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pH, Definition and Measurement at High Temperatures*

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ABSTRACT

The acidity of aqueous solutions is of great importance because of the prominent role the hydrogen ion plays in chemical equilibria, in many industrial processes, and in biochemical, geochemical, and basic solution chemical applications. The NBS standardized definition of pH in terms of -log a_H with an arbitrary definition of ion activity, has led to much confusion and ambiguity in the measurement of acidity. For many years, physical chemists have recognized and dealt with this problem, but still some continue the use of unnecessarily ambiguous assumptions. Several methods for defining pH are discussed and strong arguments are given for the use of a concentration or molality scale, especially for measurements in concentrated brines. Applications of hydrogen electrode concentration cells will be emphasized, and data available for calibrations for cells at high temperatures are given. Also, problems originating from the association of electrolytes near the critical conditions on the choice of standards for electrochemical measurements are discussed.

1. INTRODUCTION

As a measure of the acidity of aqueous media, pH, especially from measurements using the glass electrode, has been widely used since the 1920's in many scientific, industrial, medical, and geological applications at ambient conditions. The involvement of hydrogen ions is pervasive in reactions in aqueous media because of their availability from the self-ionization of the solvent, as well as the many other sources of acidity that can be introduced. Most of the ions of the elements of the periodic table undergo reactions with the solvent, hydrolysis, to produce hydroxy complexes; as the acidity decreases, ultimately solid hydroxides or basic precipitates are formed.(1-3)

Much has been written(4) about the conventions in the measurement of pH, the features of the glass electrode, and its use. The book by Bates(4) is the most recent major work on this subject, and it gives a thorough discussion of modern thought about the issues. Recently Midgley(5) has reviewed attempts to measure pH at high temperatures. Unfortunately, the nature of the response of the glass electrode and the need for calibration has led to the definition of arbitrary scales to represent acidity or "pH". It is important to distinguish those uses of electrodes for which precisely correct thermodynamic quantities are essential and those for which arbitrariness is no liability. There are many applications, especially industrial ones, that require a precisely reproducible measurement but do not demand a thermodynamically rigorous quantity, e.g., the use of glass electrodes to provide the end-point for a mixing process or as a measure for quality control of a product. There may, however, be relatively severe demands for precision in these measurements. The emphasis of this discussion is on those applications in basic studies requiring thermodynamic rigor with a minimum of assumptions such as is required for the derivation of equilibrium constants and the thermodynamic quantities for reactions.

2. THE NBS pH SCALE(4)

The operational NBS pH scale pH(S) is defined in the following way:

(1) The quantity $p(a_H\gamma_{Cl})$ is determined using the relationship

$$p(a_H\gamma_{Cl}) = (E-E^\circ)(F/\{RT \ln 10\}) + \log m_{Cl} \tag{1}$$

where $p(a_H\gamma_{Cl})$ is the negative logarithm of the product of the activity of the hydrogen ion and the activity coefficient of the Cl^- ion from measurements using $Pt,H_2 \mid solution \mid AgCl,Ag$ cells at several concentrations of chloride in a buffer mixture, and the value of $p(a_H\gamma_{Cl})^\circ$ is determined for zero chloride.

(2) pa_H is computed from $p(a_H\gamma_{Cl})^\circ$ where

$$pa_H = p(a_H\gamma_{Cl})^\circ + \log \gamma_{Cl} \tag{2}$$

using the Bates-Guggenheim convention for the activity coefficient of the chloride ion,

$$\log \gamma_{Cl} = -AI^{1/2}/(1+1.5I^{1/2}) \tag{3}$$

where A is the Debye-Huckel slope.

(3) pa_H values are then assigned to selected buffer mixtures in the range 2.5 to 11.5 that are chosen for reproducibility, stability, buffer capacity, and ease of preparation.

The two principal difficulties in setting up an arbitrary scale such as this are (1) the need for a definition of an individual ion activity coefficient and (2) the probable existence of a liquid junction that differs between the standardizing solution and the unknown solution. Both are extrathermodynamic considerations and must be addressed with some care.

3. LIQUID JUNCTION POTENTIALS

When two solutions of electrolytes are brought together, a potential is established due to the spontaneous tendency for the ions of the concentrated electrolyte to pass into the more dilute solution . The differing mobilities of the cations and anions leads to the liquid junction potential, E_J. Several models for estimating these potentials and their measurement have been made(1,4,6) and will be discussed briefly here. The following presents some estimates of the magnitude of these potentials under several circumstances in concentration cells.

The potential for the cell with liquid junction

$$\mathrm{Pt,H_2|Solution(1)||Solution(2)|RE} \tag{4}$$

is given by the following

$$E = E_{RE} + E_J - E_H \tag{5}$$

where the potentials refer to the reference electrode, the liquid junction, and the hydrogen electrode, respectively, (all written as reduction potentials), and therefore

$$E = -E_H^{\circ} - (RT/F)\ln(a_H/f_{H_2}^{1/2}) + E_J + E_{RE}. \tag{6}$$

The potential between the two solutions is given by(4,6)

$$E_J = -RT/F \int_1^2 \sum_i t_i \, d \ln m_i - RT/F \int_1^2 \sum_i t_i \, d \ln \gamma_i \qquad (7)$$

Here t_i is the number of moles of i transferred per faraday passed. In terms of equivalent conductance of the ion, λ_i,

$$t_i = z_i \lambda_i m_i / (|z_i| \Sigma |z_i| \lambda_i m_i) \qquad (8)$$

where the summation is over all ions in the solution. The Henderson equation for E_J assumes (1) λ_i is independent of solution composition and can therefore be represented by the infinite dilution values, (2) that the composition at any point across the junction can be represented as a mixture of the two solutions, and (3) that the activity coefficient term can be neglected in Eq. (7). E_J becomes

$$E_J = -\frac{RT}{F} \bullet \frac{\Sigma (z_i/|z_i|) \lambda_i \ (m_{2,i} - m_{1,i})}{\Sigma |z_i| \lambda_i \ (m_{2,i} - m_{1,i})} \ln \frac{\Sigma |z_i| \lambda_i \, m_{2,i}}{\Sigma |z_i| \lambda_i \, m_{1,i}} \qquad (9)$$

When a supporting electrolyte is present Eq. (9) reduces to

$$E_J = \Sigma D_i \ (m_{1,i} - m_{2,i}) . \qquad (10)$$

This equation contains a term for each in the two solutions, where

$$D_i = (RT/F) \ (z_i \lambda_i) / (|z_i| \Sigma |z_i| \lambda_i m_i) \qquad (11)$$

Values for the limiting equivalent conductances for a number of ions to 300°C have been given by Marshall and Quist.(7)

Bates used the Henderson equation to compute potentials for a number of liquid junctions, for example, when the one solution is either saturated KCl (4.16 M) or 0.1 M KCl and the temperature is 25°C.(4) The results in Table I demonstrate that KCl in no way eliminates liquid junction potentials, and the magnitudes of the potentials are large for HCl due to the high limiting equivalent conductance of the hydrogen ion compared to other cations.

