

# Ion product of water substance, 0–1000 °C, 1–10,000 bars New International Formulation and its background

Cite as: Journal of Physical and Chemical Reference Data **10**, 295 (1981); <https://doi.org/10.1063/1.555643>  
Published Online: 15 October 2009

William L. Marshall, and E. U. Franck



View Online



Export Citation

## ARTICLES YOU MAY BE INTERESTED IN

### The Ionization Constant of Water over Wide Ranges of Temperature and Density

Journal of Physical and Chemical Reference Data **35**, 15 (2006); <https://doi.org/10.1063/1.1928231>

### Static Dielectric Constant of Water and Steam

Journal of Physical and Chemical Reference Data **9**, 1291 (1980); <https://doi.org/10.1063/1.555632>

### The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use

Journal of Physical and Chemical Reference Data **31**, 387 (2002); <https://doi.org/10.1063/1.1461829>



# Ion Product of Water Substance, 0–1000 °C, 1–10,000 Bars

## New International Formulation and Its Background

William L. Marshall

*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830*

and

E. U. Franck

*Institute for Physical Chemistry and Electrochemistry, University of Karlsruhe  
7500 Karlsruhe, Federal Republic of Germany*

This paper is the background for a new international formulation for the ion product of water substance (May 1980) issued by the International Association for the Properties of Steam. The ion product of water ( $K_w$ ) is represented by an equation, based on density and two quadratic functions of reciprocal absolute temperature, for use from 0 to 1000 °C and 1 to 10,000 bars pressure. The equation is believed to describe within  $\pm 0.01$  units of  $\log K_w^*$  (where  $K_w^*$  equals  $K_w/(\text{mol kg}^{-1})^2$ ) many of the measurements at saturated vapor pressure up to 200 °C, and to within  $\pm 0.02$  units up to the critical temperature (374 °C). It also describes within the experimental uncertainty the several sets of measurements at high pressures and should provide values within  $\pm 0.05$  and 0.30 units at low and high temperatures, respectively.

**Key words:** Equation; formulation; high pressure; high temperature; International Association for the Properties of Steam; IAPS; ion product; ionization; ionization constant; review; water; water substance.

### 1. Introduction

During the Eighth International Conference on the Properties of Steam (Giens, France, September 1974), Working Group III of the International Association for the Properties of Steam (IAPS) was designated to establish representations of particular properties of water substance. One property studied was its ionization behavior for which an international formulation (release) has been issued (May 1980) by IAPS. Appendix 1 gives the release verbatim but with references to tables already included in this paper.

Needs have arisen for a general equation to describe the ionization behavior of water over wide ranges of temperature and pressure. Those concerned with mechanisms of corrosion and the chemistry of steam generators [7,21]<sup>1</sup> may require accurately calculated values of the ion product of water ( $K_w$ ), defined throughout this paper as the molality of hydrogen ion times the molality of hydroxide ion, in the temperature (300–600 °C) and pressure (100–500 bars) ranges of interest. (Because of the very low concentrations of ions over the full range considered (0–1000 °C, 1–10,000 bars), activities can be replaced by molalities.) Chemical oceanographers wish to calculate the ion product in water at both low and high

temperatures and pressures but with corrections for dissolved salt [44,45]. Similarly, hydrothermal geochemists are interested in a quantitative description of the ionic behavior of water in interpreting behavior of geothermal solutions [1,18]. To the aqueous electrolyte chemist, quantitative knowledge of  $K_w$  provides additional information for interpreting aqueous electrolyte behavior [12].

Many studies on the ion product of water at saturated vapor pressure have been published over the years. The experimental determinations of  $K_w$  at high temperatures started with the pioneering work of Noyes et al. [33,34] and have culminated with many relatively recent studies [2,8–10,13–15,19,20,26–28, 32,35,36,38,42,45]. Most of those appearing up to the year 1957 have been reviewed and referenced by Harned and Owen [16]. Clever made another review in 1968 [5]. Also, Cobble [6] in 1964 evaluated  $K_w$  at high temperatures along the liquid-vapor curve.

In most of the recent work on  $K_w$ , comparative figures and tables have been given. For example, Sweeton, Mesmer, and Baes [42], in presenting new, highly precise values and an excellent review, showed a deviation plot for  $\log K_w^*$  (where  $K_w^*$  in the present paper equals  $K_w/(\text{mol kg}^{-1})^2$ ) that compared several independent studies in the range, 0 to 300 °C. They gave an equation describing many measurements of  $\log K_w^*$  to  $\pm 0.02$  units along the liquid-vapor curve, and also at hydrostatic pressures up to 75 bars. Olofsson and Hepler [35], in another very good review, evaluated  $\log K_w^*$  both along the liquid-vapor curve and at high pressures and temperatures.

<sup>1</sup> Numbers in brackets indicate literature references.

Determinations of  $K_w$  at very high pressures are much less abundant because of the difficulties involved. At temperatures below 100 °C, however, the results of several important studies give confidence in establishing a quantitative variation of  $K_w$  with pressure [15,24,26,27,32,45].

At temperatures above 100 °C there are the recent studies at pressures up to 75 bars and 250 °C [42]. In the supercritical region there are studies of Quist to 4000 bars and 800 °C by electrical conductance measurements [38], of Holzapfel and Franck to 100,000 bars and 1000 °C by instantaneous static pressurization [20], and of Hamann et al. to 133,000 bars and 800 °C by explosion techniques [8,13,14].

The values of  $K_w$  at saturated vapor pressure by different investigators at temperatures up to 300 °C correlate well [42], as do those of Quist up to 800 °C. Those of Holzapfel and Franck and of Hamann also correlate sufficiently well although, as we can appreciate, there are relatively large uncertainties in values of  $K_w$  obtained at the extreme ranges of pressure.

