J. Chem. Eng. Data 1987, 32, 221-226

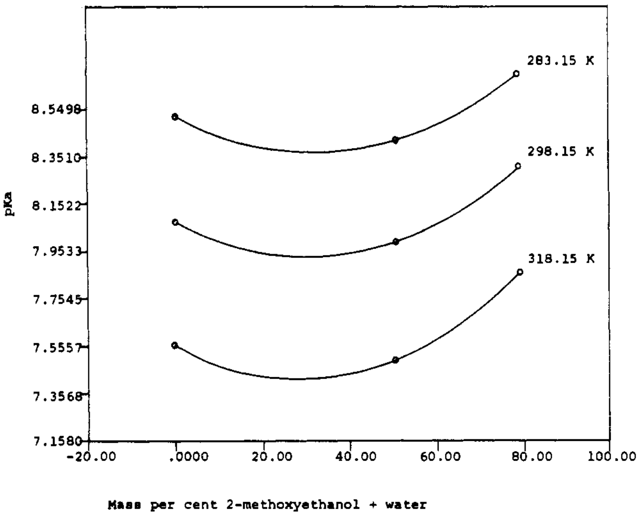

Figure 2. pK_a as a function of mass percent 2-methoxyethanol + water.

By use of the constants A, B, and C of the polynomials representing pK_a as a function of T, the standard molar thermodynamic quantities ($\Delta_t G°_m$, $\Delta_t S°_m$, $\Delta_t H°_m$) for the transfer process

$$\mathrm{TrisH^+(W) = TrisH^+(D)} \qquad (17)$$

were calculated and are listed in Table V.

Literature Cited

(1) Durst, R. A.; Staples, B. R. *Clin. Chem.* **1972**, *18*, 206.
(2) Bates, R. G. *Ann. N.Y. Acad. Sci.* **1961**, *92*, 341.
(3) Smith, W. H.; Hood, D. W. In *Recent Researches in the Fields of Hydrosphere, Atmosphere, and Nuclear Geochemistry*; Maruzen: Tokyo, 1964; p 185.
(4) Hetzer, H. B.; Bates, R. G. *J. Phys. Chem.* **1962**, *66*, 308.
(5) Woodhead, M.; Paabo, M.; Robinson, R. A.; Bates, R. G. *J. Res. Natl. Bur. Stand.* **1965**, *69A*, 263.
(6) Schindler, P.; Robinson, R. A.; Bates, R. G. *J. Res. Natl. Bur. Stand.* **1968**, *72A*, 141.
(7) Kundu, K. K.; De, A. L.; Das, M. N. *J. Chem. Soc., Dalton. Trans.* **1972**, *3*, 386.
(8) Vega, C. A.; Butler, R. A.; Perez, B.; Torres, C. *J. Chem. Eng. Data* **1985**, *30*, 376.
(9) Butler, R. A.; Vega, C. A.; Bates, R. G. *J. Solution Chem.* **1980**, *9*(4), 293.
(10) Ruehle, A. E. *Ind. Eng. Chem. Anal. Ed.* **1938**, *10*, 130.
(11) Simon, W. *Uber die Mikrobestimmung Sheinbaren Dissociations-konstanten in Nechtwasserigen Medien*; Tesis E.T.H., Juris-Verlag, Zurich, 1956.
(12) Thun, H. P.; Staples, B. R.; Bates, R. G. *J. Res. Natl. Bur. Stand.* **1970**, *74A*, 641.
(13) Shanbhag, P. M.; Vega, C. A.; Bates, R. G. *Bull. Soc. Chim. Belg.* **1981**, *90*(1), 1.
(14) Vega, C. A.; Delgado, S. *J. Chem. Eng. Data* **1986**, *31*, 74.

Received for review June 16, 1986. Accepted January 27, 1987.

Electrical Conductance of Liquid and Supercritical Water Evaluated from 0 °C and 0.1 MPa to High Temperatures and Pressures. Reduced-State Relationships

William L. Marshall

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

The electrical conductance of liquid and supercritical water to high temperatures and pressures is represented by an equation that incorporates some earlier observed trends and a newly discovered reduced-state relationship presented here. Calculations with the equation are believed to describe within ±1 to ±5% the specific conductance of liquid water at temperatures from 0 to 374 °C and at pressures from saturated vapor pressure to 1000 MPa (10 kbar). For supercritical water at fluid densities from about 0.3 to 1 g cm^{-3} and at temperatures from 374 to 1000 °C, the uncertainties probably will increase from 5% to perhaps 15% at the highest temperatures and pressures. Some general conclusions on conductance behavior are presented based on the observations.

1. Introduction

Reliable values of the electrical conductance of pure water at high temperatures are useful as background conditions for estimating ionic impurities by conductance measurements in steam cycles as well as for their fundamental value. However, there are only a few experimental measurements on the electrical conductance of water at high temperatures. It is very difficult to obtain and keep absolutely pure water in a containment system at high temperatures and pressures, with the result that most experimentally determined conductances (of water) generally include also the conductances of the unremoved (or introduced by corrosion of the containment vessel) electrolyte impurities. The earlier careful measurements that have been made are mostly at temperatures between 0 and 25 °C at saturated vapor pressures, and these are reviewed in detail by Bignold, Brewer, and Hearn (*1*) and by Light (*2*).

