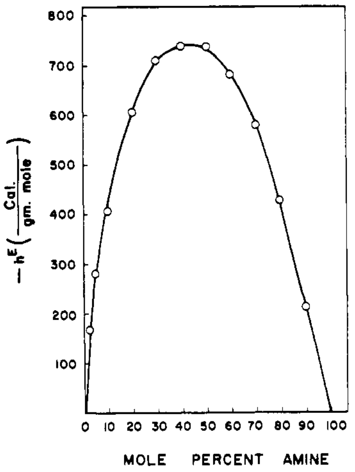

Figure 3. Calculated excess enthalpies for ethyl isopropylamine–water

at this concentration γ_w is always below 1.006. Then the mole fraction amine is given approximately by

$$y_a = \frac{P - P_w{}^0 x_w}{P} \tag{3}$$

The dotted line in Figures 1 and 2 were calculated by this equation. Figure 3 shows average excess enthalpies for ethyl isopropylamine–water calculated from the slopes of plots of g^E/T vs. $1/T$ at various mole fractions over the range of 10–40°C.

An attempt was made to represent the excess free energy of these systems by a thermodynamically consistent polynomial. As with other amine–water systems, this could not be done satisfactorily even with seven arbitrary constants.

NOMENCLATURE

f = fugacity
g^E = excess Gibbs free energy in cal/g-mol
h^E = excess enthalpy in cal/g-mol
P = pressure in mm of Hg
x = mole fraction in the liquid
y = mole fraction in the vapor

GREEK

γ = activity coefficient, f/f^0x
Φ = the ratio of the fugacity coefficient of a pure component vapor to that in the vapor mixture

SUBSCRIPTS

1 = component 1
2 = component 2
a = amine
w = water

SUPERSCRIPTS

0 = pure component

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RECEIVED for review May 17, 1971. Accepted December 12, 1971. Two tables of complete data on the calculated vapor-liquid equilibria of dimethyl isopropylamine–water and of ethyl isopropylamine–water will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D.C. 20036, by referring to author, title of article, volume, and page number. Remit by check or money order $3.00 for photocopy or $2.00 for microfiche.

Self-Ionization of Water in Dilute Sodium Chloride Solutions from 5–35°C and 1–2000 Bars

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An improved form of glass electrode cell was used to estimate the degree of self-ionization of water over the oceanographically interesting temperature and pressure range. The results indicate that the estimates of Owen and Brinkley may be in serious error at temperatures below 25°C. This conclusion is supported by the compressibility data of Kearns and by recent studies of the self-ionization of water over a broad temperature and pressure range (to 1000°C and 133K bars).

Because of its pivotal importance in aqueous solution chemistry, the self-ionization of water has been intensively studied over a wide temperature range at atmospheric pressure (*6,13,22*) and at very high temperatures and pressures in the supercritical region (*5, 9, 16, 20, 21, 25, 26, 38*). However, little attention has been paid to the more moderate temperature and pressure range of interest to biologists and marine scientists, mainly because of the lack of a suitable experimental method.

The potentiometric method was used by Hamann (*19*) in the first experimental study of water ionization in this region, and recent improvements in techniques for using glass electrodes at high pressures (*41–43*) now make it possible to ex-

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tend the data to include most of the oceanographically significant temperature-pressure range. The need for such an analysis is emphasized by the persistence of several authoritative sources (*2, 17, 24*) in quoting the values of K_w calculated by Owen and Brinkley (*35*) on the basis of a standard partial molal volume change that has since been shown to be in error by nearly 2 $cm^3\ mol^{-1}$ (*3, 15, 19*).