In some of the recent papers, equations are presented to describe values of  $K_w$  (or  $\log K_w^*$ ) as functions of temperature and pressure. Generally, these equations contain many parameters which may present difficulties in predicting behavior outside the range of experiments. Helgeson and Kirkham [18] present calculations of  $\Delta V$  (the change in molar volume upon ionization) from which changes in  $\log K_w^*$  with pressure can be calculated. However, a value of  $\log K_w^*$  must be known at one pressure for calculating at other pressures. A recent equation of Svistunov et al. [41] relates  $\log K_w^*$  to a complex function of density, together with temperature, as does an equation of Holzapfel [19]. A simpler approach would appear to be that described by Franck [11] and later followed by Quist [38] and Sweeton, Mesmer, and Baes [42] for  $\log K_w^*$ , which applies the observed straight line relation of  $\log K^*$  (of ionization of a dissolved electrolyte or of water) plotted against  $\log \rho^*$  ( $\rho^*$ , where  $\rho^*$  equals  $\rho/(\text{g cm}^{-3})$ ) of the solvent.

The straight line relation was proposed by Franck [11] to describe the ionization behavior of both water and dissolved electrolytes at high temperatures. It was later applied at low temperatures by Marshall and Quist [30,31,40]. Water and many electrolytes conform well, the best adherence observed with the most precise values of  $\log K^*$ , for example, those at low temperature (0–100 °C). The value of the slope,  $(\delta \log K^*/\delta \log \rho_w^*)_T = k$ , appears to change only with temperature, and for neutral salts [39,46] and water [38] to become essentially independent of temperature above 350 °C.

The equation presented in this paper follows from the straight line relation from which the slope ( $k$ ) is obtained. The slope is obtained also from published values of the change in molar volumes upon ionization ( $\Delta V$ ) at atmospheric pressure whereby,

$$k = -\Delta V/(RT\beta) \quad (1)$$

where  $\beta$  is the coefficient of isothermal compressibility of the solvent at the pressure of interest,  $R$  is the gas constant,

and  $T$  is the absolute temperature [30b]. Values of  $\log K_w^*$  (where  $\rho_w^*=1$ ) are described as functions only of  $(1/T)^*$ . Values of  $\log K_w^*$  at given temperatures and pressures are calculated from values of  $\rho_w^*$  inserted directly into the equation,  $\log K_w^* = \log K_w'^* + k \log \rho_w^*$ , or from an equation of state to obtain  $\rho_w^*$  from pressure, available from several publications.

The present equation expands the one of Quist [38] to include parameters to account for changes in  $k$  with temperature (predominantly observed at low temperatures) and thereby to calculate more closely the observed values of  $\log K_w^*$  at low temperatures. The equation contains the same number of parameters (seven) as that of Sweeton, Mesmer, and Baes [42] applied to zero ionic strength, but appears to describe  $\log K_w$  over a wider range of temperature and pressure.

## 2. Graphical Description of the Ion Product

Experimental values of  $K_w$  (molal units) along the liquid-vapor saturated curve from the many studies mentioned above are well summarized by Sweeton, Mesmer, and Baes [42], and by Olofsson and Hepler [35]. The latter authors also summarize studies at very high pressures at both low and high temperatures. We have chosen to use the experimental values of Sweeton, Mesmer, and Baes as the baseline values at saturated vapor pressure (0–300 °C), believing that these measurements are the most accurate. Other comprehensive studies [2,9,10,16,17,29,33,34,37] at saturated vapor pressure generally fit within 0.04 logarithmic units of these values although the other studies were not used specifically in the evaluations. At high pressures at both low and high temperatures, there are several extensive sets of experimental values of  $K_w$  that should be considered. These sets are those of Linov and Kryukov [26], 18–75 °C, 1–8000 bars; Kryukov, Starostina, and Larionov [24], 25–150 °C, 1–6000 bars; Hamann [15], 25 °C, 1–2000 bars; Whitfield [45], 5–35 °C, 1–2000 bars; Quist [38], 300–800 °C, 1000–4000 bars; Holzapfel and Franck [20], to 1000 °C, 100,000 bars; and Hamann and Linton [13], to 804 °C, 133,000 bars.

Figures 1–4 show  $\log K_w^*$ , or the ratio,  $\log [K_w(P)/K_w(1)]$ , plotted against  $\log \rho_w^*$  for the values of Linov and Kryukov [26] at 18–75 °C, of Hamann [15] and of Whitfield [45] combined at 25 °C, of Whitfield at 5–35 °C, and of Quist [38] at 300 to 800 °C. Quist presented his values in units of (molarity)<sup>2</sup>, and they are converted to units of (molality)<sup>2</sup> for consideration here. Moreover, slopes based on  $K_w$  (molal basis) are two units less than those on a molar basis [30c]. For these plots and all later evaluations, densities were obtained from the 1967 IFC formulation [22] and from those of Burnham, Holloway, and Davis [3,4], Köster and Franck [23], and Maier and Franck [29] at the extremes of pressure and temperature. These sets of densities essentially agree with each other to much better than 1%. The plots generally show excellent straight line relations. It is significant to observe essential agreement with this relation in the results of Linov and Kryukov [26] at pressures even up to 8000 bars. The most recent values of Kryukov, Starostina, and

Larionov [24] also agree at temperatures up to 150 °C and pressures to 6000 bars.

Figure 5 shows the various values for the slopes from figures 1–4, obtained by least squares fitting, plotted against  $1/(T/K)$  (0–800 °C). Included also are values obtained by Sweeton, Mesmer, and Baes from measurements over a small range of pressure (up to 75 bars), and from values of  $\Delta V$  [35] by use of eq (1). The values of the slope ( $k$ ) from the results of Hamann [15] and Whitfield [45] at 25 °C (19.3 and 19.2, respectively) are very close to that of 19.7 calculated from a "best" value of  $\Delta V$  of 22.1 cm<sup>3</sup> mol<sup>-1</sup> [35]. The average of these three values is 19.4.

The values of  $k$  shown on figure 5, with some preference for 19.4 at 25 °C, were treated by a method of least squares [25] to yield parameters  $E$ ,  $F$ , and  $G$  of an empirical equation:

$$k = E + F/T + G/T^2 \quad (2)$$

where  $T$  is in kelvins. The curve as drawn on figure 5 corresponds to that from eq (2) and its obtained parameters.

