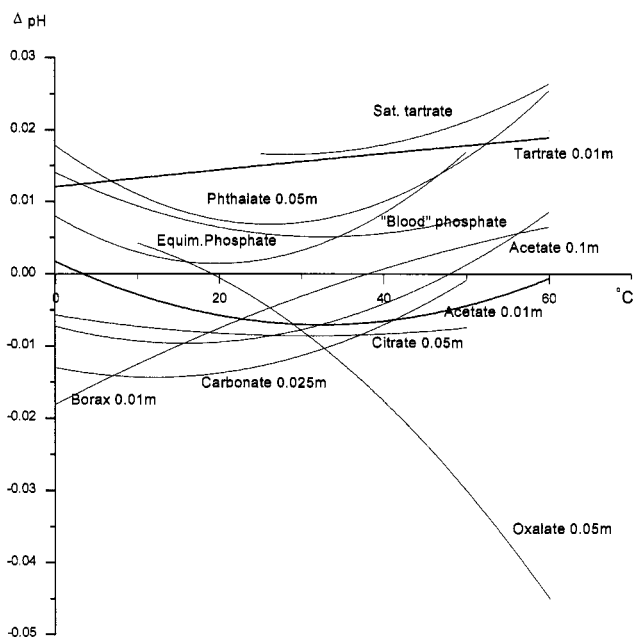


Fig.4. Differences between pH(S) values and those calculated as a function of temperature.
 $\Delta\text{pH} = \text{pH}(\text{calc}) - \text{pH}(\text{S})$

performed with $Ba = 1.0$ and 2.0 . Moreover, the species distribution fractions, α_i , buffer capacities, β , species activity coefficients, γ_i , ionic strength, I and pH values are given. The iterative computer program was developed on the basis of the flow chart shown in Fig. 2.

The activity coefficients, γ_i , may also be calculated by means of the Pitzer theory [9] in which specific ion interactions are taken into account. Determination of γ_i values by following a similar methodology, enables one to evaluate pH and related quantities, as shown in Fig. 3.

RESULTS

Table 2 shows the differences between pH values calculated from K_1 , K_2 , K_3 , by using Debye-Hückel equation ($Ba = 1.0$; 1.5 ; 2.0) or from Pitzer theory at 25°C and those conventionally assigned at 0 , 25 and 50°C .

Figure 4 shows differences between the pH(calc) and pH(S) values when the Bates-Guggenheim convention is adopted. For all standard buffers studied [10–18], except carbonate and tartrate, the consistency between pH(S) and pH(calc) is satisfactory, i.e. it equals to ± 0.01 in the temperature range 10 – 40°C . For the tartrate buffer much closer agreement can be reached if different literature values [19] of acidity constants are used. This may bring questions about the correctness of the reported values [18] which have been, nevertheless, selected for the consistency of data source. At lower and higher temperatures results may indicate incorrect pH(S) or pK values.

With the use of literature data of Pitzer parameters [9, 20], for the standard pH buffers [21], the evaluation of pH for the acetate buffers as well as for the equimolar phosphate buffer, the blood phosphate buffer and the carbonate buffer at 25°C was possible [20]. Recently published value for the potassium hydrogen phthalate buffer [22] is also included in the calculation of the differences relative to conventionally assigned pH values, presented in Table 2.

DISCUSSION AND CONCLUSIONS

If the Bates-Guggenheim convention is used for calculating the ionic activity coefficients for the standard buffer solutions studied, then differences between the assigned pH values and those calculated here are smaller than 0.01 , in the temperature range 10 – 40°C , except carbonate and tartrate. With the individual species activity coefficients evaluated by means of the Pitzer theory, the pH (calc. Pitzer) equals pH(S) for the phosphate and 0.01m acetate systems. This difference is larger for the carbonate buffer and equals to -0.016 but this is reduced to -0.008 when the calculations were repeated with the pK_1 and pK_2 values of

TABLE 1 Conventionally assigned pH(S) values for standard buffer solutions (S, PS), and RVS) of well defined compositions at various temperatures. The symbol m is used to denote mol kg⁻¹