There are, however, two carefully determined sets of experimental measurements: those of Bignold et al. (*1*) up to 271 °C and, recently, of Light up to 70 °C (*2*). Although limited to liquid water under saturated vapor, these two sets provide essentially the only reasonably accurate, directly obtained values for comparing with calculated values at temperatures much above 25 °C by any equations that might be developed.

The best procedure to obtain the conductance of water is by an indirect method that applies (i) the extent of ionization of water as expressed by its ion product (K_w) and (ii) the limiting ionic conductances of the hydrogen ion [$\lambda_0(H^+)$] and the hydroxide ion [$\lambda_0(OH^-)$]. If these or their estimated values are available at a given temperature and pressure (or density), then the specific conductance of water can be calculated without assumptions. Its accuracy will depend upon the accuracy of the values of K_w, $\lambda_0(H^+)$, and $\lambda_0(OH^-)$ used in the calculation. An equation providing values of K_w as a function of temperature from 0 to 1000 °C and pressures up to 1000 MPa is available elsewhere as an International Association for the Properties of Steam (IAPS) standard (*3*). The problem then is to obtain

0021-9568/87/1732-0221$01.50/0

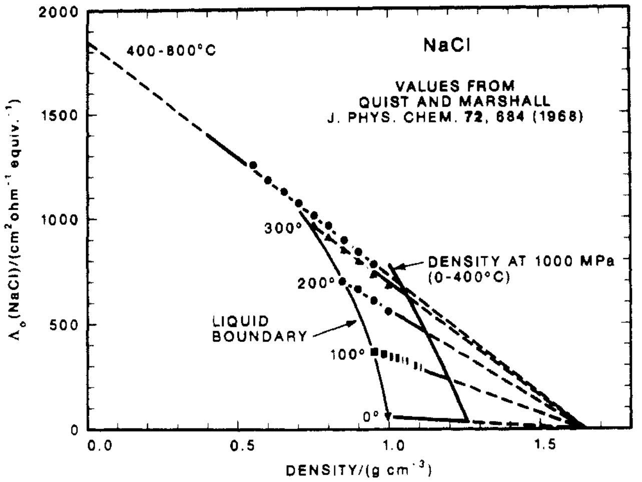

Figure 1. Limiting equivalent conductances of aqueous sodium chloride solutions vs. density, 0–800 °C. Limits of the proposed application up to 1000 MPa are indicated.

values of $\lambda_0(H^+)$ and $\lambda_0(OH^-)$ for which the sum may be expressed as $\Lambda_0(H^+,OH^-)$. There are published values of $\lambda_0(H^+)$ and $\lambda_0(OH^-)$ (*4*) for liquid water but only at saturated vapor pressures up to the vicinity of the critical temperature. Our present goal is to correlate available conductance measurements in quantitatively obtaining the sum of these two limiting conductances over a wide range of both temperature and pressure (or density).

To do this, we have applied some relationships for limiting conductances of several electrolytes at temperatures from 0 to 800 °C and pressures to 400 MPa, as first observed and interpreted in the pioneering studies of Franck (*5–7*) and later, with refinements and extensions, at this laboratory (*4*, *8–18*). These relationships are useful for extrapolating to regions where data do not exist. The procedure in developing an equation for describing the specific electrical conductance of water over a wide range of temperature and pressure is established by relating these earlier observed behaviors and some additional ones presented here. The resulting equation is given together with a comparison of its calculated values with the few directly measured values and the estimates of its accuracy over its suggested possible range of application (0–1000 °C; up to 1000 MPa).

2. Graphical Description and Initial Equations Applied for Representation of the Electrical Conductance

There are available, in addition to the earlier classic papers of Franck (*5–7*), several studies of the conductance–association behavior of aqueous electrolyte solutions at temperatures up to 800 °C and at pressures to 400 MPa (*8–18*). These studies show that an isothermal plot of the limiting equivalent conductance (Λ_0) for a given 1–1 valence electrolyte vs. the density yields essentially a straight line over the experimental range of pressure. A further observation is that at 400–800 °C, the values of Λ_0 for the different 1–1 valence *salts* fall essentially on the same straight line, and thus they provide approximately the same value of Λ_0 at an *extrapolated* limit of zero density (Λ_{00}). [Although presently it can be hypothesized that this conductance relationship will apply to very low densities (*10*, *11*), the only necessary condition here is that it applies over the proposed range of application.]

Another trend observed previously is that at 400–700 °C values of Λ_0 for the 1–1 valence aqueous electrolyte acids HCl and HBr plotted against density, although yielding smaller slopes than for the 1–1 salts, nevertheless extrapolate to zero density to yield about the same value of Λ_{00} as that for the salts (*10*, *14*). [Again, whether conductances actually follow this behavior to the lower limit is not of consequence for application in describing conductances over the proposed limited ranges of density.]

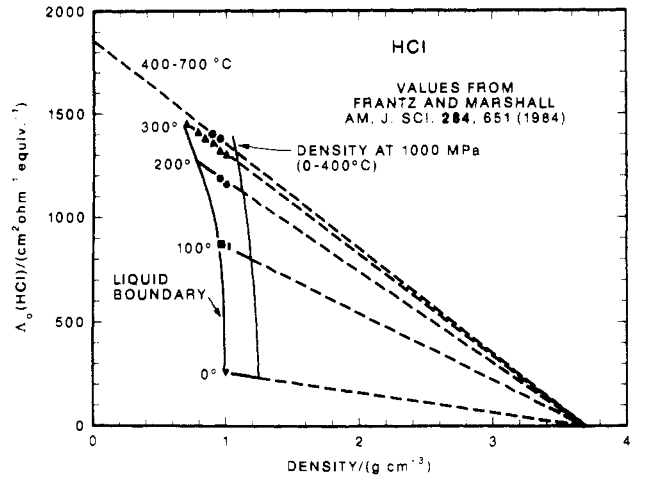

Figure 2. Limiting equivalent conductances of aqueous hydrochloric acid solutions vs. density, 0–700 °C. Limits of the proposed application up to 1000 MPa are indicated.