With the observed relation,

$$\log K_w^* = \log K_w'^* (\rho_w^*=1) + k \log \rho_w^* \quad (3)$$

and the use of eq (2) for  $k$ , values of  $\log K_w'^* (\rho_w^*=1)$  were calculated from those for  $\log K_w^*$  of Sweeton, Mesmer, and Baes along the saturated curve from 25 to 300 °C. Values of  $\log K_w'^* (\rho_w^*=1)$  in the supercritical fluid region were extrapolated and interpolated from the values of  $\log K_w^*$  of Quist, 400–800 °C.

### 3. The Equation for $\log K_w^*$ and Comparison with Experiments

The resulting values of  $\log K_w'^* (\rho_w^*=1)$  plotted against  $1/(T/K)$  are shown on figure 6, and we observe that a straight line appears to be approached as the temperature continues to rise. The values shown were fitted to a cubic function of  $1/(T/K)$  to yield, together with eq (2), the following equation for  $\log K_w^*$  as a function of temperature and density.

$$\log K_w^* = A + B/T + C/T^2 + D/T^3 + (E + F/T + G/T^2) \log \rho_w^* \quad (4)$$

where

$$K_w^* = K_w/(\text{mol kg}^{-1})^2, \rho_w^* = \rho_w/(\text{g cm}^{-3})$$

and values for the parameters are

$$\begin{aligned} A &= -4.098 \\ B &= -3245.2 \text{ K} \\ C &= +2.2362 \times 10^5 \text{ K}^2 \\ D &= -3.984 \times 10^7 \text{ K}^3 \\ E &= +13.957 \\ F &= -1262.3 \text{ K} \\ G &= +8.5641 \times 10^5 \text{ K}^2 \end{aligned}$$

Table 1 compares values of  $\log K_w^*$  calculated by eq (4) with those presented by Sweeton, Mesmer, and Baes (SMB) at saturated vapor pressure. Some differences between other values calculated by eq (4) and experimentally obtained at high pressures and temperatures are shown in table 2. Included also in table 2 are comparisons with the values at extremely high pressures [13,20] which probably have relatively large uncertainties. Nevertheless, the very small differences (0.09–0.32 units) at 45 to 373 °C at pressures up to 71,000 bars are remarkable. The relatively large differences (1 to 3 units) in the supercritical region at the highest pressures and temperatures could result from uncertainties in estimating conductance, temperature, pressure, or density, from the use of molality rather than activity where  $K_w$  approaches a large value, or from applying eq (4) at pressures greatly in excess of 10,000 bars.

The best fit with eq (4) is certainly with the values of SMB from which parameters  $A$ ,  $B$ ,  $C$ , and  $D$  were chiefly obtained. Moreover, the SMB values are considered to be the most accurate. The part of eq (4) which expresses the variation of  $\log K_w'^* (\rho_w^*=1)$  with temperature,

$$\log K_w'^* (\rho_w^*=1) = A + B/T + C/T^2 + D/T^3 \quad (5)$$

approaches the straight line relation of an elementary Van't Hoff isochore as the temperature becomes very large, but where molar heat capacities are for constant volume and are assumed to be independent of temperature. The ability to extrapolate to high temperatures from accurate values of  $\log K_w'^*$  (constant density) at low temperatures becomes great.

Similarly, the form of eq (2) for  $k$  allows the approach to a straight line relation as the temperature rises. Again, the form of eq (2), relying for the most part on accuracy of values of  $k$  at low temperatures, should provide relatively good extrapolation at the high temperatures.

With the above considerations, it would appear that uncertainties in values of  $\log K_w^*$  calculated by eq (4) are less than those of experimentally determined values at the high temperatures and pressures. Accordingly, we believe that eq (4) describes  $\log K_w^*$  within  $\pm 0.01$  units at saturated vapor pressure and within  $\pm 0.03$  units at pressures up to 10,000 bars when the temperature is below 250 °C. At temperatures from 250 to 1000 °C and pressures up to 10,000 bars the equation may still provide accuracies of  $\pm 0.03$  to 0.10 units although upper limits of uncertainty at this time should probably be  $\pm 0.05$  to 0.3 units of  $\log K_w^*$ .

Some values of  $\log K_w^*$  calculated by eq (4) are tabulated in table 3. Table 4 gives calculated values of  $\log K_w^*$  (with eq (4)) in a limited range of temperature (300–600 °C) and pressure (100–500 bars) of particular interest to those concerned with power plant steam generators [21] and hydrothermal geochemistry [1]. Equation 4 may also be used to generate values of the other thermodynamic functions,  $\Delta G$ ,  $\Delta H$ ,  $\Delta E$ ,  $\Delta S$ ,  $\Delta V$ , at related temperatures and pressures. By differentiation at constant pressure, eq (4) yields an enthalpy of ionization ( $\Delta H$ ) of 55.65 kJ mol<sup>-1</sup> (13.30 kcal mol<sup>-1</sup>) at 25 °C and saturation vapor pressure. This value may be compared with 55.798 kJ mol<sup>-1</sup> (13.336 kcal mol<sup>-1</sup>) by

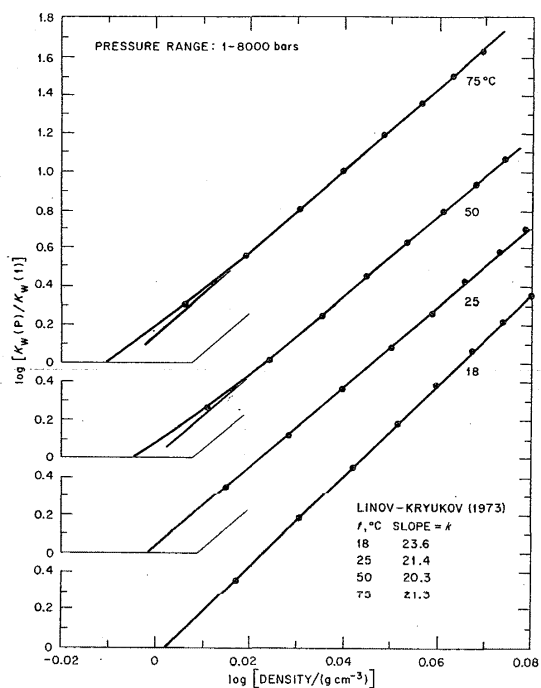


Figure 1. Observed  $\log [K_w(P)/K_w(1)]$  vs  $\log [\text{Density}/(\text{g cm}^{-3})]$  for Water; Values of Linov and Kryukov (1973), 1-8000 bars, 18-75°C,  $K_w/(\text{mol kg}^{-1})^2$ .

