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Effect of Pressure and Temperature on the Conductivity and Ionic Dissociation of Water up to 100 kbar and 1000°C*

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The effect of pressure and temperature on the equivalent conductance of water is derived from recent conductivity measurements. The results together with experimental data on the ionic conductivity of water at temperatures up to 1000°C and pressures up to 100 kbar are discussed. The ionic product of water and the corresponding thermodynamic data for water dissociation at high pressures and temperatures are derived.

I. INTRODUCTION

The knowledge about the properties of liquids and liquid solutions has been extended substantially during the last years because of developments in high-pressure techniques.

Shock-wave experiments[1–5] and static measurements of the ionic conductivity[6,7] of water at high pressures and temperatures indicated that the ionic dissociation of water increases steeply with rising pressure and temperature. Recent conductivity measurements at intermediate pressures[8] and the determination of the pressure and temperature dependence of the equivalent conductance of water make it possible to deduce quantitatively the ionic products of water for a wide pressure and temperature range.

II. CONDUCTIVITY OF WATER

The conductivity of pure water σw can be expressed in terms of equivalent conductances, λ_{H^+} and λ_{OH^-}, and concentrations, c_{H^+} and c_{OH^-}, of the hydrated H^+ and OH^- ions:

$$\sigma w=\lambda_{H^+}c_{H^+}+\lambda_{OH^-}c_{OH^-}. \qquad (1)$$

The concentrations are related to the ionic product Kw by

$$Kw=f_{H^+}f_{OH^-}c_{H^+}c_{OH^-}.$$

The activity coefficients f_{H^+} and f_{OH^-} are equal to 1 at infinite dilution. An estimate shows that the value of the activity coefficients at 1 atm and 25°C corresponding to the ion concentrations $c_{H^+}=c_{OH^-}=10^{-7}$ mole/liter is only 0.04% smaller than 1. The decrease of the activity coefficients caused by the higher ion concentrations at higher pressures and temperatures is likewise negligible within the experimental accuracy. For similar reasons, the "limiting equivalent conductance of water," $\Lambda w^0=\lambda_{H}{}^{+0}+\lambda_{OH}{}^{-0}$, can be used, neglecting

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[1] H. D. David and S. D. Hamann, Trans. Faraday Soc. **55**, 72 (1959).

[2] H. D. David and S. D. Hamann, Trans. Faraday Soc. **56**, 1043 (1960).

[3] S. D. Hamann and M. Linton, Trans. Faraday Soc. **62**, 2234 (1966).

[4] M. M. Yuknavech, Ballistic Research Laboratories, Aberdeen Proving Ground, Md., Memorandum Rept. No. 1563 (1964).

[5] A. A. Brish, M. S. Tarasov, and V. A. Tsukerman, Sov. Phys.—JETP **11**, 15 (1960).

[6] T. E. Gier and H. S. Young, reported by Lawson and Hughes in *High Pressure Physics and Chemistry*, R. S. Bradley, Ed. (Academic Press, London, 1963), Vol. 1, p. 215.

[7] W. Holzapfel and E. U. Franck, Ber. Bunsenges. Physik. Chem. **70**, 1105 (1966).

[8] K. Mangold, dissertation, Universität Karlsruhe, 1967.

corrections for finite ion concentrations. This gives for the present purpose

$$\log\sigma w = \log\Lambda w^0 + \tfrac{1}{2}\log Kw. \qquad (2)$$

Values of Λw^0 at temperatures up to 300°C and at densities between 0.75 and 1.1 g cm^{-3} are available from recent conductivity measurements on acids, bases, and salt solutions at high pressures and temperatures.[9–11] As shown by the different notations in Fig. 1, the density or pressure dependence of Λw^0 at constant temperature is surprisingly small in the measured range. An explanation for this unusual behavior results from the assumption that the decrease of the "normal" mobility of the H^+ and OH^- ions with pressure is just compensated by the increase of the "extra" mobility.[9]

The temperature dependence of Λw^0 may be fitted by the equation

$$\Lambda w^0(T) = 3.4 \times 10^{-100°K/(T-175°K)} \text{ liters}/\Omega\cdot\text{cm}\cdot\text{mole}, \qquad (3)$$

which is represented by the straight line in Fig. 1.