Likewise, the potentials for NaOH solutions are high because of the high conductance of the hydroxide ion. At the bottom of the table, the potentials for junctions with 0.1 M KCl are also quite large for both strong acid and strong base.

Liquid junction potentials measured using a Ag/AgCl concentration cell by MacInnes and Yeh(8) are compared with calculated potentials based essentially on the Henderson equation for selected cases shown in Table II. The greatest values occur for junctions involving HCl, again, because of the high mobility of the hydrogen ion. These estimations involve the extrathermodynamic assumption that γ_{Cl} is the same in both solutions, an assumption which is questionable but is no doubt better at the low concentrations examined than at much higher concentrations. For perspective, we should keep in mind that 0.26 mV is equivalent to 1% change in activity at 25°C.

Results of measurements of pH by Bates et al.(9) with cells with liquid junction, pH(l.j.), and cells without liquid junction, pa_H, are compared in Figure 1. Measurements were made successively on 24 solutions containing strong and weak acids. In the cell with liquid junction, measurements were made against a 0.025 m standard phosphate buffer (pa_H = 6.855 at 25°C). The figure shows errors of 0.04 log units from this source that are especially large at pH values below 2 and above 11. The length of the lines on the plot represent the variation of ln γ_{Cl} with choice of the ion size term in Eq. (3) where a value of 1.5 is used. Likewise, the results of Tables I and II show that the liquid junction potentials introduced become rapidly unacceptable for high molalities of electrolytes even when saturated KCl is the bridge solution.

4. THE MOLALITY OR CONCENTRATION SCALE

The activity of an individual ion is an extrathermodynamic quantity requiring arbitrary assumptions, and its use can and should be avoided if possible. There is no compelling reason to define an acidity scale for physical chemical measurements based on a_H since chemical issues can always be addressed in terms of the neutral component quantity.

$$\gamma^{\nu}_{\pm(M_{\nu_M}X_{\nu_X})} = \gamma_M^{\nu_M}\,\gamma_X^{\nu_X} \tag{12}$$

Where $\gamma^{\nu}_{\pm(M_{\nu_M}X_{\nu_X})}$ represents the mean activity coefficient for the electrolyte $(M_{\nu_M}X_{\nu_X})$. Since mean coefficients are experimentally measurable and available for many single and mixed electrolyte systems, a molality (or concentration) scale is the appropriate ionic quantity to consider. The molality of hydrogen ions is obtained from the activity product, a_Ha_X, and $\gamma_{\pm(HX)}$ as given by

$$-\log m_H = -\log a_Ha_X + \log \gamma^2_{\pm(HX)} + \log m_X \,. \tag{13}$$

The activity product, a_Ha_X, is measurable from electrochemical cells without liquid junction, the molality of the anion X is known, and $\gamma_{\pm(HX)}$ can be computed from available literature data if the composition of the solution is known. This applies to pure acidic solutions as well as electrolyte mixtures containing HX for which interaction parameters are known. The exact approach used to obtain $\gamma_{\pm(MX)}$ is not important, as it can be computed from any one of the models for excess thermodynamics or from direct experimental data in the literature. Notice, this is just the reverse of the normal use of Harned cells (or other reversible cells) to obtain activity coefficients. In this case, the molality m_H is desired and the other quantities in Eq. (13) are known. In Eqs. (12) and (13) the mean activity is represented as $\gamma_{\pm(MX)}$, but often in the literature the ± subscript is omitted in representing these quantities.

a. Cells Without Liquid Junction

The activity product a_Ha_{Cl} is known from electrochemical measurements of Leitzke and his coworkers at high temperatures for a number of mixtures of electrolytes with chloride as the common anion. These results are summarized in Section 6. The availability of such information provides the basis for calibration of cells without liquid junction, such as glass or zirconia electrodes vs. Ag/AgCl for use in concentrated brines. Such a cell gives a_Ha_{Cl}, and if $\gamma_{\pm(HCl)}$ can be computed, i.e., all the parameters needed for use of the Pitzer ion interaction treatment(10,11) are available, then m_H can be determined. Knauss et al.(12) described a number of such cells with a similar goal involving a different assumption for γ_H.

The most commonly used cell without liquid junction is the following:

$$\mathrm{Pt, H_2|HCl\,(m_1), MCl\,(m_2),\ etc.\,|Ag,\ AgCl} \tag{14}$$

The cell potential is given by (in terms of reduction potentials)

$$E = E_{Ag,AgCl} - E_H \tag{15}$$

$$E = E^{\circ}_{Ag,AgCl} - RT/F \ln(a_Ha_{Cl}/f_{H_2}{}^{1/2}) \tag{16}$$

Because of the difficulty with the stability and behavior of reference electrodes at high temperatures, one is generally compelled to use a reference electrode located outside the cell, and different approaches have been used.(13,17) One approach(13) employs a wick of asbestos passing through a Teflon tube which is squeezed in a compression fitting to restrict the flow of solution from the cell to a reference cell held at ambient temperature and pressure (see Fig. 2a). Potentials due to the flowing solution and gradients in temperature and pressure are present but can be kept relatively constant. Another and better approach uses a pressurized reference cell (Fig. 2b) held at a lower temperature from the cell. Macdonald and his coworkers(15,17) have used this approach with the zirconia electrode in measurements related to steam generator chemistry issues. Although zirconia electrodes do not have the precision of hydrogen electrodes, their applicability in oxidizing systems and in plant facilities is advantageous. The properties and use of these electrodes(14,15-17) have been described previously, and we will not endeavor to cover their use in this review. Medgley(5) indicates that, thus far, glass electrodes are limited to about 150°C. Above that temperature the zirconia electrodes are more applicable. Both electrodes are usually employed in cells having bridge solutions and therefore involve liquid junctions.

b. Cells With Liquid Junction

Even a glass electrode in combination with a reference electrode involves a liquid junction in its customary use. At high temperatures, the difficulties with ordinary reference electrodes have led to the use of hydrogen electrodes as are both the test and reference electrodes in concentration cells. Such cells have been used extensively at ORNL(18-22) and their use is described briefly here. The cell representation, either for hydrogen electrode concentration cells or for a hydrogen electrode vs. a reference electrode where one point in a titration is the reference condition, is given as:

$$\mathrm{Pt, H_2|HCl(m_1), MCl(m_2)||HCl(m_3), MCl(m_2)|Pt, H_2} \quad (17)$$

The cell potential is given by

$$E-E_r = -(RT/F)\ \ln\ (m_H/m_{H,r}) + \Sigma\ D_i\ (m_i - m_{r,i}) \quad (18)$$

where activity coefficients and hydrogen fugacities are assumed to cancel for this cell.