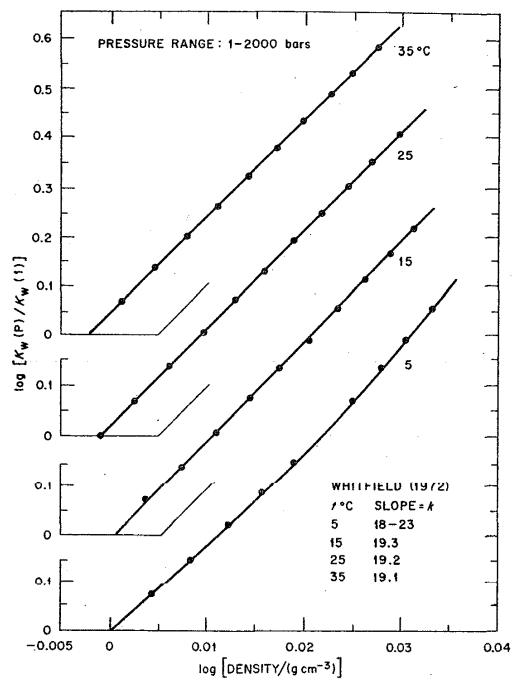


Figure 3.  $\log [K_w(P)/K_w(1)]$  of Whitfield (1972) vs  $\log [\text{Density}/(\text{g cm}^{-3})]$ ; 5-35°C, 1-2000 bars.

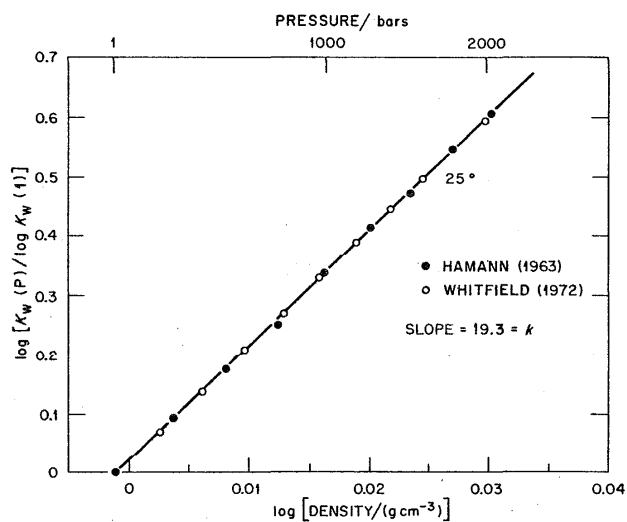


Figure 2.  $\log [K_w(P)/K_w(1)]$  of Hamann (1963) and Whitfield (1972) vs  $\log [\text{Density}/(\text{g cm}^{-3})]$ , 25°C.

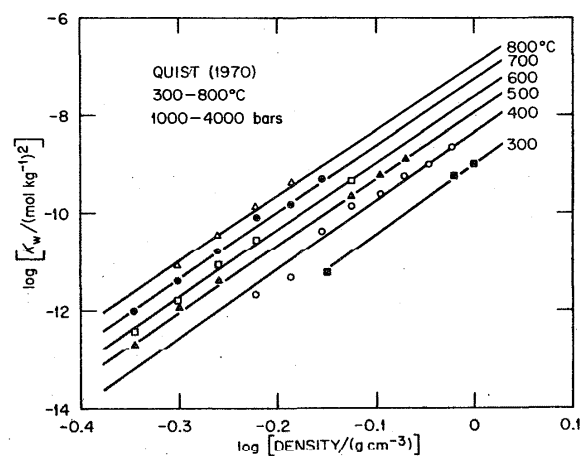


Figure 4. Observed  $\log [K_w/(\text{mol kg}^{-1})^2]$  for Water vs  $\log [\text{Density}/(\text{g cm}^{-3})]$ , Quist (1970); 300-800°C, 1000-4000 bars. Slopes (k) Drawn Calculated by Equation 2.

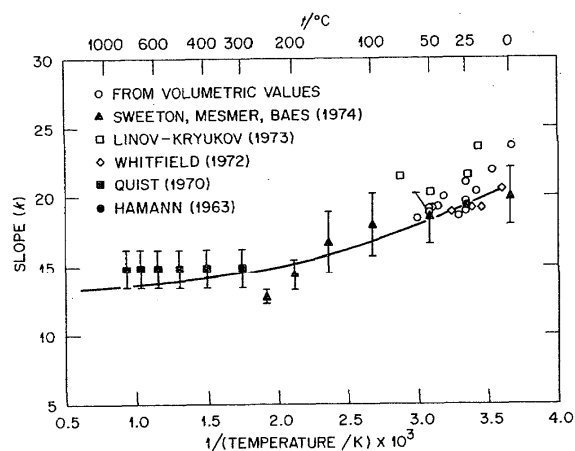


Figure 5. The Slope (k) of  $\log [\text{Ion Product of Water}/(\text{mol kg}^{-1})^2]$  vs  $\log [\text{Density}/(\text{g cm}^{-3})]$  Plotted Against  $1/(T/K)$ ; Curve Calculated by Equation 2.

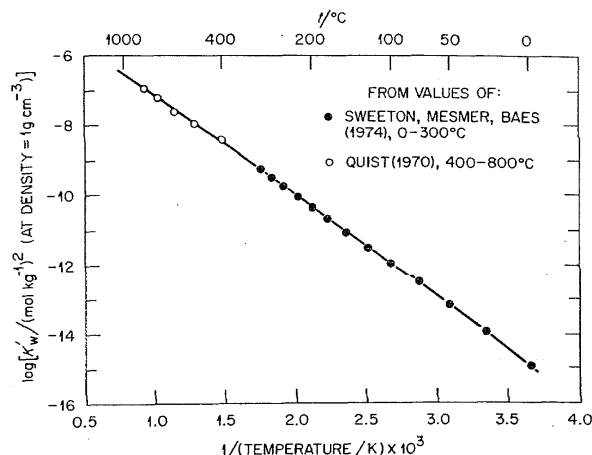


Figure 6.  $\log [K_w/(\text{mol kg}^{-1})^2]$  at a Density of  $1 \text{ g cm}^{-3}$  ( $\log K_w^*$ ) Plotted Against  $1/(T/K)$ , 0-1000°C; Curve Calculated by Equation 4.