At lower pressures and temperatures, where small amounts of dissociating impurities make a direct measurement of σw very difficult, some values of σw are calculated from the available Kw values. The early results of Noyes *et al.*[12] and later measurements of higher precision in the lower temperature range[13–16] determined the variation of Kw along the coexistence curve of liquid water and steam up to 306°C. The increase of Kw with increasing pressure up to 2 kbar at room temperature was measured by Hamann.[17] The corresponding σw values are shown by squares and triangles in Fig. 2.

At higher pressures and temperatures one principal problem of static conductance measurements is still the possible influence of impurities.

Gier and Young,[6] using a platinum cell with sapphire insulators, therefore regarded their measured values only as upper limits for the conductivity of pure water, bearing in mind especially some possible contributions from soluted and disassociated Al_2O_3. Their values are shown by open circles in Fig. 2. Similarly Mangold's measurements, shown by heavy dots in Fig. 2, represent at least an upper limit for σw. From an experimental point of view it seems that the good reproducibility, found by Mangold[8] for his measurements above 600°C and 6 kbar compared with the poor reproducibility and time dependence below 300°C, indicates that the conductivity in these measurements above 600°C and 6 kbar was essentially because of the dissociation of the water itself.

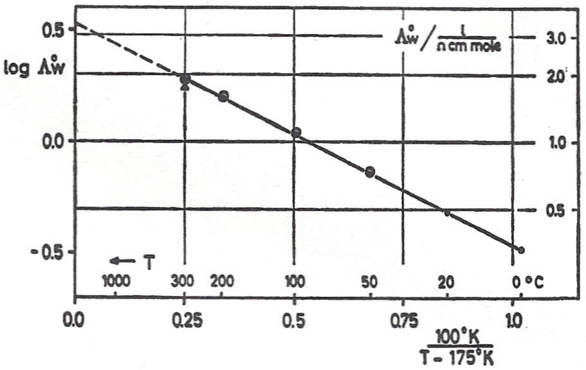

FIG. 1. Equivalent conductance of water at high pressures and temperatures. Experimental values for different densities: △ at 0.75, ● at 1.0, and ○ at 1.1 g cm^{-3} (from Refs. 9 and 10).

In the highest pressure range, the conductivity measurements under static pressures by Holzapfel and Franck,[7] indicated by crosses in Fig. 2, can be compared with shock-wave results of different groups.[1–6] The mean values of Hamann and Linton[3] are indicated by points with surrounding circles. Yukhnavech's values[4] are represented by the open hexagons. The larger scatter of the shock-wave data below about 400°C may possibly be explained by partial freezing or by effects of the short measuring time, which could be too small in this range of higher viscosity to attain the equilibrium of the ionic dissociation. Since the possible effect of impurities can be avoided in the shock-wave experiments, these results may rather be considered as lower limits for σw.

Regarding all the experimental problems not only of the shock-wave technique but also of the static measurements at the highest pressures, it seems that the agreement between both results is fairly good.

The density dependence of the different sets of conductivity data can be interpolated by an equation of the form

$$\log\sigma w(\rho, T) = [A + (B\rho/\rho_0)]\log(\rho/\rho_0) + \log\sigma w(\rho_0, T). \qquad (4)$$

The slope at $\rho=\rho_0=1.0$ g cm^{-3} results $A+B=9.7\pm0.5$. The less well-determined curvature gives $B=2.5\pm1$. The interpolating curves in Fig. 2 correspond to $A=7.2$ and $B=2.5$ and indicate that no temperature dependence of A or B is necessary within the present experimental accuracy. The boundaries of the liquid

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[9] E. U. Franck, D. Hartmann, and F. Hensel, Discussions Faraday Soc. **39,** 200 (1965).