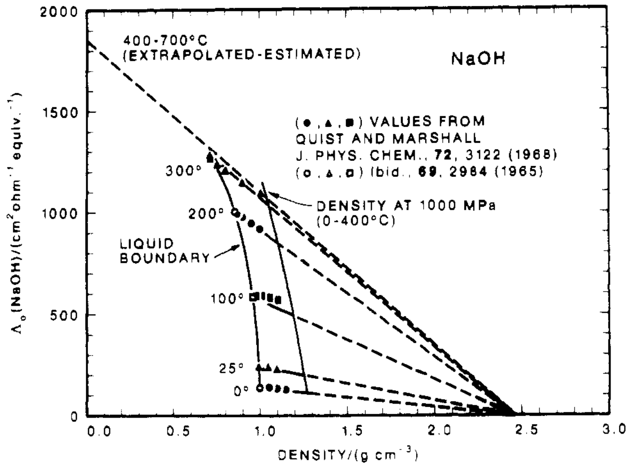

Figure 3. Limiting equivalent conductances of aqueous sodium hydroxide solutions vs. density, 0–700 °C. Limits of the proposed application up to 1000 MPa are indicated.

In the present study, we have discovered that the above-described isothermal straight lines for any given electrolyte (from the several studies referenced above) over a range of temperature from 100 to 400 °C *appear* to converge to a common point of *high* density (ρ_h) where Λ_0 becomes equal to zero. [This common point of density is physically unattainable, but still can be applied as a constant in an equation for describing conductances over experimentally attainable regions, where only relatively short extrapolations of density are required.] Some examples of this behavior, for application here, are shown in Figures 1–3 by plots of the limiting equivalent conductances of aqueous NaCl, HCl, and NaOH (*10*, *12*, *15*), where for illustration the dashed straight lines are extended beyond the experimental ranges to the hypothetical convergence point.

Figure 4 gives comparative behavior at temperatures of 400 to 700 °C for Λ_0(HCl), Λ_0(NaOH), and Λ_0(NaCl). It shows for Λ_0(NaOH) that the straight line for its estimated behavior at 400–700 °C, extrapolated from the straight lines in Figure 3 describing low-temperature (0–300 °C) behavior, also produces about the same value of Λ_{00} as that for NaCl and HCl at the high temperatures (1850 cm^2 ohm^{-1} equiv^{-1}). Since limiting conductances are additive

$$\Lambda_0(H^+,OH^-) = \Lambda_0(HCl) + \Lambda_0(NaOH) - \Lambda_0(NaCl) \qquad (1)$$

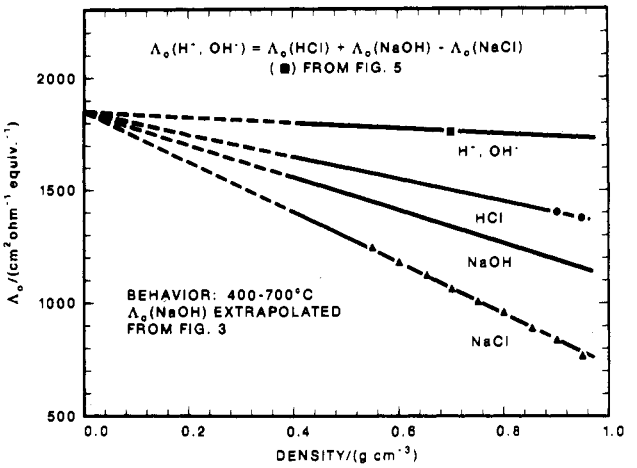

Figure 4. Limiting equivalent conductances of aqueous NaCl, HCl, NAOH, and $[H^+,OH^-]$ at 400–700 °C plotted against density. [Included are values from ref *10* (HCl), *12* (NaOH), and *15* (NaCl).] Limits of the proposed application are indicated by the continuous (undashed) lines.

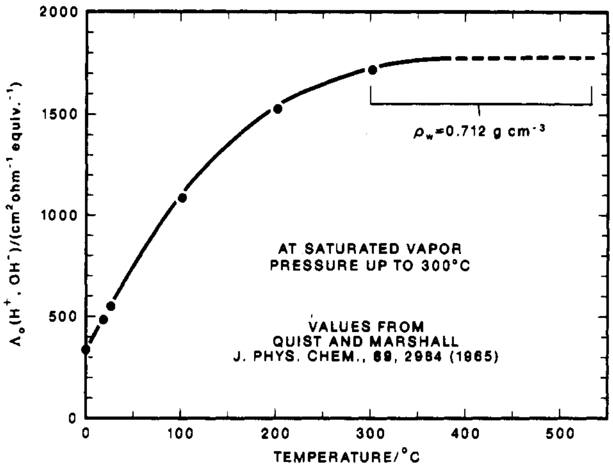

Figure 5. Limiting equivalent conductances of H^+ plus OH^- ions $[\Lambda_0(H^+,OH^-)]$ in aqueous solution under saturated vapor pressure vs. temperature.