THEORY

If the glass electrode is considered as an ideal hydrogen ion sensor, then the cell used in this study (cell I):

$$\text{Ag, AgCl; HCl } (m_1), \text{ NaCl } (m_2)|\text{glass membrane}|\text{NaOH } (m_1), \text{ NaCl } (m_2); \text{ AgCl, Ag}$$

is equivalent to the combination of cells used by Harned (*22*) and his co-workers to eliminate the standard cell potential from the cell equation. The near theoretical response of the glass electrode at high pressures has been established by a number of independent investigations (*8, 10, 19, 41*) and so the cell potential may be written as

$$E/S = (E_c - E_a)/S = -\ln (a_H\gamma_{Cl})/(\bar{a}_H\bar{\gamma}_{Cl}) - \ln (m_{Cl}/\bar{m}_{Cl}) \tag{1}$$

where the properties of the NaCl/HCl mixture are indicated by barred symbols. $S = RT/F$ if the electrodes are behaving ideally. The cell potential (E_c) has to be corrected for a residual asymmetry effect (E_a) across the glass membrane which alters slightly with age and is a function of temperature and pressure (*41*).

The cell responds to changes in $a_H\gamma_{Cl}$ as the pressure and temperature are altered (*31*). This parameter may be related to the self-ionization constant for water (K_w) by the equation

$$\begin{aligned}\ln K_w &= \ln (a_H\gamma_{OH}\cdot m_{OH})/a_{H_2O}\\ &= \ln a_H\gamma_{Cl} + \ln (\gamma_{OH})/(a_{H_2O}\gamma_{Cl}) + \ln m_{OH}\end{aligned} \tag{2}$$

Substituting for $\ln (a_H\gamma_{Cl})$ from Equation 2 into Equation 1 and rearranging give

$$E/S = -\ln K_w + \ln \gamma_w + \ln M + \ln (\bar{\gamma}_H\bar{\gamma}_{Cl})/(\gamma_H\gamma_{Cl}) \tag{3}$$

where

$$\ln \gamma_w = \ln (\gamma_{OH}\gamma_H)/(a_{H_2O}); \ \ln M = \ln (\bar{m}_H\cdot m_{OH}\cdot \bar{m}_{Cl})/(m_{Cl})$$

If the solutions are sufficiently dilute ($m_1 + m_2 < 0.1M$) and if $m_1 \ll m_2$ then the value of the term $\ln (\bar{\gamma}_H\bar{\gamma}_{Cl})/\gamma_H\gamma_{Cl})$ will be small (*22*) (approx 0.03 mV). Its contribution to the temperature and pressure coefficients of the cell potential will certainly be negligible. The effect of pressure on γ_w will also be small (*11*). If the solution compositions are expressed in molalities the term $\ln M$ is a constant independent of temperature and pressure. Variations in m_{OH} caused by changes in K_w will be negligible in the alkaline solutions considered here and Equation 3 may be simplified to

$$\Delta E/S = -\ln (K_p/K_1) \tag{4}$$

where K_1 and K_p represent the values of K_w at 1 bar and P bars, respectively, and ΔE represents the change in cell potential resulting from the pressure step from 1 to P bars.

If the measured ΔE values are corrected for changes in the asymmetry potential and for small deviations in S (Equation 1) from the theoretical value, then Equation 4 may be written as

$$F\Delta\bar{E}/RT = -\ln (K_p/K_1) \tag{5}$$

The experimental data are analyzed on the basis of this equation.

EXPERIMENTAL

Solutions were prepared by the weight titration of constant boiling, bromide-free hydrochloric acid (*27*) into carbonate-free sodium hydroxide solution (*40*) under a nitrogen atmosphere. The hydrochloric acid was standardized by titration against sodium carbonate solutions (prepared from Mallinckrodt primary standard grade Na_2CO_3). The composition of the final mixture was checked by back titration of the excess acid or alkali against standard solutions of sodium carbonate or hydrochloric acid, respectively. The solutions were stored under a nitrogen atmosphere over soda lime to minimize the absorption of carbon dioxide. Occasional tests of solution samples with a few drops of barium hydroxide throughout the experimental series showed no evidence of carbonate formation. The solutions were saturated with silver chloride by the addition of a few drops of silver nitrate. Working solutions were prepared by weight dilution of the concentrated stock solutions ($m_1 = 0.153M$, $m_2 = 0.547$) with carbon dioxide–free quartz-distilled water under a nitrogen atmosphere.