Liquid junction potentials have been represented in this manner by a number of investigators when using supporting electrolytes. Liquid junction coefficients applicable to replacing a small amount of an alkali metal ion by H^+ in presence of a common anion (D_H - D_M) are summarized in Table III from several studies. Generally, the Henderson equation, with limiting equivalent conductances, is accurate to about 25%.

The magnitude of the liquid junction potential decreases with temperature since the limiting conductances of ions are becoming more nearly equal. The significance of the contribution of the E_J diminishes as shown in Fig. 3, because of the increase in the magnitude of the Nernst slop, RT/F. For example, in 1 m NaCl solution D_H - D_{Na} goes from 61 mV at 25° to 20 mV at 300°C. Replacing 1% of the sodium with hydrogen ions leads to 0.6 mV at 25°C and 0.2 mV at 300°C. Generally, experiments can be designed to limit the E_J to less than 2 mV and often less than 1 mV.

c. Measurements in Brines

For acidity measurements in brines at ambient conditions the following approaches could be used. Where the major ion content of a brine is known, a reference solution can be prepared with the same composition plus a small amount of HCl (e.g., 0.01 m). Then the potential of the cell (e.g., glass vs Ref) is

$$E - E_r = -(RT/F) \ln (m_H/m_{H,r}) \tag{19}$$

neglecting the liquid junction term where the highest accuracy is not needed. An alternative procedure could be used in some circumstances. Acidity could be added to an unknown brine by making a standard addition of HCl to the brine in such a way that only a slight dilution of the brine occurs. A modestly concentrated source (e.g., 6 m HCl) could be used to produce 0.01 m H^+ in the brine. In order to ascertain if protolytic substances were present, successive additions (a titration) could be made. For example, if the molality of H^+ is doubled, the potential should increase by 18 mV in the absence of buffers at 25°C.

d. Measurements Near the Critical Temperature

Near the critical conditions for water, $t_c = 374°C$ and $P_c = 220.6$ bars, the degree of association of most electrolytes becomes very high.(18) Under conditions were there is strong association of hydrogen ions with anions present, it becomes essential to define the reference acidity in terms of the free hydrogen ion concentration in order to derive equilibrium information, such as the ionization constants of acids. This is necessary because of the difficulty of extrapolation to infinite dilution of apparent ionization constants such as

$$Q_{HX} = (m_H + m_{HCl})(m_X + m_{MX})/m_{HX} \tag{20}$$

where m_H, m_X, m_{HCl}, and m_{MX} refer to the actual concentrations of the species present and where MCl is the supporting electrolyte in which the ionization of the acid HX is studied. The real constant involving only the ions becomes

$$Q^{\bullet}_{HX} = m_H m_X/m_{HX} = Q_{HX}[1+Q_{HCl}\ m_{Cl}]^{-1}[1+Q_{MX}\ m_M]^{-1} \tag{21}$$

where Q_{HCl} and Q_{MX} are association quotients for HCl and MX. At lower temperatures the association quotients for HCl and MX are sufficiently small that extrapolations can be made from measurements at modest concentrations (ca. 0.1 m) of MCl. In the region of transition from strong electrolyte behavior to weak electrolyte behavior, near critical conditions, use of Eq. (21) becomes a difficult matter because of the lack of information on all the necessary association quotients.

Another concern is the use of the Henderson equation to compute liquid junction potentials in this region. If the supporting electrolyte is appreciably associated, then calculated potentials require a knowledge of all association processes. However, assuming the diminishing significance of liquid junction potentials at high temperatures as indicated in Fig. 3, this problem might be expected to be minimal.

5. A PITZER pH SCALE

Although we have emphasized that it is unnecessary to make an assumption about individual ion activity coefficients, some will choose to do so. For the NBS scale, the previously stated assumption for γ_{Cl} (Eq. 3) is made. Other reasonable assumptions are possible. The use of the Pitzer treatment$^{(10,11)}$ for individual ion activity coefficients is an interesting choice, although the indeterminable terms (third line in Eq. 24) would have to be omitted when addressing individual ion activity coefficients. For all chemically interesting combinations such as charge balanced products and quotients and for neutral combinations of ions only mean activity coefficients would be needed, which are unambiguously defined. The advantage of this choice of the Pitzer treatment for individual ions is the large database being accumulated today of the parameters needed for this approach. A variation of this approach has recently been suggested by Knauss et al.(12)

To be more explicit, the quantity pa_H could be defined

$$pa_H = p(a_H a_{Cl}) + \log m_{Cl} + \log \gamma_{Cl}{}^P \tag{22}$$

which is equivalent to

$$pa_H \equiv p(m_H \gamma_H{}^P) \tag{23}$$

where $\gamma_H{}^P$ is given by Eq. (24) omitting the third line, the undeterminable part. Then, as long as one is carefully consistent in using only ionic activity coefficient on this basis for processes in this solution, no errors are introduced into calculations; i.e., products or quotients such as $a_H a_{Cl}$ or a_H/a_K are computed correctly.