T °C	S	PS	S	PS	RVS	PS	S	PS	S	PS	PS	PS	PS
	KH ₃ C ₄ O ₈ 0.05m	KHtart sat 25°C	KHtart 0.01m	KH ₂ cit 0.05m	KHphht 0.05m		CH ₃ COONa 0.1m + CH ₃ COONa 0.1m		CH ₃ COOH 0.01m + CH ₃ COONa 0.01m		KH ₂ PO ₄ 0.025m + Na ₂ HPO ₄ 0.025m		NaHCO ₃ 0.025m + Na ₂ CO ₃ 0.025m
0			3.711	3.863	4.000		4.683		4.737		6.984		10.317
5			3.691	3.840	3.998		4.673		4.730		6.954		10.245
10	1.670		3.672	3.820	3.997		4.665		4.725		6.923		10.179
15	1.672		3.656	3.802	3.998		4.656		4.722		6.900		10.118
20	1.675		3.647	3.788	4.001		4.656		4.720		6.881		10.062
25	1.679	3.557	3.637	3.773	4.005		4.654		4.720		6.865		10.012
30	1.683	3.552	3.633	3.766	4.001		4.654		4.722		6.853		9.966
35		3.549	3.630	3.759	4.018						6.844		9.926
37	1.691	3.548		3.756	4.022						6.841		9.910
40	1.694	3.547	3.630	3.754	4.027		4.660		4.730		6.838		9.989
50	1.707	3.549	3.640	3.749	4.050		4.675		4.745		6.833		9.828
60	1.723	3.560	3.654		4.080		4.684		4.768		6.836		
70	1.743	3.580			4.116						6.845		
80	1.766	3.610			4.159						6.859		
90	2.44	3.650			4.21						6.876		
95	2.49	3.674			4.24						6.886		

TABLE 2 Differences (ΔpH) = $\text{pH}(\text{calc}) - \text{pH}(\text{S})$ between pH values calculated from known acid dissociation, K_1 , K_2 , K_3 , (*) by using Debye-Hückel equation (Ba) and those conventionally assigned at 0, 25 and 50°C, or by Pitzer theory, at 25°C.

SOLUTION (*)	0°C			25°C				50°C		
	$Ba=1.0$	$Ba=1.5$	$Ba=2.0$	$Ba=1.0$	$Ba=1.5$	$Ba=2.0$	Pitzer	$Ba=1.0$	$Ba=1.5$	$Ba=2.0$
$\text{KH}_3\text{C}_4\text{O}_8$ 0.05m				-0.002	-0.004	-0.005		-0.028	-0.030	-0.032
KHtart sat 25°C				0.000	0.013	0.024		0.008	0.021	0.033
KHtart 0.01m	0.008	0.012	0.016	0.012	0.016	0.020		0.012	0.016	0.020
KH2cit 0.05m	-0.023	-0.006	0.008	-0.025	-0.008	0.007		-0.025	-0.007	0.008
KHph 0.05m	0.003	0.018	0.031	-0.009	0.007	0.021	-0.002	0.000	0.017	0.031
CH_3COOH 0.1m + CH_3COONa 0.1m	-0.020	-0.008	0.003	-0.021	-0.008	0.003	-0.001	-0.016	-0.003	0.009
CH_3COOH 0.01m + CH_3COONa 0.01m	0.001	0.003	0.004	-0.009	-0.007	-0.005	0.000	-0.005	-0.003	-0.001
KH_2PO_4 0.025m + Na_2HPO_4 0.025m	-0.024	0.014	0.044	-0.035	0.004	0.036	0.000	-0.034	0.007	0.041
KH_2PO_4 0.008695m Na_2HPO_4 0.03043m	-0.031	0.007	0.038	-0.039	0.000	0.032	0.000	-0.024	0.017	0.051
$\text{Na}_2\text{B}_4\text{O}_7$ 0.01m	-0.023	-0.020	-0.017	-0.008	-0.004	-0.001		-0.002	0.001	0.005
NaHCO_3 0.025m + Na_2CO_3 0.025m	-0.051	-0.013	0.017	-0.053	-0.014	0.018	-0.016 -0.008	-0.042	-0.001	0.032

carbonic acid as redetermined by Peiper and Pitzer [23]. This shows that there is a good consistency of the pH reference values with the corresponding thermodynamic acid dissociation constants, when either the Bates-Guggenheim convention or the Pitzer equations are used for evaluation of the activity coefficients, provided that the ionic strength of these solutions is not higher than 0.1 mol kg⁻¹.

The adoption of the Pitzer approach leads to the assignment of pH values to reference buffers in a wide range of ionic strengths. This assignment is based on a sound scientific model which takes into account specific interactions of ions. The presented methodology is universal; it overcomes the limitations of Bates-Guggenheim convention.

Unfortunately, data for other systems are insufficiently extensive to allow the calculation of the required Pitzer coefficients.

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