Table 1. Comparisons of  $\log K_w^*$  (base 10) at Saturated Vapor Pressure Calculated by Equation 4 with those Calculated by Sweeton, Mesmer, and Baes (SMB)<sup>a,b</sup>

$t^\circ\text{C}$	$\log K_w^*$ (SMB)	$\log K_w^*$ (Calcd. by Eqn. 4)	Difference
0	-14.941	-14.938	-0.003
25	-13.993	-13.995	+0.002
50	-13.272	-13.275	+0.003
75	-12.709	-12.712	+0.003
100	-12.264	-12.265	+0.001
125	-11.914	-11.912	-0.002
150	-11.642	-11.638	-0.004
175	-11.441	-11.432	-0.009
200	-11.302	-11.289	-0.013
225	-11.222	-11.208	-0.014
250	-11.196	-11.191	-0.005
275	-11.224	-11.251	+0.027
300	-11.301	-11.406	+0.105

<sup>a</sup>Densities used were obtained from the 1967 Formulation for Industrial Use as prepared by the International Formulation Committee (IFC) [22]. This committee was established by the Sixth International Conference on the Properties of Steam (New York, October 1963). Steam tables based upon the 1967 IFC formulation are published in several member countries of the International Association for the Properties of Steam.

<sup>b</sup> $K_w^* = K_w/(\text{mol kg}^{-1})^2$ ;  $K_w$  in (molality)<sup>2</sup>

Table 2. Differences Between Some Calculated (with Equation 4) and Observed Values of  $\log K_w^*$  at High Pressures and Temperatures<sup>a</sup>

Researchers	Conditions	Average Difference (Calcd. vs Obs.)
Whitfield (1972)	5-35°C 1-2,000 Bars	0.016
Hamann (1963)	25°C 1-2,000 Bars	0.007
Linov-Kryukov (1972)	18-75°C 1-8,000 Bars	0.022 (up to 2,000 Bars)
Kryukov-Linov- Starostina (1979)	25-150°C 1-6,000 Bars	0.022 (up to 2,000 Bars)
Quist (1970)	300-800°C 1,000-4,000 Bars	0.2
Hamann- Linton (1969) <sup>b</sup>	45°C, 7,500 Bars 240°C, 48,000 Bars 304°C, 59,000 Bars 373°C, 71,000 Bars 444-804°C 82,000- 133,000 Bars	0.09 0.13 0.20 0.32 1.0-2.7
Holzappel- Franck (1966) <sup>b</sup>	500-1000°C 40,000- 104,000 Bars	2.2-2.6

<sup>a</sup> $K_w^* = K_w/(\text{mol kg}^{-1})^2$ ;  $K_w$  in (molality)<sup>2</sup>.

<sup>b</sup>Values not used in obtaining Eq. (4), and outside the range of stated application (exception: 45°C, 7,500 Bars).

Table 3. The Negative Logarithm (Base 10) of the Ion Product of Water  
 Divided by  $(\text{mol kg}^{-1})^2$ ,  $-\log K_w^*$ ; 0-1000°C, 1-10,000 Bars  
 Calculated by Equation 4.<sup>a,b</sup>

Pressure (bars)	Temperature (°C)													
	0	25	50	75	100	150	200	250	300	350	400	450	500	600
Sat'd Vapor	14.938	13.995	13.275	12.712	12.265	11.638	11.289	11.191	11.406	12.30	----	----	----	----
250	14.83	13.90	13.19	12.63	12.18	11.54	11.16	11.01	11.14	11.77	19.43	21.59	22.40	23.27
500	14.72	13.82	13.11	12.55	12.10	11.45	11.05	10.85	10.86	11.14	11.88	13.74	16.13	18.30
750	14.62	13.73	13.04	12.48	12.03	11.36	10.95	10.72	10.66	10.79	11.17	11.89	13.01	15.25
1,000	14.53	13.66	12.96	12.41	11.96	11.29	10.86	10.60	10.50	10.54	10.77	11.19	11.81	13.40
1,500	14.34	13.53	12.85	12.29	11.84	11.16	10.71	10.43	10.26	10.22	10.29	10.48	10.77	11.59
2,000	14.21	13.40	12.73	12.18	11.72	11.04	10.57	10.27	10.08	9.98	9.98	10.07	10.23	10.73
2,500	14.08	13.28	12.62	12.07	11.61	10.92	10.45	10.12	9.91	9.79	9.74	9.77	9.86	10.18
3,000	13.97	13.18	12.53	11.98	11.53	10.83	10.34	9.99	9.76	9.61	9.54	9.53	9.57	9.78
3,500	13.87	13.09	12.44	11.90	11.44	10.74	10.24	9.88	9.63	9.47	9.37	9.33	9.34	9.48
4,000	13.77	13.00	12.35	11.82	11.37	10.66	10.16	9.79	9.52	9.34	9.22	9.16	9.15	9.23
5,000	13.60	12.83	12.19	11.66	11.22	10.52	10.00	9.62	9.34	9.13	8.99	8.90	8.85	8.85
6,000	13.44	12.68	12.05	11.53	11.09	10.39	9.87	9.48	9.18	8.96	8.80	8.69	8.62	8.57
7,000	13.31	12.55	11.93	11.41	10.97	10.27	9.75	9.35	9.04	8.81	8.64	8.51	8.42	8.34
8,000	13.18	12.43	11.82	11.30	10.86	10.17	9.64	9.24	8.93	8.68	8.50	8.36	8.25	8.13
9,000	13.04	12.31	11.71	11.20	10.77	10.07	9.54	9.13	8.82	8.57	8.37	8.22	8.10	7.95
10,000	12.91	12.21	11.62	11.11	10.68	9.98	9.45	9.04	8.71	8.46	8.25	8.09	7.96	7.78