Equation (24) gives the activity coefficient of H^+ in a mixture of electrolytes by the Pitzer treatment,(11)

$$\begin{aligned} \ln \gamma_H = z_H^2 F \sum_a m_a (2B_{Ha} + ZC_{Ha}) + \sum_c m_c (2\Phi_{Hc} + \sum_a m_a \psi_{Hca}) \\ + \sum_{a<a'}\sum m_a m_{a'} \psi_{Haa'} + |z_H| \sum_c \sum_a m_c m_a C_{ca} \\ + |z_H| [\sum_c m_c \lambda_{cc}/z_c - \sum_a m_a \lambda_{aa}/|z_a| + (3/2) \sum_c \sum_a m_c m_a (\mu_{cca}/z_c - \mu_{caa}/|z_a|)] . \end{aligned} \tag{24}$$

where c and c' are cations and a and a' are anions and their ion charges are z_c and z_a. The B and C terms are obtained experimentally from binary electrolyte systems while Φ and Ψ arise from mixed electrolyte solutions and are measured from common ion mixtures. The term in brackets in the last line of the equation for $\ln \gamma_H$ contains λ_{ij} and μ_{ijk} that are second and third virial coefficients in the expression for the total excess free energy of the solution. These terms are not individually measurable as a result of the electrical neutrality of any real solution. However, the bracketed term drops out for all mean activity coefficients or any combination of ions that maintain electrical neutrality such as an ion exchange reaction equilibrium.

The quantity F contains the long range electrostatic term plus additional terms and is given by

$$\begin{aligned} F = & -A_\phi[I^{1/2}/(1+bI^{1/2})+(2/b)\ln(1+bI^{1/2})] \\ & + \sum_c\sum_a m_c m_a B'_{ca} + \sum\sum_{c<c'} m_c m_{c'} \Phi'_{cc'} + \sum\sum_{a<a'} m_a m_{a'} \Phi'_{aa'} \end{aligned} \quad (25)$$

where,

$$Z = \sum_i m_i|z_i|. \quad (26)$$

The double summation terms include all distinguishable pairs of dissimilar cations or anions represented as a<a′ and c<c′. The terms C_{ca}, Ψ_{Hca}, and $\Psi_{Haa'}$, are assumed independent of concentrations.

The ionic strength dependence of B_{HX} is given by

$$B_{HX} = \beta_{HX}^{(0)} + \beta_{HX}^{(1)} g(\alpha_1 I^{1/2}) \quad (27)$$

where g is given by

$$g(x) = 2[1 - (1 + x)\exp(-x)]/x^2 \quad (28)$$

$\beta^{(0)}$ and $\beta^{(1)}$ are solute specific parameters obtained from measurements on binary systems where concentration is varied. For electrolytes in which one of the ions is univalent, α_1 is 2.0 $kg^{1/2}$ $mol^{1/2}$. The above equations require the five types of empirical parameters, $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, C_{MX}, Φ_{MN}, Ψ_{MNX}, (or Ψ_{MXY}). The parameter Φ_{MN} is equal to θ_{MN} where M and N have the same charge, i.e., the electrostatic contribution to mixing is zero.

Likewise, the mean activity coefficient for the electrolyte ($M_{\nu_M}X_{\nu_X}$) in a mixture where $\nu = \nu_M + \nu_X$ is given by the following:

$$\begin{aligned}\ln \gamma_{\pm(M_{\nu_M}X_{\nu_X})} &= |z_M z_X|F + (\nu_M/\nu)\sum_a m_a[2B_{Ma} + ZC_{Ma} + 2(\nu_X/\nu_M)\,\Phi_{Mc}] \\ &\quad + (\nu_X/\nu)\sum_c m_c[2B_{cX} + Z\,C_{cX} + 2(\nu_M/\nu_X)\Phi_{Mc}] \\ &\quad + \sum_c\sum_a m_c m_a \nu^{-1}\,[2\nu_M z_M C_{ca} + \nu_M\Psi_{Mca} + \nu_X\Psi_{caX}] \qquad (29) \\ &\quad + \sum\sum_{c<c'} m_c m_{c'}\,(\nu_X/\nu)\,\psi_{cc'X} + \sum\sum_{a<a'} m_a m_{a'}(\nu_M/\nu)\psi_{Maa'}\end{aligned}$$

6. REFERENCE DATA FOR ELEVATED TEMPERATURES

Table IV lists the conditions in studies of HCl, DCl, HBr, and HCl mixtures with a number of electrolytes made by Leitzke and coworkers$^{(30-40)}$ using the Pt,H_2 vs. Ag,AgX cells. These results provide activity coefficient information on HCl for a number of electrolyte mixtures mostly to a total ionic strength of about 1 mol•kg^{-1} and to about 150-175°C. Such information is needed for the use of the molality scale in electrochemical measurements of pH without liquid junction, in effect to calibrate the electrode or to determine the apparent E° for the cell. If analyzed in terms of the Pitzer treatment, the results in Table IV could also provide $\gamma_H{}^P$ for the Pitzer pH scale defined here. For pure HCl solutions, $\gamma_H{}^P = \gamma_{\pm(HCl)} = \gamma_{Cl}{}^P$.

Table V lists results for both γ_H and $\gamma_\pm$ for HCl in mixtures with NaCl from the results of Lietzke et al.$^{(34)}$ for use in the two approaches mentioned above, i.e., pH = $-\log m_H\gamma_H{}^P$, or pH = $-\log m_H$. The ln $\gamma_{\pm(HCl)}$ was obtained from

Eq. (24) where the pure electrolyte parameters for HCl were taken from Holmes et al.(41) and for NaCl from Pitzer et al.(42) Data of Harned(43) were used at 25° and 60°C and from Leitzke et al.(34) at 25°-175°C. The only mixing parameter derived is θ_{HNa}, which is given by

$$\theta_{HNa} = 0.02576 + 3.00 \times 10^{-6} (T - 298.15)^2 \tag{30}$$

Probably the most accurate values of the activity coefficients for HCl(aq) are those based on enthalpy of dilution data and reported by Holmes et al.(41) (see Table VI) to 250°C and the analysis by Simonson et al.(44) for temperatures to 375°C based on the same measurements.

Other reference values for m_H can be obtained from buffer solutions. The temperature dependence for the ionization constants for fourteen acids and bases previously measured are shown in Fig. 4 and the literature references are given by Mesmer et al.(18) for all but acetic acid(19) and bisulfate.(20) For most of these the dependence on ionic strength has also been determined to 1.0 m and often to 3 m. Similar information is now available for the Tris(21) and Bis-Tris(22) buffers over more limited temperature ranges. This information provides additional data for establishing the m_H scale in electrolyte media to 300°C. Here,

$$m_H = m_{HA}\, Q/m_A = K\ (\gamma_{HA}/\gamma^2_{\pm(HA)})\ (m_{HA}/m_A) \tag{31}$$

where Q and K are the ionization quotient and constant for the acid HA. For measurements at higher temperatures, attention must be given to ion association behavior as discussed in Section 4b.