The high-pressure equipment has been described in detail elsewhere (*42, 43*). To prevent dissolution of the halide coating from the reference electrodes a few small pieces of silver chloride were placed in the bottom of the cell. At the higher temperatures (25–35°C) the silver chloride together with the alkaline cell solution reacted with the mercury normally used for pressure transmission (*42*). The solution became cloudy and the cell potential became erratic. In consequence, the cells were modified to allow pressure transmission via the cap that carries the leads and the electrodes (Figure 1). The cell solutions were injected through a hole in the cap that could be closed by an O-ring sealed screw. A nest of four cells was mounted inside a thick-walled steel pressure vessel (*42*) which was suspended in the center of a constant temperature bath (stability ±0.001°, accuracy ±0.005°). The pressure was

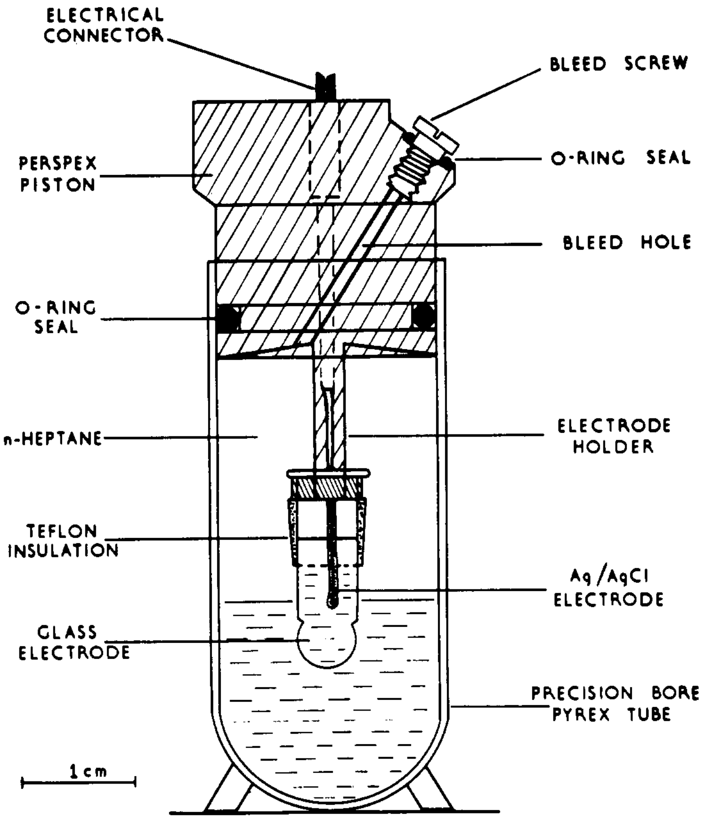

Figure 1. High pressure cell

Second silver–silver chloride electrode lies behind the glass electrode in sketch

Table I. Smoothed Values for Function $(0.4343\ F \cdot \Delta\bar{E})/RT = \log_{10}(K_p/K_1)$ for Solutions Where $M_1/M_2 = 0.281$

(a) 0.07M total ionic strength. (b) 0.007M total ionic strength

Pressure bars	Temp, °C 5 (a)	 15 (a)	 25 (a)	 (b)	 35 (a)
200	0.0743	0.0717	0.0696	0.0688	0.0674
400	0.1455	0.1413	0.1378	0.1377	0.1341
600	0.2129	0.2090	0.2032	0.2017	0.1977
800	0.2794	0.2746	0.2667	0.2660	0.2584
1000	0.3434	0.3362	0.3281	0.3268	0.3176
1200	0.4068	0.3970	0.3859	0.3898	0.3745
1400	0.4688	0.4565	0.4420	0.4440	0.4302
1600	0.5282	0.5120	0.4975	0.4980	0.4822
1800	0.5880	0.5639	0.5519	0.5470	0.5319
2000	0.6447	0.6136	0.6048	0.5930	0.5795
SD[a]	0.08	0.16	0.18	0.35	0.32

[a] Standard deviation of all experimental points from fitted curve (mV).