[10] E. U. Franck, H. Renkert, G. Ritzert, W. von Osten, and G. Treiber (to be published); H. Renkert, diplomarbeit, Universität Karlsruhe, 1965; G. Ritzert, dissertation, Universität Karlsruhe, 1965; W. von Osten, diplomarbeit, Universität Karlsruhe, 1966; G. Treiber, diplomarbeit, Universität Karlsruhe, 1967.

[11] A. S. Quist and W. L. Marshall, J. Phys. Chem. **69,** 3165 (1965).

[12] A. A. Noyes, K. Yogoro, and R. B. Sosman, Z. Physik. Chem. **73,** 1 (1910).

[13] H. S. Harned and R. A. Robinson, Trans. Faraday Soc. **36,** 973 (1940).

[14] K. Schwabe, Chem. Tech. Berlin **11,** 554 (1959).

[15] J. W. Cobble, J. Am. Chem. Soc. **86,** 5399 (1964).

[16] A. K. Covington, R. A. Robinson, and R. G. Bates, J. Phys. Chem. **70,** 3820 (1966).

[17] S. D. Hamann, J. Phys. Chem. **67,** 2233 (1963).

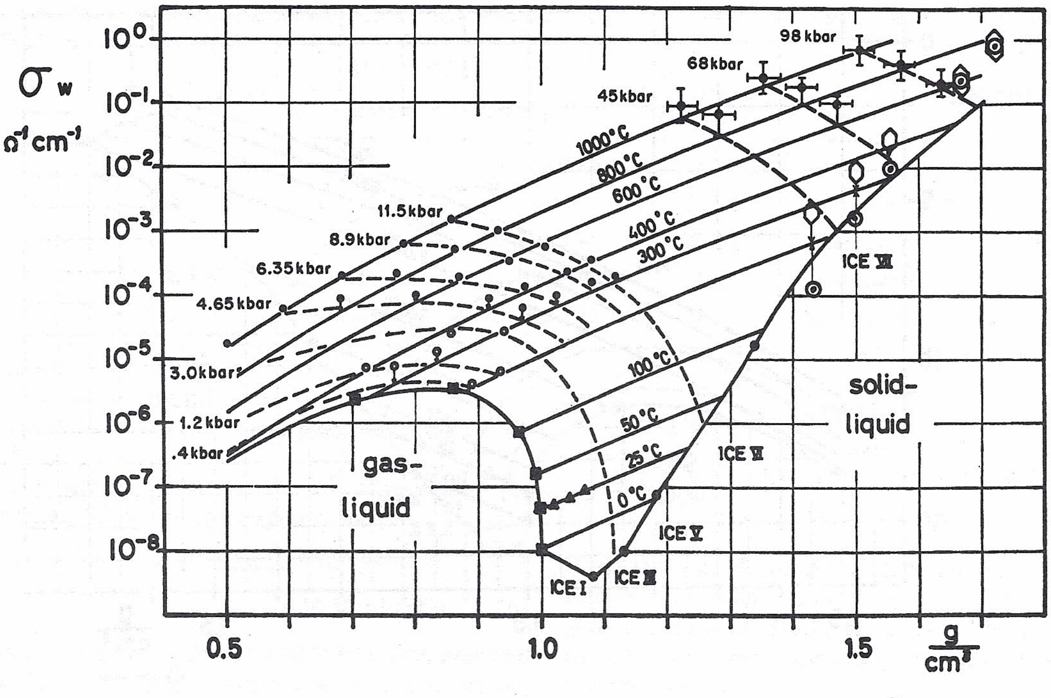

FIG. 2. Conductivity of water measurements at static high pressures: open circles, Gier and Young[6]; filled circles with horizontal and vertical error bars, Holzapfel and Franck[7]; filled circles, Mangold.[8] Shock-wave data: open circle with dot, Hamann and Linton[3]; hexagon, Yuknavech.[4] Values calculated from Kw: filled squares, Noyes *et al.*[12]; filled triangles, Hamann.[17]

phase are determined from the phase diagram[18–21] with corresponding *PVT* data.[22–28]