7. CONCLUSIONS

1. The operational NBS scale for pH is based on an approximation for γ_{Cl} that is a good approximation only at ionic strength below 0.1, and in customary measurements liquid junction potentials are encountered that prevent assignment of exact meaning to the observations.
2. The Henderson equation does not accurately take into account the non-ideal term for liquid junction potentials but has been shown to approximate these potentials to 20-30% for a number of cases using limiting equivalent conductivities for the ions.
3. Using cells without liquid junction, measurements of the molality of hydrogen ion can be made directly if $\gamma_{\pm(HX)}$ is known from the literature for the solution of interest.
4. Using cells without liquid junction a useful pH scale can be defined as (-log a_H) based on representing all ion activity coefficients (including γ_H) by the Pitzer ion-interaction treatment ignoring the undeterminable terms, since these terms cancel for any neutral component or ion-exchange consideration.
5. In the presence of a supporting electrolyte, molalities of hydrogen ion can be measured to 0.01 log units with concentration cells or with other cells having a bridge solution joining to a reference electrode, if the calibration is made on the molality basis and corrections for liquid junction potentials are made with the Henderson equation.
6. Data are summarized for calibration of hydrogen ion responding cells at high temperatures using available data on acid-base

buffers or HCl solutions and mixtures of HCl with other metal chloride salts.

7. Measurements for electrochemical cells near the critical conditions for water require a knowledge of the association behavior of all electrolytes present in order to give useful information on acidity.

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Table I. Liquid Junction Potentials from the Henderson Equation at 25°C (Bates, 1973) Using Limiting Mobilities.

Junction: Solution X ‖ KCl (satd.)

Solution X	E_J(mV)	Solution X	E_J(mV)
1 M HCl	14.1	0.01 M NaOH	2.3
0.1 M HCl	4.6	0.1 M NaOH	-0.4
0.01 M HCl	3.0	1.0 M NaOH	-8.6
0.01 M HCl, 0.09 M NaCl	1.9	1.0 M KOH	-6.9

Junction: Solution X ‖ 0.1 M KCl

Solution X	E_J(mV)
0.1 M HCl	26.9
0.01 M HCl	9.1
0.1 M NaOH	-19.2
0.01 M NaOH	-4.5

Table II. Liquid Junction Potentials for Ag/AgCl Concentration Cells with Junctions of the Type (m_1 MCl ∥ m_1 NCl) from MacInnes and Yeh.

Concentrations	Electrolytes	E_J (observed) (mV)	E_J (calculated)[a] (mV)
0.1 M	HCl: KCl	26.8	28.5
	HCl: NaCl	33.1	33.4
	HCl: LiCl	34.9	36.1
	KCl: LiCl	8.8	7.6
	KCl: NaCl	6.4	4.9
0.01 M	HCl: KCl	25.7	27.5
	HCl: NaCl	31.2	32.0
	HCl: LiCl	33.8	34.6

[a] Using Henderson equation equivalent and the extrathermodynamic assumption that γ_{Cl^-} is equal in the two solutions.

Table III. Comparison of Observed and Calculated Effects of Composition Change on the Potential of Cells with Liquid Junction at 25°C.

Medium	$\Delta E + 59.16 \log (m_H/m_{H,r})$ $m_H - m_{H,r}$ (mV liters mole^{-1} or mV kg mole^{-1}) Observed	Calculated	Ref.
0.5 M KNO_3	105	98	23
1 m NaCl	63	61	24
0.7 M $ThCl_4$ + 0.2 M NaCl	22-25	20	25
1 M $NaClO_4$	64	66	26
3 M $NaClO_4$	16.7	22	27
0.4 M $UO_2(ClO_4)_2$ + 0.2 M $NaClO_4$	51	65	28
3 M $LiClO_4$	15.8	25	29
0.967 M $La(ClO_4)_3$ + 0.1 M $LiClO_4$	20	19	29

Table IV. Experimental Results for HX Activities to Temperatures Above 100°C Mostly from EMF Studies of Lietzke and Coworkers.

Solutions	t/°C	Ionic Strength/mol kg^{-1}	Ref.
HCl	25-275	0-1	30
	25-375	0-16	41,44
DCl	25-225	0-1	33
HBr	25-200	0-1	31
HBr-KBr	25-150	0.4, 1	32
HCl-LiCl	25-175	0.5, 1	39
HCl-NaCl	25-175	0.4, 1	34
HCl-KCl	25-175	0.5, 1	38
HCl-RbCl	25-175	0.5, 1	38
HCl-CsCl	25-175	0.5, 0.9	38
HCl-$BaCl_2$	25-175	0.5, 1	35
HCl-$LaCl_3$	25-175	0.5, 1	36
HCl-$GdCl_3$	25-150	0.5, 1	37
HCl-CsCl-$BaCl_2$	23-176	0.5	40

Table V. Activity Coefficient of HCl and Single (Pitzer) Ion Activity Coefficient of H^+ in HCl + NaCl Mixtures.

---------------Molality of HCl = 0.01---------------

t/°C	$\gamma_{\pm(HCl)}$	γ_H^P	$\gamma_{\pm(HCl)}$	γ_H^P	$\gamma_{\pm(HCl)}$	γ_H^P
	Total m = 0.1		Total m = 0.5		Total m = 1.0	
25	0.795	0.796	0.758	0.759	0.810	0.812
50	0.783	0.784	0.735	0.735	0.773	0.774
75	0.770	0.771	0.708	0.709	0.733	0.734
100	0.754	0.755	0.679	0.680	0.691	0.692
125	0.736	0.737	0.647	0.647	0.645	0.646
150	0.715	0.716	0.610	0.611	0.595	0.596
175	0.691	0.691	0.569	0.570	0.542	0.543
200	0.662	0.663	0.523	0.524	0.484	0.485

---------------Mole Fraction of HCl = 0.5---------------

t/°C	$\gamma_{\pm(HCl)}$	γ_H^P	$\gamma_{\pm(HCl)}$	γ_H^P	$\gamma_{\pm(HCl)}$	γ_H^P
	Total m = 0.1		Total m = 0.5		Total m = 1.0	
25	0.792	0.798	0.744	0.769	0.780	0.834
50	0.782	0.786	0.725	0.746	0.753	0.796
75	0.769	0.773	0.703	0.721	0.722	0.759
100	0.754	0.758	0.678	0.694	0.688	0.721
125	0.737	0.740	0.649	0.665	0.649	0.682
150	0.716	0.720	0.616	0.632	0.607	0.639
175	0.693	0.696	0.579	0.595	0.561	0.592
200	0.666	0.669	0.537	0.552	0.509	0.540