Table I. Best Estimated Values of the Parameter Λ_{00}[a] for NaCl, HCl, NaOH, and (H^+,OH^-) and the Parameter, ρ_h[b]

	$\Lambda_{00}/(cm^2\ ohm^{-1}\ equiv^{-1})$				$\rho_{wh}(H^+,OH^-)/$ (g cm^{-3})
T/°C	NaCl	HCl	NaOH	(H^+,OH^-)	
0	150	355	235	440	4.38
100	865	1132	1000	1267	6.54
200	1445	1590	1535	1680	9.39
300	1755	1800	1777	1822	12.06
400	1850	1850	1850	1850	14.12
500–1000[c]	1850	1850	1850	1850	15.3–15.9

Best Estimates of ρ_h/(g cm^{-3})

T/°C	NaCl	HCl	NaOH
0–1000[c,d]	1.65	3.70	2.46

[a] Limiting equivalent conductance at zero density. [b] Density at which Λ_0 hypothetically equals zero. [c] Values above 400 °C based on extrapolation only. [d] Values of ρ_h for NaCl, HCl, and NaOH appear to be independent of temperature within the accuracy of the extrapolations, while ρ_{wh} (for H^+,OH^-) changes significantly with temperature.

$\Lambda_0(H^+,OH^-)$ must follow also a straight line relationship and extrapolate to the same value of Λ_{00} (at 400–700 °C), provided the above observations and interpretations are correct. From Figures 1–3, the following equations for the straight lines taken to represent the behavior over the experimental ranges of density at 400–700 °C can be written

$$\Lambda_0^*(HCl) = \Lambda_{00}^* - 500\rho^* \tag{2}$$

$$\Lambda_0^*(NaOH) = \Lambda_{00}^* - 752\rho^* \tag{3}$$

$$\Lambda_0^*(NaCl) = \Lambda_{00}^* - 1121\rho^* \tag{4}$$

from which by application of eq 1

$$\Lambda_0^*(H^+,OH^-) = \Lambda_{00}^* - 131\rho^* \tag{5}$$

at 400–700 °C where Λ_{00}^* is taken to equal 1850. In eq 2–5, the superscript * denotes dimensionless units as applied in the later equations. Thus, $\Lambda_0^*(HCl)$ equals $\Lambda_0(HCl)/(cm^2\ ohm^{-1}\ equiv^{-1})$. Several additional examples for electrolytes adhering to these straight line relationships are given elsewhere (*11*, *13*, *16–18*).

By application of eq 1 and the eq 2–5 derived from the descriptions given in Figures 1–3, values of $\Lambda_0(H^+,OH^-)$ are obtained. These values are thus represented also in Figure 4 by a straight line that extrapolates to the perceived common value of Λ_{00}. The extension to high densities of the resulting straight line for $\Lambda_0(H^+,OH^-)$ in Figure 4 provides a value of density (ρ_{wh}) at the intercept where $\Lambda_0(H^+,OH^-)$ will (by extrapolation only) equal zero.

Values of $\lambda_0(H^+)$ and $\lambda_0(OH^-)$ at temperatures from 0 to 300 °C (*4*), at saturated vapor pressures, were used also to obtain corresponding values of $\Lambda_0(H^+,OH^-)$. These values of $\Lambda_0(H^+,OH^-)$ agree well with those obtained by application of eq 1 with the descriptions of Figures 1–3. They are plotted in Figure 5 to show their rapid increase with increasing temperature and also to show the approach to a constant value. [Since at 400 °C a published (but extrapolated) value of $\Lambda_0(H^+,OH^-)$ was available, the corresponding value of density at 300 °C was used in Figure 5 for the description at the temperatures above 300 °C. The purpose of Figure 5 is to show graphically that $\Lambda_0(H^+,OH^-)$ appears to approach temperature independence at a constant density in the supercritical temperature region.]

The form of eq 2–5

$$\Lambda_0^* = \Lambda_{00}^* + S^*\rho^* \tag{6}$$

was applied to the experimental values for NaCl, HCl, and NaOH shown in Figures 1–3, respectively, to yield values of Λ_{00}^* and the slopes S^* (with a negative sign) for each electrolyte and accordingly for (H^+,OH^-), as described at the several temperatures. Calculated values of $\Lambda_{00}(H^+,OH^-)$ and ρ_{wh} together with calculated values of Λ_{00} and ρ_h for the several electrolytes are given in Table I. However, to make the calculations for $\Lambda_{00}(H^+,OH^-)$ (Table I), the values of $\lambda_0(H^+)$ and $\lambda_0(OH^-)$ from the published ionic conductances at saturated vapor pressure (*4*) were used as standards rather than those obtained by averaging and summing the separate high-temperature results in Figures 1–3. The low-temperature values used for $\lambda_0(OH^-)$ closely agreed with the excellent values at 15–75 °C of Marsh and Stokes (*19*). It was felt that these published values obtained (and evaluated) from several sources probably were the more accurate, although there is insignificant difference in Λ_{00} calculated from either approach. The slopes, S^*, are easily calculated since they equal $-\Lambda_{00}^*/\rho_h^*$.