III. IONIC PRODUCT

For densities between 0.5 and 1.8 g cm^{-3}, the pressure dependence of $\log\Lambda w^0$ is at least an order of magnitude smaller than the pressure dependence of $\log\sigma w$. A good approximation for the density dependence of the ionic product Kw results therefore from the combination of Eqs. (2) and (4) in the form

$$\log Kw(\rho,T)=2[A+(B\rho/\rho_0)]\log(\rho/\rho_0)+\log Kw(\rho_0,T). \tag{5}$$

The temperature dependence of $\log Kw(\rho_0, T)$ at the density $\rho_0=1.0$ g cm^{-3} can be derived in the lower-temperature range from the Kw values along the coexistence curve,[12–16] when the corrections for higher density use Hamann's results.[17] These values are shown in Fig. 3 by dots. Values of $\log Kw(\rho_0, T)$ at higher temperatures are derived from the conductivity data Fig. 2 using Eqs. (2) and (3). These points are indicated in Fig. 3 by circles with estimated error bars.

These possible errors result from the uncertainty of the conductivity measurements and above 300°C additionally from the extrapolation of Λw^0. As suggested by Fig. 1, it seems very plausible that the accuracy of

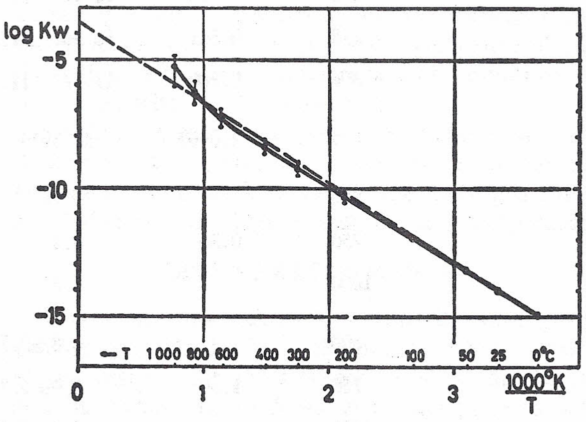

FIG. 3. Temperature dependence of $\log Kw$ at constant density $\rho=1.0$ g cm^{-3} (Kw in square moles per square liter). Open circles are from atmospheric[12–17] with corrections for constant density. Filled circles with vertical error bars, derived from conductivity data; solid line, interpolated by Eq. (6); dashed line, interpolated by Eq. (7).

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[18] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **47**, 441 (1911).

[19] P. W. Bridgman, J. Chem. Phys. **5**, 969 (1937).

[20] C. W. F. T. Pistorius, M. Pistorius, J. B. Blakey, and L. J. Admiral, J. Chem. Phys. **38**, 600 (1963).

[21] W. Holzapfel, J. Phys. Chem. Solids (to be published).

[22] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **74**, 419 (1942).

[23] H. M. Rice and J. M. Walsh, J. Chem. Phys. **26**, 815 (1957).

[24] W. T. Holser and G. L. Kennedy, Am. J. Sci. **257**, 71 (1959).

[25] W. E. Sharp, UCRL-7118, University of California, Los Angeles, Calif., 1962.

[26] E. Schmidt, *VDI-Wasserdampftafel 6. Auflage* (Springer-Verlag, Berlin, 1963).

[27] S. Maier and E. U. Franck, Ber. Bunsenges. Physik. Chem. **70**, 639 (1966).

[28] R. Vedam and G. Holton, J. Acoust. Soc. Am. **43**, 108 (1968).