Values for constants used in this paper

$R = 83.14\ \mathrm{cm^3\ bar\ deg^{-1}\ mol^{-1}} = 1.9872\ \mathrm{cal\ deg^{-1}\ mol^{-1}}$

$F = 96{,}487\ \mathrm{C\ equiv^{-1}}$

T_0 (ice point) = 273.15°A

$\mathrm{Log}_e = 2.3026\ \log_{10}$

measured with Heise Bourdon tube gauges calibrated against a dead-weight tester. The uncertainty in the measured pressure was ±4 bars.

For the lower temperatures (5 and 15°C), flat membrane electrodes, prepared from commercial high pH glass, were used to minimize errors caused by uncertainties in the asymmetry potentials and to reduce the resistance of the cells (*41*). At higher temperatures (25° and 35°C), such electrodes had a limited life, probably because of the relatively rapid dissolution of the fine glass membrane in the alkaline solution. Consequently, commercial high pH bulb electrodes were used and corrections had to be made for the effect of pressure and temperature on the asymmetry potentials of the cells (*41*). The asymmetry potential was measured in acid solutions [HCl (m_1), NaCl (m_2)] as a function of temperature and pressure before and after each run with NaOH/NaCl mixtures, and the mean value for the correction factor was applied. The slope factor (S) for all glass electrodes was checked at frequent intervals at 25°C and 1 atm pressure using a series of NBS buffers. In addition, the slope factor was checked at each working temperature at the beginning and end of the experimental series.

Silver–silver chloride electrodes were prepared electrolytically and electrodes with a bias potential of < 0.02 mV were selected for the high-pressure cells. The cells were assembled and the solutions loaded under a nitrogen atmosphere. The cells were pressurized to 2000 bars the day before the measurements were made, and the pressure was allowed to fall gradually to 1 bar overnight.

The cell potentials together with the pressure and the cell temperature were recorded on a potentiometric recorder (*41*, *42*), and readings were taken when the drift in cell potential was less than 0.1 mV/hr. The initial potentials of the cells were backed off against a Leeds & Northrup Model K4 Potentiometer using a Dynamco DM2022 digital voltmeter (Dynamco, Hanworth Lane, Chertsey, Surrey, England) as a nul instrument and a Keithley Model 610BR electrometer as impedance matching amplifier; ΔE values were then read directly from the digital voltmeter. The maximum spread of results varied from 0.3 mV at 5°C to 0.8 mV at 35°C. However, the standard deviation about the fitted curve was much smaller than this (Table I). Tables of raw data and of pK_w values calculated from the smoothed values have been placed with the American Chemical Society Microfilm Depository Service.

RESULTS AND DISCUSSION

Experimental values for the ratio $\Delta\bar{E}/S$ (Equation 5) were plotted against the pressure, and a smooth curve was drawn through the points (Figure 2). The data plotted are for solutions where $m_1 + m_2 = 0.07M$, as no significant difference was observed between the pressure coefficients of cell I at ionic strengths of 0.07M and 0.007M at 25°C (Table I) and the cells were less reproducible at the lower ionic strength. Consequently, it was not possible to employ an extrapolation procedure (*22*) to determine K_w at infinite dilution. $\Delta\bar{E}/S$ values were read off from the smooth curve at 200-bar intervals (Table I). These values were used in the subsequent analysis.

The values obtained at 25°C agree well with those obtained by Hamann (*19*) at a similar ionic strength (Figure 3). As there are no data available at other temperatures for this ionic strength, it is instructive to compare the values obtained here with values for K_w calculated at infinite dilution. To make this comparison, it is first necessary to estimate the deviation from infinite dilution behavior that might be expected with a background ionic strength of 0.07M.

The effect of pressure on the dissociation constant at infinite dilution may be expressed by the following equation if the standard partial molal compressibility ($\Delta\bar{K}_1°$) is not a function of pressure over the range considered (*32*),

$$RT \ln (K_p/K_1) = -\Delta\bar{V}_1°(P - 1) + (\Delta\bar{K}_1°/2)(P - 1)^2 \quad (6)$$

where $\Delta\bar{V}_1°$ is the standard partial molal volume change for the neutralization reaction.