Surprisingly, ρ_{wh} changes moderately with temperature, in contrast to the essentially temperature-independent but different values of ρ_h for NaCl, HCl, and NaOH, respectively. While the mathematical relationships are sound [that is, $\rho_{wh}(H^+,OH^-)$ can vary while the three separate values of ρ_h remain temperature-independent constants, with the four systems still showing mathematical agreement with both eq 1 and the form of eq 6], this differing behavior for ρ_{wh} might appear to be inconsistent in describing a physical picture of separate ionic conductances. Nevertheless, the representation of Figures 1–3 based on the experimental observations appear to approximate reality within

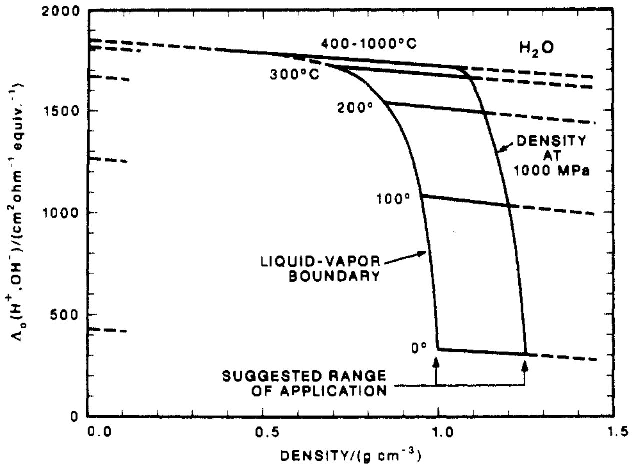

Figure 6. Limiting equivalent conductances of H^+ plus OH^- ions [$\Lambda_0(H^+,OH^-)$] vs. density at several constant temperatures. Limits of the proposed application up to 1000 MPa are indicated.

and near the experimentally attainable regions of density. Rather than try forcing ρ_{wh} to be temperature-independent, we have taken it to vary as indicated from the NaCl, HCl, and NaOH measurements with their presumed accuracies. Further discussion is given in section 5.

Figure 6 shows representative calculated lines for $\Lambda_0(H^+,OH^-)$ vs. ρ, with the proposed ranges for application. The limiting boundaries shown represent the density at saturated vapor pressure (below 374 °C) and that at 1000 MPa. The suggested limiting densities for application at 400–1000 °C will decrease with increasing temperature to values at 1000 °C of about 0.1 and 0.8 g cm^{-3} at 50 and 1000 MPa, respectively. With the possible exception that the description may be less reliable at the low densities (0.1–0.4 g cm^{-3}), these ranges are those of application proposed for the equation presented in section 3. With this restriction that application should be *limited* to conditions described *only* between the indicated boundaries (Figure 6), the isothermal behavior of $\Lambda_0(H^+,OH^-)$ is represented by the following equation

$$\Lambda_0^*(H^+,OH^-) = [\rho_w^* - \rho_{wh}^*]S^* \tag{7}$$

where $\Lambda_0(H^+,OH^-)$ is the limiting equivalent conductance (cm^2 ohm^{-1} equiv^{-1}), $\Lambda_0^*(H^+,OH^-)$ is $\Lambda_0(H^+,OH^-)$/(cm^2 ohm^{-1} equiv^{-1}), ρ_w is the density of water (g cm^{-3}), $\rho_w^* = \rho_w$/(g cm^{-3}), ρ_{wh} is the hypothetical density (g cm^{-3}) at $\Lambda_0(H^+,OH^-) = 0$, $\rho_{wh}^* = \rho_{wh}$/(g cm^{-3}), S is the slope of $\Lambda_0(H^+,OH^-)$ vs. density (cm^5 ohm^{-1} equiv^{-1} g^{-1}), and $S^* = S$/(cm^5 ohm^{-1} equiv^{-1} g^{-1}).

Values of $\Lambda_{00}(H^+,OH^-)$ and of ρ_{wh} as a function of temperature, as given in Table I, were fitted, respectively, to the following two empirical equations

$$\Lambda_{00}^*(H^+,OH^-) = 1850 - 1/[1/1410 + A_1t^* + A_2t^{*2} + A_3t^{*3} + A_4t^{*4}] \tag{8}$$

$$\rho_{wh}^* = 16.0 - 1/[1/11.6 + B_1t^* + B_2t^{*2} + B_3t^{*3}] \tag{9}$$

where the slope S^* of eq 7 equals $-\Lambda_{00}^*/\rho_{wh}^*$, t is temperature (°C), t^* equals t/°C, and the parameters determined by a method of nonlinear least squares (*20*) are given as A_1 = +2.164 17 E-6; A_2 = +1.816 09 E-7; A_3 = −1.752 97 E-9; A_4 = +7.207 08 E-12; B_1 = +3.26 E-4; B_2 = −2.30 E-6; and B_3 = +1.10 E-8, where E represents the base 10 of the exponent (thus, 1.0 E-2 = 0.01). Equations 8 and 9 fit the Table I values of $\Lambda_{00}(H^+,OH^-)$ and ρ_{wh} with an average deviation of 0.3% and 1.0%, respectively. The full equation for the electrical conductance of water is given in the next section.