Table 3. The Negative Logarithm (Base 10) of the Ion Product of Water  
 Divided by  $(\text{mol kg}^{-1})^2$ ,  $-\log K_w^*$ ; 0-1000°C, 1-10,000 bars  
 Calculated by Equation 4.a,b

(CONTINUED)

Pressure (bars)	Temperature (°C)			
	700	800	900	1000
Sat'd Vapor	----	----	----	----
250	23.81	24.23	24.59	24.93
500	19.29	19.92	20.39	20.80
750	16.55	17.35	17.93	18.39
1,000	14.70	15.58	16.22	16.72
1,500	12.50	13.30	13.97	14.50
2,000	11.36	11.98	12.54	12.97
2,500	10.63	11.11	11.59	12.02
3,000	10.11	10.49	10.89	11.24
3,500	9.71	10.02	10.35	10.62
4,000	9.41	9.65	9.93	10.13
5,000	8.95	9.11	9.30	9.42
6,000	8.61	8.72	8.86	8.97
7,000	8.34	8.40	8.51	8.64
8,000	8.10	8.13	8.21	8.38
9,000	7.89	7.89	7.95	8.12
10,000	7.70	7.68	7.70	7.85

<sup>a</sup>Values were calculated by Equation 4. Densities used were obtained from the 1967 IFC Formulation [22] (Footnote a of Table 1) and from the smoothed experimental values, up to the highest temperatures and pressures, of Burnham, Holloway, and Davis [3,4], of Köster and Franck [23], and of Maier and Franck [29]. These sets of densities generally agree with each other to much better than 1%. A 1% deviation in density corresponds to a difference of 0.06 units in calculated  $\log K_w$  at 1000°C, well within the projected uncertainties in the higher range of temperature and pressure.

<sup>b</sup> $K_w^* = K_w / (\text{mol kg}^{-1})^2$ ;  $K_w$  in (molality)<sup>2</sup>.



Table 4. The Negative Logarithm (Base 10) of the Ion Product of Water Divided by  $(\text{mol kg}^{-1})^2$ ,  $-\log K_w^*$ , in a Range of Interest to Power Production and Hydrothermal Geochemistry; 340–600°C, 50–500 Bars.<sup>a,b</sup>

Pressure (bars)	Temperature (°C)								
	340	360	380	400	440	480	520	560	600
50	33.14	33.15	33.17	33.18	33.20	33.24	33.29	33.35	33.44
100	27.85	28.11	28.29	28.42	28.63	28.79	28.92	29.05	29.18
150	† 11.97	24.33	24.91	25.22	25.71	26.02	26.25	26.44	26.62
200	11.74	12.51	† 21.55	22.46	23.40	23.92	24.26	24.53	24.76
250	11.57	12.06	13.64	19.43	21.33	22.14	22.63	22.98	23.27
300	11.44	11.80	12.57	14.78	19.33	20.55	21.23	21.67	22.02
350	11.32	11.62	12.17	13.10	17.24	19.08	19.96	20.52	20.93
400	11.22	11.47	11.88	12.49	15.35	17.69	18.81	19.48	19.96
450	11.13	11.35	11.68	12.14	13.99	16.42	17.75	18.53	19.09
500	11.06	11.24	11.51	11.88	13.26	15.32	16.78	17.67	18.30

† Demarcation Line Between Values for Vapor (Above) and Liquid (Below). Values of  $-\log K_w^*$  at 340 and 360°C at saturated vapor pressure are 12.01 and 12.73, respectively.

<sup>a</sup>Footnote a of Table 3 applies.

<sup>b</sup>  $K_w^* = K_w / (\text{mol kg}^{-1})^2$ ;  $K_w$  in (molality)<sup>2</sup>.

Van der Zee and Swanson [43] obtained by calorimetry, and 55.814 kJ mol<sup>-1</sup> (13.340 kcal mol<sup>-1</sup>) by Sweeton, Mesmer, and Baes [42] and 58.6 kJ mol<sup>-1</sup> (14.0 kcal mol<sup>-1</sup>) by Quist [38] by essentially the same interpretation as here.

#### 4. Conclusion

A general equation is presented for calculating the ion product of water over a wide range of temperature and pressure. The form of the equation is such that the higher order terms ( $C/T^2$ ,  $D/T^3$ ,  $G/T^3$ ) diminish in importance at high temperatures. The observed straight line relation at constant temperature of  $\log K_w^*$  versus  $\log \rho_w^*$  should extend well outside the range of experimental measurement. The power of prediction therefore appears to be great.

It seems to be highly significant that plots of  $\log K_w^*$  versus  $1/(T/K)$  at constant density produce essentially straight lines (fig. 6), as proposed earlier [11] and observed more recently [19,38]. The present observations again emphasize that much simpler behavior is exhibited for these relations at constant density than at constant pressure.

#### 5. Acknowledgements

The work presented was initiated and encouraged by participation in the Working Groups of the International Association for the Properties of Steam. We especially thank the members of all the Working Groups for their contributions during the course of this study. Present members of Working Group III, in which this study was specifically made, are Professor Koichi Watanabe, Department of Mechanical Engineering, Keio University, Yokohama, 223, Japan, Klaus Scheffler, Institute A for Thermodynamics, Technical University of Munich, Federal Republic of Germany, and the authors.

Research conducted by William L. Marshall was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