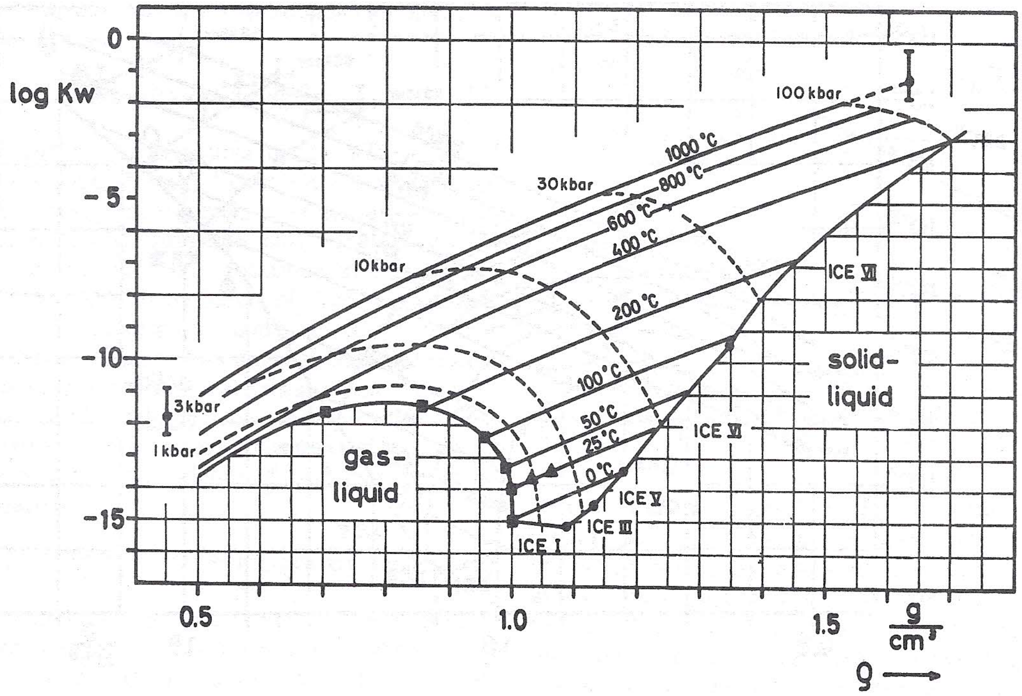

FIG. 4. Ionic product of water: ■ Measurements of Noyes *et al.*,[12] ▲ Measurements of Hamann,[17] —— calculated from conductivity data by Eq. (5) with Eq. (6), ● Water–ice triple points. logKw is in square moles per square liter.

TABLE I. Comparison of logKw values from different authors.

T (°C)	ρ (g cm^{-3})	$-\log Kw$ Literature	Kw (moles^2 liter^{-2}) Eq. (6)	Eq. (7)	Estimated error ±
0	0.9999	14.928[a]	14.91	14.928	0.01
25	0.9971	14.000	14.00	14.000	0.01
50	0.9880	13.272	13.29	13.272	0.01
100	0.958	12.32[b] 12.27[c]	11.28	12.25	0.03
218	0.843	11.34 11.36	11.37	11.31	0.06
306	0.700	11.77 11.4	11.86	11.79	0.1
25	1.0707	13.397[d]	13.39	13.397	0.01
500		9.7[e]	9.5	9.4	0.3
750	0.80	8.2	8.4	8.4	0.5
1000		7.3	7.1	7.8	0.7
500		2.8±0.7[f]	3.7	3.6	0.4
750	1.50	1.9±0.7	2.5	2.6	0.6
1000		1.2±0.7	1.3	2.0	0.8

[a] Reference 16.
[b] Reference 12.
[c] Reference 14.
[d] Reference 17.
[e] E. U. Franck, Z. Physik. Chem. 8, 192 (1956).
[f] Reference 7.

TABLE II. Thermodynamic quantities for the self-dissociation of water (referring to the molarity scale. Errors are estimated.)