This equation may be combined with Equation 5 to give

$$F\Delta\bar{E} = -\bar{V}_1°(P - 1) + (\Delta\bar{K}_1°/2)(P - 1)^2 \quad (7)$$

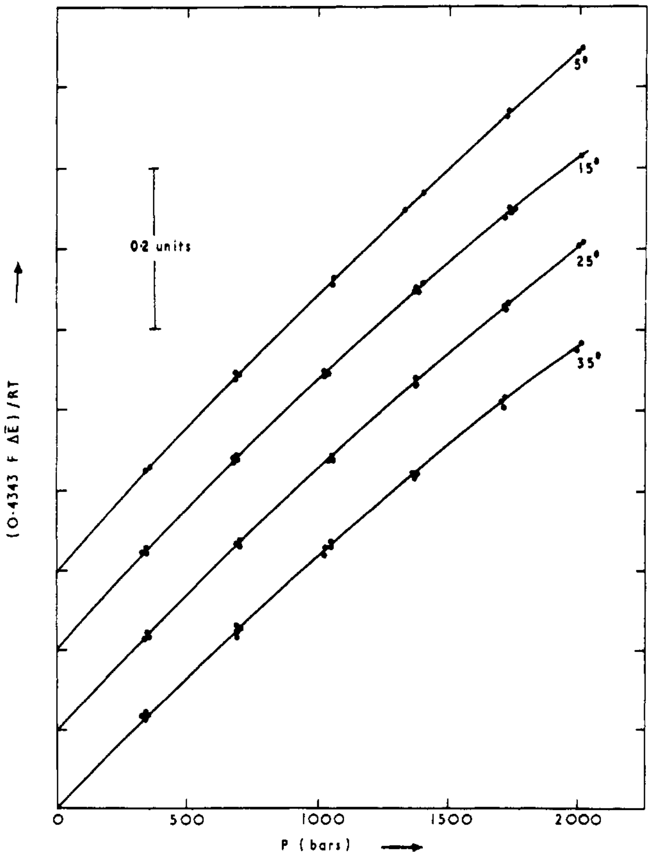

Figure 2. Effect of pressure on potential of cell I

Data have been corrected for slight variations in slope factor and asymmetry potential. Smooth curves drawn through points have coordinates listed in Table I. Lines have been displaced vertically to clarify presentation. Solid circles show experimental points

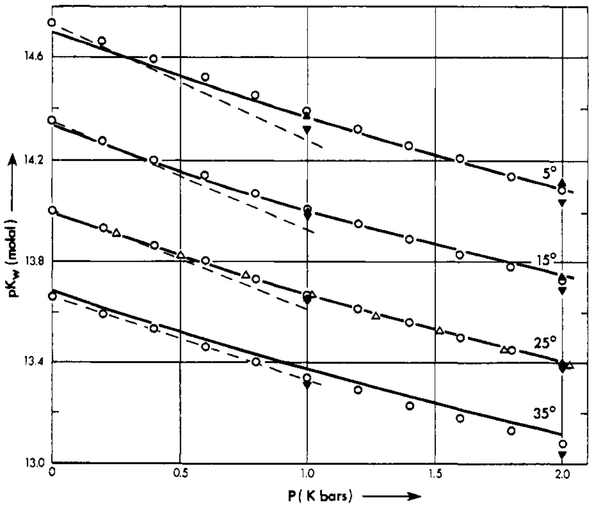

Figure 3. Effect of pressure on the self-ionization of water

Experimental values: ○ This work △ Homann (19)
Calculated values (infinite dilution): ▲ Kearns (28) ▼ Millero et al. (34)
Solid line drawn according to Equation 11
Dashed line follows estimates of Owen and Brinkley (35)