#### References

- [1] Barnes, H. L., Editor, "Geochemistry of Hydrothermal Ore Deposits," Holt, Rinehart, and Winston, Publ., New York, 1967.
- [2] Bignold, G. J., Brewer, A. D., and Hearn, B., Trans. Faraday Soc. **67**, 2419 (1971).
- [3] Burnham, C. W., Holloway, J. R., and Davis, N. F., Am. J. Sci. **267A**, 70 (1969).
- [4] Burnham, C. W., Holloway, J. R., and Davis, N. F., "Thermodynamic Properties of Water to 1000°C and 10,000 Bars," Geological Society of America Publ., Special Paper No. 132.
- [5] Clever, H. L., J. Chem. Educ. **45**, 231 (1968).
- [6] Cobble, J. W., J. Am. Chem. Soc. **86**, 5394 (1964).
- [7] Cohen, P., "Water Coolant Technology of Power Reactors," Amer. Nucl. Soc. Monograph, Gordon and Breach Publ., New York, 1969.
- [8] David, H. G., and Hamann, S. D., Trans. Faraday Soc. **55**, 72 (1959).
- [9] Dobson, J. V., and Thirsk, H. R., Electrochim. Acta. **16**, 315 (1971).
- [10] Fisher, J. R., and Barnes, H. L., J. Phys. Chem. **76**, 90 (1972).
- [11] Franck, E. U., Z. Phys. Chem. (Frankfurt) **8**, 107, 192 (1956).
- [12] Franks, F., Editor, "Water, A Comprehensive Treatise," Plenum Press Publ., Vols. 1–5, London, 1972.
- [13] Hamann, S. D., and Linton, M., Trans. Faraday Soc. **65**, 2186 (1969).
- [14] Hamann, S. D., and Linton, M., Trans. Faraday Soc. **62**, 2234 (1966).
- [15] Hamann, S. D., J. Phys. Chem. **67**, 2233 (1963).
- [16] Harned, H. S., and Owen, B. B., "Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Press, New York, pp. 634–643 (1958).
- [17] Harned, H. S., and Hamer, W. J., J. Am. Chem. Soc. **55**, 2194 (1933).
- [18] Helgeson, H. C., and Kirkham, D. H., Am. J. Sci. **274**, 1089, 1199 (1974); *ibid.* **276**, 97 (1976); plus numerous earlier papers by Helgeson.
- [19] Holzappel, W. B., J. Chem. Phys. **50**, 4424 (1969).
- [20] Holzappel, W. B., and Franck, E. U., Ber. Bunsenges. Phys. Chem. **70**, 1105 (1966).
- [21] International Association for the Properties of Steam, "Proceedings of

- the Working Groups," H. J. White, Secretary, U.S. National Bureau of Standards, Washington, D.C., U.S.A. (1975-78).
- [22] International Formulation Committee 1967 Steam Tables; Committee established by Sixth International Conference on the Properties of Steam (New York, October 1963).
- [23] Köster, H., and Franck, E. U., *Ber. Bunsenges. Phys. Chem.* **73**, 716 (1969).
- [24] Kryukov, P. A., Starostina, L. I., and Larionov, E. G., in "Water and Steam", J. Straub and K. Scheffler, Editors, *Proc. 9th. Intl. Conf. Prop. Steam*, Munich, 1979; Pergamon Press, p. 513 (1980).
- [25] Lietzke, M. H., Oak Ridge National Laboratory Report ORNL-3259 (1962).
- [26] Linov, E. D., and Kryukov, P. A., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, No. 4, 10 (1972).
- [27] Lown, D. A., Thirsk, H. R., and Wynne-Jones, L., *Trans. Faraday Soc.* **64**, 2073 (1968).
- [28] MacDonald, D. D., Butler, P., and Owen, D., *Can. J. Chem.* **51**, 2590 (1973).
- [29] Maier, S., and Franck, E. U., *Ber. Bunsenges. Phys. Chem.* **70**, 639 (1966).
- [30] Marshall, W. L., (a) *J. Phys. Chem.* **76**, 720 (1972); (b) *ibid.* **74**, 346 (1970); (c) *Rec. Chem. Prog.* **30**, 61 (1969).
- [31] Marshall, W. L., and Quist, A. S., *Proc. Natl. Acad. Sci. U.S.A.* **58**, 901 (1967).
- [32] Millero, F. J., Hoff, E. V., and Kahn, L., *J. Soln. Chem.* **1**, 309 (1972).
- [33] Noyes, A. A., Kato, Y., and Sosman, R. B., *J. Am. Chem. Soc.* **32**, 159 (1910).
- [34] Noyes, A. A., et al., "The Electrical Conductivity of Aqueous Solutions," Carnegie Institution of Washington, Washington, D.C., Publ. No. 63 (1907).
- [35] Olofsson, G., and Hepler, L. G., *J. Soln. Chem.* **4**, 127 (1975).
- [36] Owen, B. B., and Brinkley, S. R., *Chem. Rev.* **29**, 461 (1941).
- [37] Perkovets, V. D., and Kryukov, P. A., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, No. 3, 9-12 (1969). (Trans. UDC 546.121 + [541.124.7:141.036].)
- [38] Quist, A. S., *J. Phys. Chem.* **74**, 3396 (1970).
- [39] Quist, A. S., and Marshall, W. L., *J. Phys. Chem.* **72**, 684 (1968).
- [40] Quist, A. S., and Marshall, W. L., *J. Phys. Chem.* **72**, 1536 (1968).
- [41] Svistunov, E. P., Golubev, B. P., Smirnov, S. N., and Sevast'yanov, V. P., *Teploenergica*, No. 3, 70 (1978).
- [42] Sweeton, F. H., Mesmer, R. E., and Baes, C. F., *J. Soln. Chem.* **3**, 191 (1974).
- [43] Vanderzee, C. E., and Swanson, J. A., *J. Phys. Chem.* **67**, 2608 (1963).
- [44] Whitfield, M., "Seawater as an Electrolyte Solution" in "Chemical Oceanography," Riley, J. P., and Chester, R., Editors, Page Bros. Ltd., Norwich, Great Britain, Vol. 1, 2nd Ed., p. 43 (1975).
- [45] Whitfield, M., *J. Chem. Eng. Data* **17**, 124 (1972).
- [46] Yeatts, L. B., and Marshall, W. L., *J. Phys. Chem.* **76**, 1053 (1972).

Executive Secretary:

Dr. Howard J. White, Jr.

Office of Standard Reference Data

National Bureau of Standards

Washington, D.C. 20234, U.S.A.

The General Meeting of the International Association for the Properties of Steam (IAPS) held during the Ninth International Conference on the Properties of Steam in Munich, Federal Republic of Germany, September 10-14, 1979, authorized the preparation of an official representation for the ion product of water substance. The task of preparing this representation was assigned to Working Group III of IAPS which had already carried out preliminary work leading toward preparation of a representation.

This release has been authorized by the IAPS for issue by its Secretariat and presents the *International Representation of the Ion Product of Water Substance, 1980*. In accordance with the Statutes of IAPS, the representation has been circulated to and approved by the Members of the IAPS (Canada, Czechoslovakia, Federal Republic of Germany, France, Japan, USSR, United Kingdom, and United States of America).