	At $T=25°C$, $P=1$ bar		At $T=500°C$ $\rho=1.0$ g cm^{-3}	
	from literature	from Eq. (7)	from Eq. (7)	Units
ΔU^0	...	14.22 ± 0.02	14.2 ± 3	kcal mole^{-1}
ΔV^0	20.4[a] 21.3[b]	21.4 ± 0.7	55 ± 5	cm^3 mole^{-1}
ΔG	19.099[c]	19.10 ± 0.01	26.6 ± 1	kcal mole^{-1}
ΔH	13.617[c]	13.60 ± 0.03	6 ± 3	kcal mole^{-1}
$\Delta S_P{}^0$	−18.39[c]	-18.45 ± 0.12	-27 ± 5	cal deg^{-1} mole^{-1}

[a] Reference 17. [b] Reference 30. [c] Reference 16.

the extrapolation of $\log\Lambda w^0$ even at 1000°C is better than ±0.2.

The full drawn curve in Fig. 3 interpolates the experimental values and corresponds to

$$\log Kw(\rho_0, T) = -(T_0/T) + \log(1+10^{5-(1.8T_0/T)}) + 10.30 + \log Kw_F. \quad (6)$$

with $Kw_F = Kw(1\text{ atm}, 25°\text{C}) = 10^{-14.000}$ mole^2/liter and $T_0 = 3063°$K. The upward curvature of this interpolation is not unreasonable and would correspond to an increase of the dissociation energy ΔU^0 with temperature.

Nevertheless, within the present experimental accuracy it is still possible to assume a constant dissociation energy ΔU^0. This gives

$$\Delta U^0/R\ln 10 = 3108.0°\text{K}$$

and

$$\log Kw(\rho_0, T) = (-\Delta U^0/RT\ln 10) + 10.450 + \log Kw_F \quad (7)$$

which corresponds to the straight line in Fig. 3.

In Table I values of $\log Kw$ from Eq. (5) plus either Eq. (6) or Eq. (7) are compared with some representative data from the literature. Estimated error limits are added. Especially at lower temperatures, where the experimental errors are small, Eq. (7) shows a clear superiority over Eq. (6). The differences at the higher temperatures give a measure of the actual uncertainty.

Figure 4 finally results from Eq. (5) with Eq. (7) by the use of PVT data[22–28] and the phase diagram[18–21] from literature. Some isobars, coexistence curves, error bars, and the earlier Kw values[12,17] are illustrated, too.

The thermodynamic data for the ionic dissociation of water can be derived, too, from Eq. (5) with either Eq. (6) or Eq. (7). Using the standard convention that the activity of water is 1 and Kw refers to the molarity scale, the following definitions are obtained:

$$\Delta U° = RT^2\ln 10(\partial\log Kw/\partial T)_\rho,$$

$$\Delta V° = -RT\ln 10(\partial\log Kw/\partial\rho)_T(\partial\rho/\partial P)_T,$$

$$\Delta G° = RT\ln 10(\log Kw),$$

$$\Delta H° = \Delta U^0 + RT^2\ln 10(\partial\log Kw/\partial\rho)_T(\partial\rho/\partial T)_P,$$

$$\Delta S_P° = (\Delta H° - \Delta G°)/T.$$

With the use of the PVT data for water from literature[22–28] the above equations with Eqs. (5) and (7) give the data of Table II. This table includes comparable data from literature[16,17,29] and an estimate of the possible errors.

IV. DISCUSSION

The present knowledge of the conductivity of pure water is shown in Fig. 2 with full regard to all the uncertainties of the available experimental data. The difference between the "interpolated curves" and some of the shock-wave data at intermediate temperatures seems to result from the proximity of these experimental points to the freezing curve. Shock-wave experiments along another Hugoniot curve, starting for instance at 100°C, or further static measurements could possibly resolve these uncertainties.

On the other hand, it appears that Eqs. (5) and (7) together with the corresponding thermodynamic data yield a better understanding of the particular temperature dependence of log Kw along the coexistence curve water–steam and of the physical significance of these data than the earlier interpretations. Equation (5) points explicitly to the density effects.

Finally, the pressure dependence of the conductivity data and of the related Kw values may have indicated how much such weak bonds as the hydrogen bridges are influenced by high pressures and temperatures.

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[29] A. Bodansky and W. Kauzmann, J. Phys. Chem. **66**, 177 (1962).