Table VI. Activity Coefficient of HCl(aq)[a]

	t/°C						
m	25	50	75	100	125	150	175
0.10	0.796	0.784	0.770	0.754	0.736	0.715	0.690
0.20	0.767	0.751	0.734	0.713	0.690	0.663	0.633
0.30	0.757	0.739	0.718	0.694	0.667	0.637	0.602
0.40	0.755	0.734	0.711	0.684	0.654	0.620	0.582
0.50	0.759	0.735	0.709	0.679	0.647	0.610	0.569
0.60	0.765	0.739	0.710	0.678	0.642	0.603	0.559
0.70	0.774	0.745	0.713	0.679	0.641	0.599	0.552
0.80	0.785	0.753	0.719	0.681	0.641	0.596	0.547
0.90	0.797	0.762	0.726	0.686	0.642	0.595	0.544
1.00	0.811	0.773	0.733	0.691	0.645	0.595	0.541
1.25	0.850	0.805	0.758	0.708	0.655	0.599	0.540
1.50	0.897	0.843	0.787	0.730	0.670	0.608	0.542
1.75	0.949	0.885	0.821	0.756	0.689	0.619	0.548
2.00	1.007	0.933	0.860	0.785	0.710	0.633	0.556
2.50	1.144	1.044	0.948	0.854	0.760	0.668	0.576
3.00	1.308	1.177	1.053	0.934	0.819	0.709	0.602
3.50	1.504	1.334	1.175	1.027	0.888	0.756	0.632
4.00	1.737	1.517	1.317	1.134	0.964	0.809	0.666
4.50	2.013	1.731	1.480	1.254	1.051	0.867	0.703
5.00	2.341	1.981	1.667	1.390	1.146	0.931	0.742
5.50	2.729	2.272	1.880	1.543	1.251	1.000	0.785
6.00	3.189	2.610	2.124	1.714	1.367	1.075	0.829
6.50	3.734	3.004	2.402	1.905	1.494	1.154	0.875
7.00	4.380	3.460	2.719	2.119	1.632	1.239	0.924

Table VI. Activity Coefficient of HCl(aq)[a]
(Continued)

	t/°C						
m	200	225	250	275	300	325	350
0.10	0.662	0.628	0.589	0.535	0.449	0.321	0.145
0.20	0.597	0.557	0.509	0.448	0.361	0.242	0.105
0.30	0.562	0.517	0.465	0.400	0.316	0.202	0.086
0.40	0.539	0.490	0.435	0.369	0.286	0.178	0.075
0.50	0.522	0.471	0.413	0.346	0.265	0.161	0.067
0.60	0.510	0.456	0.396	0.328	0.249	0.148	0.061
0.70	0.501	0.444	0.383	0.314	0.236	0.138	0.057
0.80	0.494	0.435	0.372	0.303	0.225	0.130	0.053
0.90	0.488	0.428	0.363	0.293	0.216	0.124	0.050
1.00	0.484	0.421	0.355	0.284	0.209	0.118	0.048
1.25	0.477	0.410	0.341	0.268	0.193	0.107	0.043
1.50	0.474	0.403	0.331	0.256	0.182	0.099	0.039
1.75	0.474	0.399	0.324	0.247	0.173	0.093	0.036
2.00	0.477	0.398	0.319	0.240	0.166	0.088	0.034
2.50	0.486	0.398	0.313	0.230	0.155		
3.00	0.500	0.402	0.310	0.223	0.147		
3.50	0.516	0.409	0.310	0.218	0.141		
4.00	0.535	0.417	0.311	0.214	0.136		
4.50	0.556	0.426	0.312	0.212	0.132		
5.00	0.578	0.436	0.314	0.209	0.128		
5.50	0.601	0.446	0.316	0.207	0.125		
6.00	0.624	0.455	0.318	0.206	0.122		
6.50	0.648	0.465	0.319	0.204	0.119		
7.00	0.672	0.473	0.319	0.202	0.116		

[a] 25°-250°C, Ref. (41) model I; 275°-300°C, Ref. (41) model III; 325°-350°C, Ref. (44) model (AI).