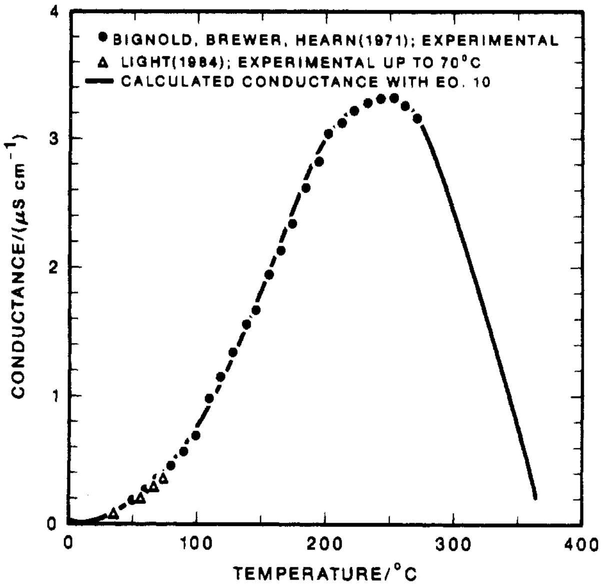

Figure 7. Comparison of the experimental values of water conductance of Bignold et al. (*1*) from 50 to 271 °C and Light (*2*) to 70 °C with the present values calculated from eq 10.

3. The Equation for the Electrical Conductance of Water

The equation for calculating the electrical conductance of liquid water (below 374 °C) and of supercritical fluid at pressures up to an estimated 1000 MPa is given as

$$\kappa_w^* = \Lambda_0^*(H^+,OH^-)K_w^{*1/2}(0.001)\rho_w^* \tag{10}$$

where κ_w is the specific conductance of water (ohm^{-1} cm^{-1}), $\kappa_w^* = \kappa_w$/(ohm^{-1} cm^{-1}), K_w is the ion product of water (mol kg^{-1})^2, and $K_w^* = K_w$/(mol kg^{-1})^2.

An equation released by the International Association for the Properties of Steam (IAPS) describing K_w^* as a function of temperature and density over the ranges proposed in this paper is available elsewhere (*3*). Needed values of ρ_w^* as a function of pressure and temperature are available from the 1984 International Formulation Committee Steam Tables (IAPS) (*21*), from which the IAPS equation for ρ_w^* (*22*) can be introduced directly into eq 10 above.

The values of $\Lambda_0(H^+,OH^-)$ obtained by summing the published, evaluated values of $\lambda_0(H^+)$ and $\lambda_0(OH^-)$ are believed to be accurate to 1%, and the methods by which the descriptions of $\Lambda_0(H^+,OH^-)$ as a function of temperature and pressure were deduced are described in Figures 1–6. The equations used are at this time empirical, and the only necessary condition suggested is that the equation given for $\Lambda_0(H^+,OH^-)$ reasonably describes the conductance behavior over the *limited* range of density for each temperature as shown in Figure 6. Again, the forms of eq 7–9 may not necessarily represent behavior outside the indicated boundaries but to this author they would appear to provide a representation *within the boundaries* within 1% to 5% of the values of $\Lambda_0(H^+,OH^-)$. The user, however, may wish to decide personally on the extent of acceptance outside the range of experimental data, and where values of $\Lambda_0(H^+,OH^-)$ can be deduced directly from experiment.

The uncertainties of eq 10 must also incorporate those of $K_w^{*1/2}$. By applying the uncertainties in log K_w^* stated elsewhere (*3*), eq 10 is estimated to describe to ±1 to ±5% the specific conductance of liquid water up to 374 °C and perhaps up to 1000 MPa. The uncertainties probably will increase from 5% at the low temperatures to perhaps 15% at the highest temperatures and pressures.

Table II. Specific Conductance/(μS cm^{-1}) of Liquid and Supercritical Water Calculated by the Conductance Equation, 0–1000 °C, up to 1000 MPa (10 kbar)

	temp/°C								
press./MPa	0	25	100	200	300	400	600	800	1000
satd vap	0.0115	0.0550	0.765	2.99	2.41				
50	0.0150	0.0686	0.942	4.08	4.87	1.17	$(2.15 \times 10^{-4})^a$	$(2.22 \times 10^{-5})^a$	$(6.16 \times 10^{-6})^a$
100	0.0189	0.0836	1.13	5.22	7.80	4.91	0.134	6.94×10^{-3}	1.40×10^{-3}
200	0.0275	0.117	1.53	7.65	14.1	14.3	4.65	0.831	0.198
400	0.0458	0.194	2.45	13.1	28.9	39.2	33.8	17.8	8.20
600	0.0667	0.291	3.51	19.5	46.5	71.3	85.7	65.4	41.6
800	*b*	0.416	4.67	26.7	66.9	110	159	148	112
1000	*b*	*b*	5.92	34.8	90.2	155	253	268	230

[a] Values in parentheses are for very low fluid densities (0.08–0.16 g cm^{-3}) and they may have much higher uncertainties of extrapolation than estimated in text. [b] Ice at these pressures and temperatures (applies to Figures 1–3 and 6).

4. Comparison with Experiment, and the Calculated Values

Figure 7 shows a plot of the experimentally determined conductances of Bignold et al. (*1*) at saturated vapor pressures. The curve drawn was calculated by eq 10, and this curve also closely reproduces the experimental values of Light (*2*) to 70 °C. Light gives several equations to describe conductances of water under saturated vapor up to 300 °C, and the curve by eq 10 also closely fits the calculated curves of Light. The fit of eq 10 to these measurements and other calculations is well within the above-stated limits of accuracy.