If we use Kearns (*28*) values for $\Delta\bar{K}_1°$ and assume a probable error in the voltage measurements of three times the standard error, this would indicate an uncertainty of ±0.4 cm³ mol⁻¹ in the values deduced for the volume change in the sodium chloride solution ($\Delta\bar{V}$). From neutralization experiments with sodium hydroxide–hydrochloric acid mixtures, Bodanszky and Kauzmann (*3*) derived the expression

$$\Delta\bar{V} - \Delta\bar{V}_1° = 2.30m^{1/2} - 0.40m \qquad (8)$$

for the process

$$H_2O \text{ (pure)} \rightarrow H^+(m) + OH^-(m) \qquad (9)$$

More recent partial molal volume determinations (*14, 15, 23*) indicate that Bodanszky and Kauzmann's measurements may be in error at ionic strengths below 0.01*M*. However, at higher ionic strengths Equation 8 can be used, without serious error, to deduce that the volume decrease for the neutralization reaction at 25°C should be about 0.6 cm³ mol⁻¹ *smaller* in the 0.07*M* salt solution than at infinite dilution. Since this difference is of the same order as the experimental error this suggests that the pressure coefficients reported here may be compared with earlier estimates at infinite dilution (Table II, Figure 3).

Good agreement is observed between the present measurements and the values of Kearns (*28*) which were based on his own compressibility data and on recalculated values for $\Delta\bar{V}_1°$.

Table II. Comparison of Literature Values of pK_w (*m*)

		pK_w					
T, °C	P (bars)	This work[a]	Kearns (*28*)[b]	Hamann (*19*)[a]	Quist (*38*)[b]	Millero et al. (*34*)[b]	Owen and Brinkley (*35*)[b]
5	1000	14.39	14.37		14.36	14.33	14.28
	2000	14.09	14.12		14.10	14.04	
15	1000	14.01	14.00		14.01	13.98	13.93
	2000	13.73	13.74		13.75	13.71	
25	1000	13.67	13.66	13.67	13.68	13.65	13.62
	2000	13.39	13.40	13.40	13.42	13.38	
35	1000	13.34			13.37	13.31	13.33
	2000	13.08			13.12	13.03	

[a] Ionic strength approximately 0.1*M*. [b] Infinite dilution.

He used the partial molal volumes of sodium hydroxide (*23*), sodium nitrate (*12, 36*) and nitric acid (*4*) to calculate $\Delta\bar{V}_1°$ at 25°C. The value obtained (−21.63 cm³ mol⁻¹) agreed favorably with that reported by Hepler et al. (*23*) (−21.86 cm³ mol⁻¹). To calculate the temperature dependence of $\Delta\bar{V}_1°$, he assumed that the standard partial molal expansibility ($\Delta\bar{E}_1°$) of Reaction 9 was independent of temperature. $\Delta\bar{E}_1°$ was estimated at 25°C from the partial molal expansibilities of sodium hydroxide (*18*), nitric acid (*4*), and sodium nitrate. This latter value was estimated from data on nitric acid (*4*), sodium chloride, and hydrochloric acid (*22*) by the principle of ionic additivity.

More recently, Quist (*38*) has measured log K_w over the intermediate temperature and pressure range (to 800°C and 4000 bars) and has derived an empirical relationship to describe the variation of log K_w (±0.02 unit) over the whole range to 1000°C and 133K bars. He derives this equation on the basis of linear relationships between log K_w and T^{-1} and between log K_w and log C_{H_2O} (logarithm of the concentration of water in the solution expressed in moles liter⁻¹) that can be shown to hold down to more moderate temperatures and pressures (*25, 33*).

If log K_w is expressed in *molar* terms, the equation has the form

$$\log K_w(T) = -33.05 - \frac{3050}{T} + 16.8 \log C_{H_2O} \qquad (10)$$

Since

$$\log K_c = \log K_m - \log C_{H_2O} - \log 0.018$$

then Equation 10 can be converted to *molal* terms to give,

$$\log K_w(T) = -34.79 - \frac{3050}{T} + 17.8 \log C_{H_2O} \qquad (11)$$

The differences between pK_w (molal) and pK_w (molar) at atmospheric pressure from 5–35°C are negligible in the present context (*7*). C_{H_2O} values were calculated from compilations of water density covering the appropriate temperature/pressure range (*1, 29, 30, 39*). The solid lines in Figure 3 are derived from this equation.