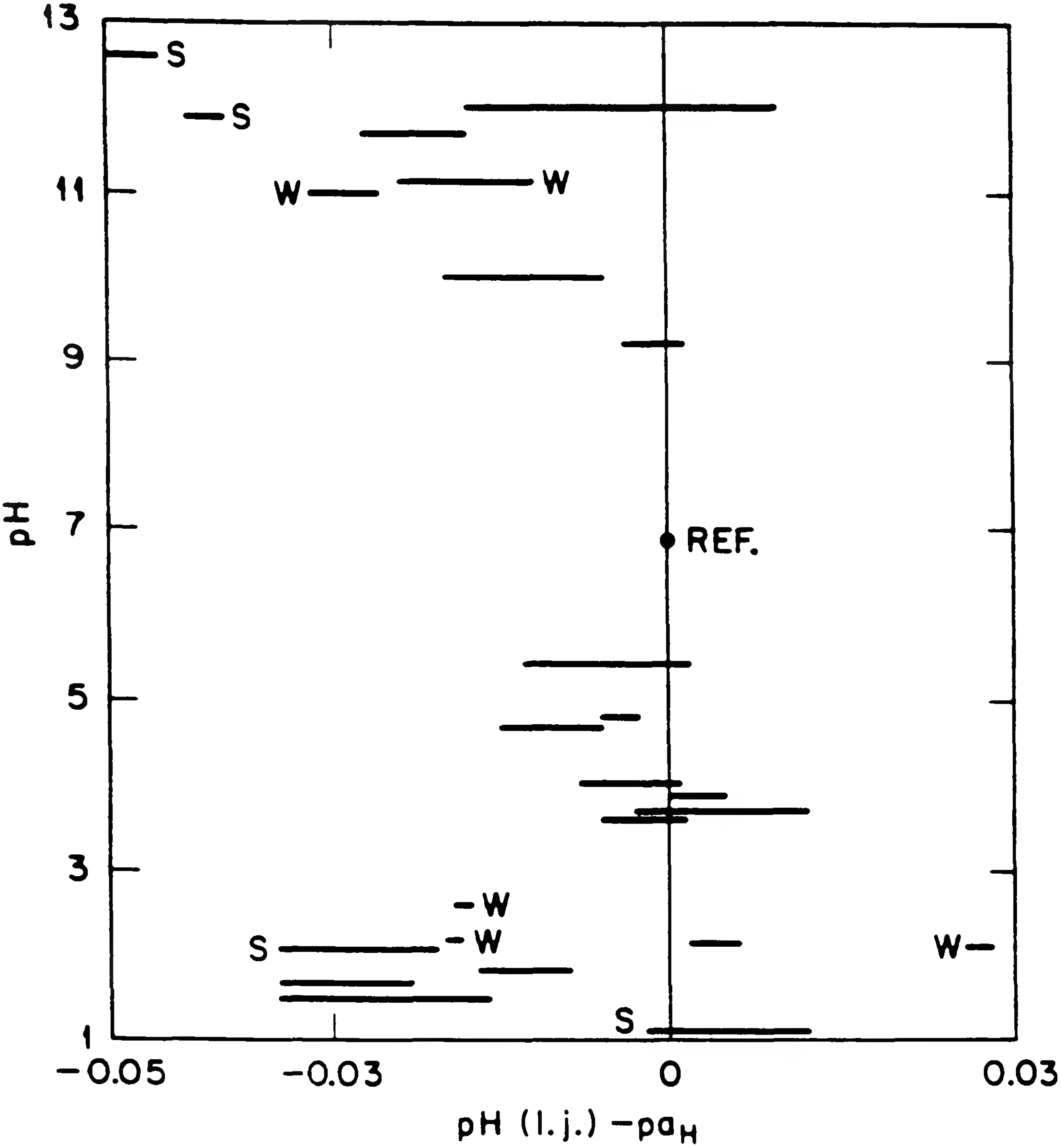
CAPTIONS

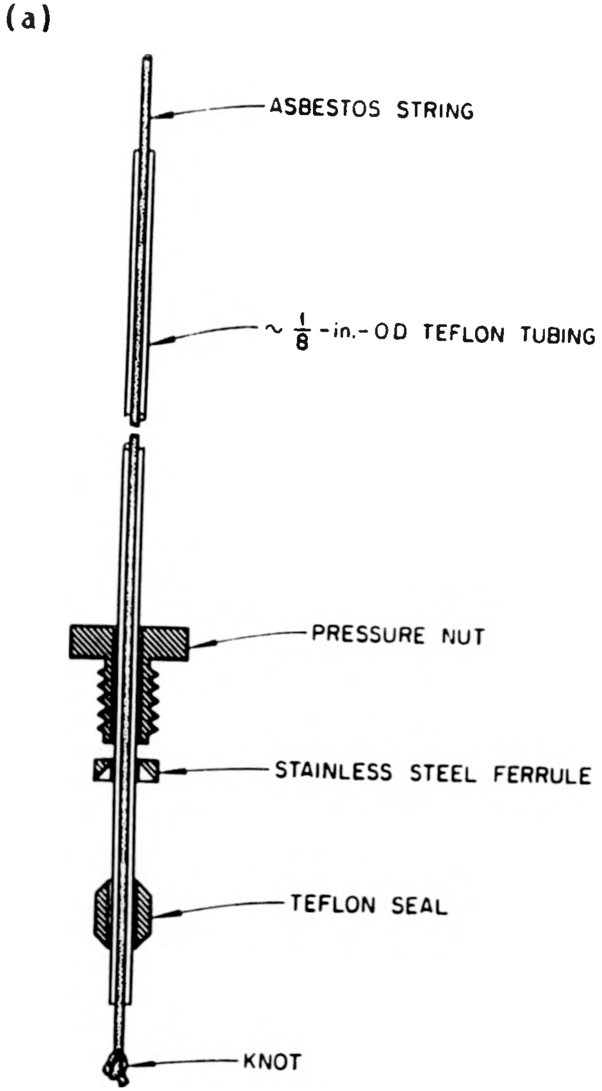
Fig. 1. Errors in determining pH of various solutions. (From Bates et al., 1950, by permission). The difference between the pH determined in cells with liquid junction - pH(l.j.) - and in cells without liquid junction - pa_H - is plotted on the abscissa. The length of each line corresponds to the estimated uncertainty in pa_H, which arises from the uncertainty in assigning γ_{Cl} - in the cell used. S and W denote strong and weak electrolytes, respectively. The other solutions were buffered.

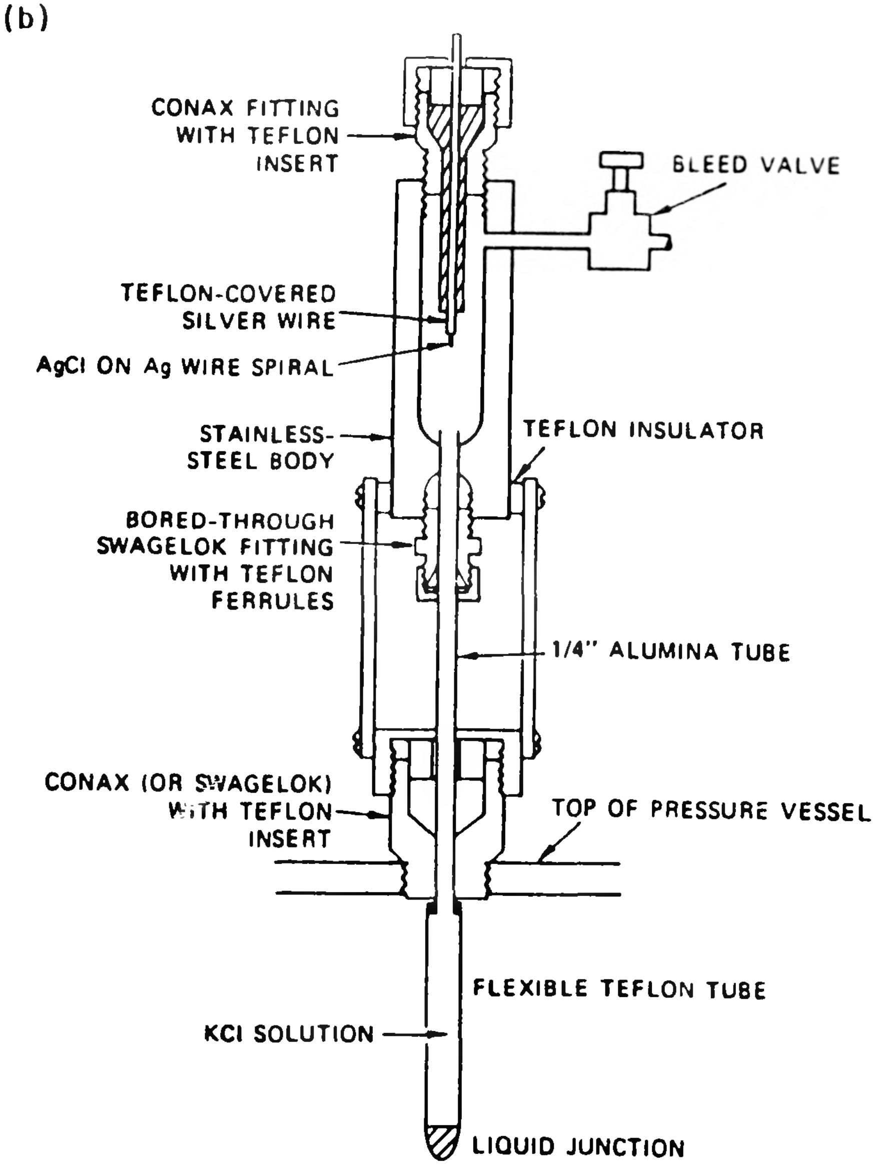
Fig. 2. (a) Salt bridge for external reference electrode held at ambient conditions by Bacarella and Sutton (1965) (by permission) and (b) pressurized bridge solution and reference electrode assembly employed by Macdonald et al. (1979)(by permission). Both are for use in autoclaves at high temperatures.