Table II provides representative values of the specific conductance of water in μS cm^{-1} (10^{-6} ohm^{-1} cm^{-1}) calculated by eq 10 by using the 1984 International Formulation Committee Steam Tables equations for the pressure–volume–temperature behavior of water substance, as published elsewhere by Haar, Gallagher, and Kell (*22*).

5. Reduced-State Equation and Other Observations

Equation 6 for any particular electrolyte (including also water in the sense of this description) may be written in a reduced form

$$\Lambda_{0r} = 1 - \rho_r \tag{11}$$

where, at a given temperature, Λ_{0r} equals Λ_0/Λ_{00} and ρ_r equals ρ/ρ_h and where, for NaCl, HCl, and NaOH, the respective values of ρ_h (1.65, 3.70, and 2.46 g cm^{-3}) are essentially independent of temperature. From plotting limiting equivalent conductances of NaBr (*13*), NaI (*9*), HBr (*14*), $CaCl_2$ (*11*), and $MgCl_2$ (*11*) vs. density (at temperatures up to 400 °C), values of ρ_h for these electrolytes of 1.65 (NaBr), 1.62 (NaI), 1.85 ($CaCl_2$), 1.75 ($MgCl_2$), and 3.46 (HBr) are obtained. These values of ρ_h for the salts are close to that of 1.65 for NaCl (Figure 1). Also, ρ_h for HBr is close to that for HCl (Figure 2). The corresponding values of Λ_{00} for the above salts agree within 1.5% of those for NaCl given in Table I while values of Λ_{00}(HBr) also agree within 1.5% of those for HCl in Table I. These agreements suggest the closeness to a universal relationship for the salts described by eq 11. The strongly differing values of Λ_{00} and of ρ_h for the acids and bases compared with the salts, however, modify the proposed universal relationship as discussed below and soon to be presented in some detail (*23*).

In contrast to the above behavior for salts at temperatures below 400 °C, the marked change in ρ_{wh} (for H^+, OH^-) with rising temperature and the differing values of Λ_{00} for (H^+,OH^-), HCl, and NaOH (Table I) is most certainly due to the effect of solvent hydrogen bonding on the mechanisms of conductance by H^+ and OH^- ions, with perhaps the major effect exhibited by the H^+ ion. At 400 °C and above, the effect of hydrogen bonding may have essentially disappeared; Λ_{00}(H^+,OH^-) thus approaches the same value as for the salts, and ρ_{wh} appears to change insignificantly above this temperature (Table I). Nevertheless, the smaller values for *S* above 400 °C than for the salts may still reflect differing intrinsic properties of the H^+ and OH^- ions.

It would seem that values of ρ_h for HCl (also for HBr) and NaOH should also change markedly with temperature, but significant changes do not occur (Figures 2 and 3). This differing behavior can be rationalized by considering that both the hydrogen and hydroxide ionic conductances at a constant temperature show only a small change with increasing density, as indicated in Figures 4 and 6, and thus the major change is due to the chloride ion (for HCl) and sodium ion (for NaOH).

Since a limiting equivalent conductance for an electrolyte under a given condition of temperature and density is the sum of the separate ionic conductances, each isothermal straight line in Figures 1–3 could be described explicitly by separate lines for ionic conductances (if they were known as a function of density). However, from the observations, it can be reasoned that the separate lines (for each ionic conductance) *cannot* reach values of zero conductance at the same value of ρ_h obtained from the behavior of Λ_0 for each separate electrolyte as described in Figures 1–3. Otherwise, *all* acids, bases, and salts would show the same quantitative behavior and approach the *same* common value of ρ_h. Since they do not all approach a common value (Figures 1–3 and the examples of other electrolytes cited above), it has to be reasoned that the values of ρ_h (Table I) are simply parameters in the descriptive equations, and that actual conductances cannot follow a straight line throughout to this high density "limit" even if "achievable".

Nevertheless, eq 11 and the preceding equations would appear to be fully valid in the generally feasible, experimental ranges of density, that is, up to about 1.25 g cm^{-3}. In this respect, it should be noted that the observed relationships do not follow the generally applied Walden's rule, which states that the product of limiting conductance and solvent viscosity is approximately a constant that is somewhat independent of temperature. Theoretical evaluation of eq 11, and the nature of changing ionic and molar conductances with increasing density and changing temperature, is a challenging endeavor. Some thoughts concerning this will be presented shortly (*23*).

6. Conclusion

An equation based on experimental correlations is presented for calculating the electrical conductance of liquid and supercritical water over a wide range of temperature and pressure. The observed, apparent straight-line relationship of limiting equivalent conductance vs. density, applied within the equation, can be expressed as a reduced-state relationship. An immediate, practical use of the equation is the calculation of the (background) conductance of water for estimating very low concentrations of electrolyte impurities in steam generator water–steam cycles. The equation can also be applied to the

J. Chem. Eng. Data **1987**, *32*, 226–229

many fundamental studies of systems involving water as a reactant, qualified by the possible uncertainties of extrapolation into regions where experimental and/or correlating data do not exist.

Acknowledgment

The work presented was initiated through participation in the Working Groups of the International Association for the Properties of Steam, and I thank the two groups for their many fruitful suggestions. It is a pleasure to acknowledge the many discussions with John M. Skarpelos (General Electric Co., San Jose, CA) and his critical analyses and checks of the equations and calculations. I also thank Truman S. Light (The Foxboro Co., Foxboro, MA) for his helpful comments and Howard F. Holmes (ORNL) for his most constructive reviews of early versions of the manuscript.