Values of $\Delta\bar{V}$ and $\Delta\bar{K}$ may be obtained from the present data using an extrapolation procedure (*32*) based on Equation 7 rearranged to give, for the salt solution,

$$F\Delta\bar{E}/(P - 1) = -\Delta\bar{V} + (\Delta\bar{K}/2)(P - 1) \qquad (12)$$

A plot of the left-hand side of Equation 12 against $(P-1)$ should give a straight line with slope $(\Delta\bar{K}/2)$ and intercept $-\Delta\bar{V}$. Unfortunately, since P is in the denominator on the left-hand side, the extrapolation is particularly sensitive to small errors in $\Delta\bar{E}$ at the lower pressures where the relative errors in the measured potential change are greatest: For example, at 200 bars the standard deviation in $\Delta\bar{E}$ from the present measurements gives an error of ±0.9 cm³ mol⁻¹ in the estimated value of $\Delta\bar{V}$, and this error has risen to ±1.8 cm³ mol⁻¹ by 100 bars. However, the results of the extrapolation indicate that $\Delta\bar{V}$ is effectively constant over the whole temperature range with a value of −20.4 ± 0.4 cm³ mol⁻¹. The mean value agrees with that obtained by Hamann (*19*) and with the value estimated from Equation 7 at 25°C. In addition, the spread of values is consistent with that estimated by Kearns (*28*) whose data indicate that $\Delta\bar{V}_1° = -22.1 \pm 0.5$ cm³ mol⁻¹ from 5–25°C. Values of $\Delta\bar{K}$ obtained ranged from -38×10^{-4} cm³ bar⁻¹ mol⁻¹ at 5 to -32×10^{-4} cm³ bar⁻¹ mol⁻¹ at 25°C indicating, as might be expected, that the system is less compressible in the electrolyte solution than in pure water (*28, 32*) and that in addition, the temperature coefficient of the compressibility is lower in the electrolyte solution (*28*).

However, recent direct measurements by Millero et al. (*34*) indicate that the standard partial molal expansibility ($\Delta\bar{E}_1°$) has a value of 0.140 cm³ deg⁻¹ mol⁻¹ which is close to that

Table III. Parameters for Equation $\Delta G = A + BT$

P (bars)	A	B
400	13770	17.22
800	13644	17.06
1200	13510	16.94
1600	13326	17.07
2000	13142	17.21

estimated by Owen and Brinkley (*35*) (0.135 $cm^3\ deg^{-1}\ mol^{-1}$). This contrasts with the effective constancy of $\Delta\bar{E}_1°$ observed in sodium chloride solutions in the present experiments. If Millero's estimate of $\Delta\bar{E}_1°$ is combined with the most recent value (*15*) of $\Delta\bar{V}_1°$ at 25°C ($-22.11\ cm^3\ mol^{-1}$) and the Kearns (*28*) estimates of $\Delta\overline{K}_1°$, then pK_w can be calculated from Equation 6. The values obtained (Figure 3) show significant deviations from the other values quoted here at 5°C. Even so, *all* the data presented indicate that the widely quoted estimates of Owen and Brinkley (*35*) are probably in error, particularly at the lower temperatures. In addition to a then unavoidable error in the estimate of $\Delta\bar{V}_1°$ at 25°C, Owen and Brinkley (*35*) used the value of $\Delta\overline{K}_1°$ at 25°C for calculations over the whole temperature range. Kearns (*28*) has since shown that $\Delta\overline{K}_1°$ increases from $-45.6 \times 10^{-4}\ cm^3\ bar^{-1}\ mol^{-1}$ at 25°C to $-64.8 \times 10^{-4}\ cm^3\ bar^{-1}\ mol^{-1}$ at 5°C, and therefore has a considerable temperature coefficient.

Values of ΔG for the self-ionization reaction were deduced from the equation

$$\Delta G = -RT \ln K_w \tag{13}$$

They may be represented by a linear equation with the parameters listed in Table III. These data can be used to interpolate log K_w values for temperatures other than those considered here. An analysis of error propagation using the method of orthogonal polynomials (*37*) indicates that the data reported here are not sufficiently precise for the determination of meaningful ΔS and ΔH values from the temperature coefficients of log K_w. Consequently, the data were not analyzed further.

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