Fig. 3. The magnitude of D_H-D_{Na} (left ordinate), and the error in m_H (%) due to neglecting E_J from replacing 1% of the Na^+ with H^+ in a 1 m NaCl solution (right ordinate).

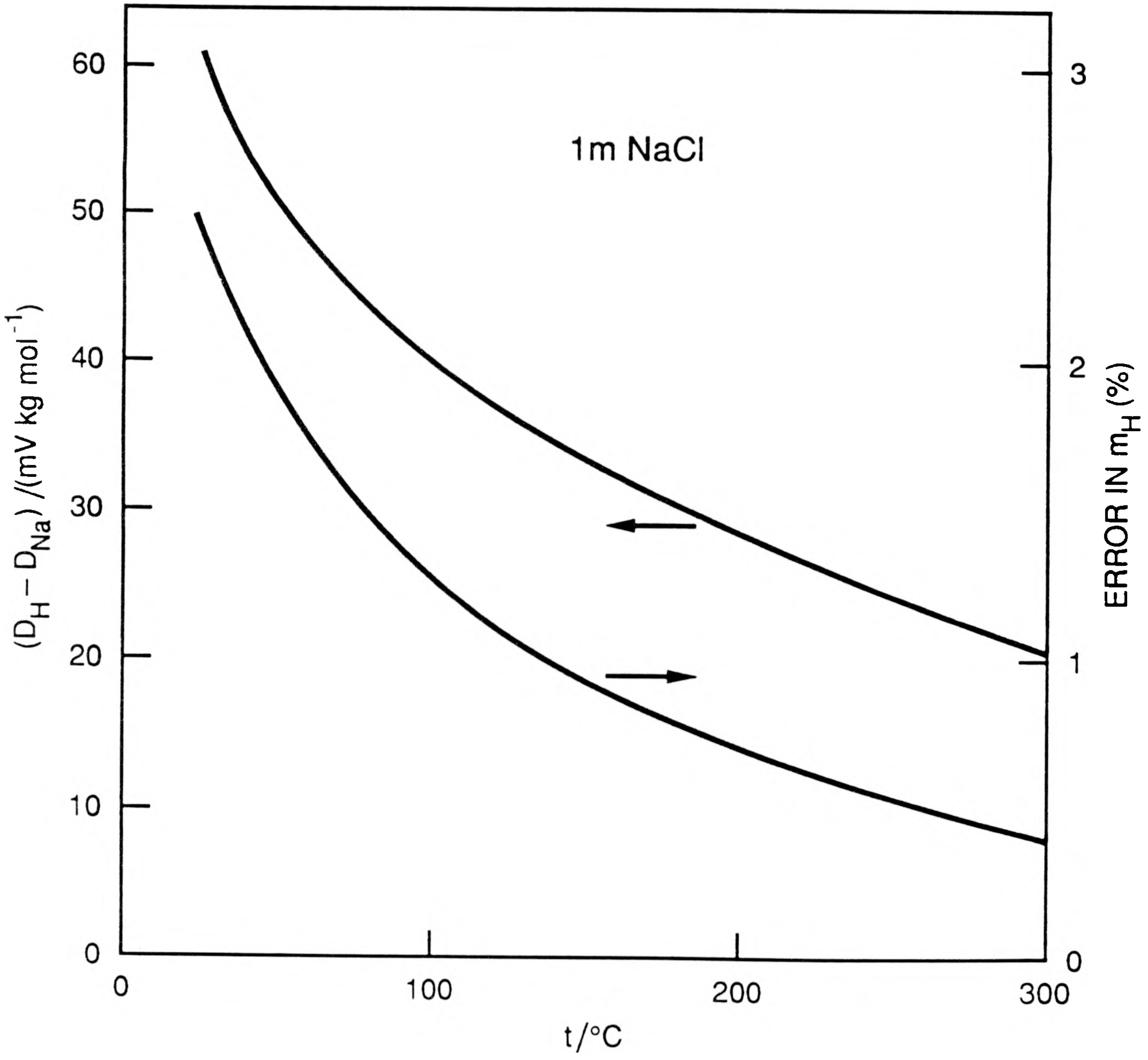
Fig. 4. Log K for ionization of acids and bases to 300°C from EMF studies.


13
11
9
7
5
3
1
pH
S
S
W
W
REF.
W
W
S
W
S
−0.05
−0.03
0
0.03
pH (l. j.) −pa_H


(a)
ASBESTOS STRING
~ 1/8 -in.-OD TEFLON TUBING
PRESSURE NUT
STAINLESS STEEL FERRULE
TEFLON SEAL
KNOT


(b)
CONAX FITTING WITH TEFLON INSERT
BLEED VALVE
TEFLON-COVERED SILVER WIRE
AgCl ON Ag WIRE SPIRAL
STAINLESS-STEEL BODY
TEFLON INSULATOR
BORED-THROUGH SWAGELOK FITTING WITH TEFLON FERRULES
1/4" ALUMINA TUBE
CONAX (OR SWAGELOK) WITH TEFLON INSERT
TOP OF PRESSURE VESSEL
FLEXIBLE TEFLON TUBE
KCl SOLUTION
LIQUID JUNCTION

ORNL-DWG 91M-9535



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