Literature Cited

(1) Bignold, G. C.; Brewer, A. D.; Hearn, B. *Trans. Faraday Soc.* **1971**, *67*, 2419.
(2) Light, T. S. *Anal. Chem.* **1984**, *56*, 1138.
(3) Marshall, W. L.; Franck, E. U. *J. Phys. Chem. Ref. Data* **1981**, *10*, 295.
(4) Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1965**, *69*, 2984.
(5) Franck, E. U. *Z. Phys. Chem., N. F.* **1956**, *8*, 192.
(6) Franck, E. U. *Z. Phys. Chem. N. F.* **1956**, *6*, 107.
(7) Franck, E. U. *Z. Phys. Chem. N. F.* **1956**, *8*, 92.
(8) Dunn, L. A.; Marshall, W. L. *J. Phys. Chem.* **1969**, *73*, 2619.
(9) Dunn, L. A.; Marshall, W. L. *J. Phys. Chem.* **1969**, *73*, 723.
(10) Frantz, J. D.; Marshall, W. L. *Am. J. Sci.* **1984**, *284*, 651.
(11) Frantz, J. D.; Marshall, W. L. *Am. J. Sci.* **1982**, *282*, 1666.
(12) Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1968**, *72*, 3122.
(13) Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1968**, *72*, 2100.
(14) Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1968**, *72*, 1545.
(15) Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1968**, *72*, 684.
(16) Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1968**, *70*, 3714.
(17) Yeatts, L. B.; Marshall, W. L. *J. Phys. Chem.* **1972**, *76*, 1053.
(18) Yeatts, L. B.; Dunn, L. A.; Marshall, W. L. *J. Phys. Chem.* **1971**, *75*, 1099.
(19) Marsh, K. N.; Stokes, R. H. *Aust. J. Chem.* **1964**, *17*, 740.
(20) Lietzke, M. H., Oak Ridge National Laboratory Report ORNL-3259, 1962.
(21) International Formulation Committee 1984 Steam Tables of the International Association for the Properties of Steam, 1984.
(22) Haar, L.; Gallagher, J. S.; Kell, G. S. *NBS/NRC Steam Tables*; Hemisphere: Washington, DC, 1984.
(23) Marshall, W. L., submitted for publication in *J. Chem. Phys.*

Received July 28, 1986. Accepted February 3, 1987. This study was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

Vapor–Liquid Equilibrium of the Mixtures 2-Furaldehyde/1-Butanol and 2-Furaldehyde/4-Methyl-2-pentanone

Torsten Hauschild,[†] **Huey S. Wu, and Stanley I. Sandler***
Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

Low-pressure isothermal vapor–liquid equilibrium has been measured for pure 2-furaldehyde and for 2-furaldehyde separately with 1-butanol and 4-methyl-2-pentanone. Because of the ease with which 2-furaldehyde both oxidizes and autoxidizes, special handling methods had to be developed. Activity coefficients derived from our data have been correlated with five thermodynamic models and used to estimate UNIFAC group contribution parameters.

Introduction

Furfural or 2-furaldehyde is used in many industrial processes, including as a selective solvent for separating saturated from unsaturated hydrocarbons, in the extractive distillation of C_4 and C_5 hydrocarbons, and as a chemical from which a variety of aliphatic and heterocyclic compounds can be synthesized. In the UNIFAC (*1*, *2*) group contribution method of predicting activity coefficients, furfural is treated as a single group. In spite of its industrial importance, relatively few data on the binary vapor–liquid of mixtures containing furfural appear in the literature (*3*). Thus, UNIFAC parameters are not available for the interactions of many groups with furfural. For this reason we chose to measure the vapor–liquid equilibrium of furfural with an alcohol and a ketone, each along two isotherms. There are no previously reported data for the systems we have measured.

Experimental Section

The general equipment and procedures we used have been discussed previously (*4*). Therefore, the discussion here will be mainly concerned with the special problems and procedures involved in using furfural. Furfural is an extremely hazardous chemical (2 ppm allowable exposure concentration over an 8-h day); in addition, it is easily absorbed through the skin and dangerous to the eyes. Furfural is not very stable; it is especially susceptible to oxidation, though it also decomposes by reactions with acid and by heat (*5–7*). A very sensitive indication of oxidation is a change in color. Immediately after purification (using a 13-stage Oldershaw column at low pressure under a nitrogen blanket) a clear liquid was obtained. Upon exposure to even small amounts of oxygen, the color changed to yellow, and then yellow/brown in several hours at room temperature, and more rapidly at elevated temperatures. Using a gas chromatograph/mass spectrograph unit, we have found that the main oxidation product is 2-fuoric acid. We tried several oxidation reaction inhibitors as suggested by Dunlop et al. (*5*) including triethylamine, tripropylamine, and hydroquinone but all were ineffective at the temperatures of our experiments.

Several major changes in our equipment and operating procedure had to be made in order to make the measurements we report here. First, all traces of water and oxygen had to be kept out of the system. This included even trace amounts used in the nitrogen blanket in the purification and measurement steps. Thus we started with Grade 5 nitrogen, which was then passed through a steel column containing one layer of manganese(II) oxide and another of molecular sieves, before entering our system. Second, tubing to permit the direct transfer

---

[†] Permanent address: Institute for Thermodynamics and Plant Design, Technical University of Berlin, D-1000 Berlin 12, West Germany.

0021-9568/87/1732-0226$01.50/0