The deliberations of Working Group III are given briefly in appendix A. In appendix B an equation for the ion product ( $K_w$ ), defined as (molality of hydrogen ion) times (molality of hydroxide ion), is given as a function of temperature and density. Auxiliary tables (apps. C, D, and E) present values of  $K_w$  calculated by the equation at selected temperatures and pressures.

Further information can be obtained from the Executive Secretary of IAPS:

Dr. Howard J. White, Jr.

National Bureau of Standards

Office of Standard Reference Data

Physics Building, Room A316

Washington, D.C. 20234 U.S.A.

#### Attachments

Appendices A, B, C, D, and E.

## Appendix 1

### International Association for the Properties of Steam

#### Release on the Ion Product of Water Substance

May 1980

Unrestricted publication allowed in all countries.

Issued by the International Association for the Properties of Steam.

President:

Prof. Dr. U. Grigull, President

Technical University of Munich

8 Munich 2

Federal Republic of Germany

## Appendix A

Working Group III of the International Association for the Properties of Steam has collected from the literature existing experimental data and treatments for the ion product of water. References were compiled and descriptions given in several documents presented at the annual meetings of working groups. These documents are: "Consideration of Present Knowledge of the Ionization Behavior of Water as a Function of Temperature and Pressure" (W. L. Marshall—Ottawa, Canada, September 15-19, 1975); "Further Evaluation of the Ionization Constant of Water; Description from 0 to 1,000 °C and from 1 to above 10,000 Bars" (W. L. Marshall—Kyoto, Japan, September 5-10, 1976); "Revised Evaluation of the Ion Product of Water; Description from 0 to 1,000 °C and from 1 to 10,000 Bars" (W. L. Marshall—Moscow, USSR, September 10-16, 1977).

Working Group III considers that enough independent determinations of  $K_w$  at vapor saturation from 0 to 374 °C have been made to describe  $K_w$  under this condition, within  $\pm 0.01$  logarithmic units (base 10). It would appear that sufficient experimental values have been obtained throughout the range of pressure, 1–10,000 bars, and temperature, 0–1,000 °C, together with a correlation by the form of equation used (app. B), to yield values of  $\log K_w^*$  (base 10), where  $K_w^*$  equals  $K_w/(\text{mol kg}^{-1})^2$ , within uncertainties of  $\pm 0.01$  near saturated vapor pressure to  $\pm 0.3$  at the extreme of temperature and pressure. Selected literature references and estimated uncertainties for particular ranges are included with the equation.

## Appendix B

### Recommended Interpolation Equation

The available data are reproduced by the equation given below, wherein,

$K_w$ : ion product, molality of  $\text{H}^+$  ion times molality of  $\text{OH}^-$ , which may be expressed by the symbols,  $m_{\text{H}^+} \cdot m_{\text{OH}^-}$ .

$K_w^*$ :  $K_w/(\text{mol kg}^{-1})^2$ .

$T$ : temperature in degrees K on the 1968 practical temperature scale.

$\rho_w$ : density in  $\text{g/cm}^3$ .

$\rho_w^*$ :  $\rho_w/(\text{g cm}^{-3})$ .

Logarithms of  $K_w^*$  and of  $\rho_w^*$  are in units of base 10.

$$\log K_w^* = A + B/T + C/T^2 + D/T^3 + (E + F/T + G/T^2) \cdot \log \rho_w^*$$

(same as eq (4) in text).

The constants in the above equation are:

$$\begin{aligned} A &= -4.098 \\ B &= -3245.2 \text{ K} \\ C &= +2.2362 \times 10^5 \text{ K}^2 \\ D &= -3.984 \times 10^7 \text{ K}^3 \\ E &= +13.957 \\ F &= -1262.3 \text{ K} \end{aligned}$$

$$G = +8.5641 \times 10^5 \text{ K}^2$$

The equation will describe  $K_w^*$  at saturated vapor pressure up to 250 °C within  $\pm 0.004$  to 0.014 units of critically determined values of Sweeton, Mesmer, and Baes (J. Soln. Chem. **3**, 191 (1974)) (app. C). Generally described within their uncertainties are experimental values of Kryukov, Larionov, and Starostina, 25–150 °C, 1–8000 bars (Ninth Intl. Conf. Prop. Steam, Munich, FRG, September 10–14, 1979), of Linov and Kryukov, 25–75 °C, 1–8000 bars (Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk **1972** (4), 10 (1972)), of Hamann, 25 °C, 1–2000 bars (J. Phys. Chem. **67**, 2233 (1963)), and of Whitfield, 25 °C, 1–2000 bars (J. Chem. Eng. Data **17**, 124 (1972)). Some values of Hamann and Linton, 45–373 °C, 7500–71,000 bars (Trans. Faraday Soc. **65**, 2186 (1969)), are calculated to within 0.10–0.35 units although not used in obtaining the parameters. At high temperatures, the equation describes values of Quist, 300–800 °C, 1000–4000 bars (J. Phys. Chem. **74**, 3396 (1970)), generally within 0.1–0.2 units, or better than stated uncertainties of  $\pm 0.3$  to 0.5 units.

Accuracies of  $\log K_w^*$  calculated by the equation are estimated to be within  $\pm 0.01$  units at saturated vapor pressure and within  $\pm 0.03$  units at pressures up to 10,000 bars when the temperature is below 250 °C. At temperatures from 250 to 1000 °C and pressures up to 10,000 bars the equation may still provide accuracies of  $\pm 0.03$  to 0.05 units although upper limits of uncertainty should probably be increased from  $\pm 0.05$  to 0.30 units of  $\log K_w^*$  as the highest temperatures and pressures are approached.

## Appendix C

$\log K_w^*$  calculated (eq (4) in text) compared with values calculated by Sweeton, Mesmer, and Baes [42] at saturated vapor pressure (same as table 1 in text).

## Appendix D

Calculated values of  $\log K_w^*$ , 0–1000 °C; 1–10,000 bars (same as table 3 in text).

## Appendix E

Calculated values of  $\log K_w^*$  in a range of interest to power production and hydrothermal geochemistry, 340–460 °C; 50–500 bars (same as table 4 in text).