evaluated at 0 K for each reaction. This was accomplished by using eq 1 where ΔH_{f0}° represents the heat of formation of

$$\Delta H_0^\circ = \sum_{P} \nu_P(\Delta H_{f0}^\circ)_P - \sum_{R} \nu_R(\Delta H_{f0}^\circ)_R \qquad (1)$$

reactants, R, and products, P, and ν_P and ν_R are the stoichiometric coefficients of the products and reactants, respectively. An equivalent method is to sum the bond dissociation energies, D_0°, of the bonds that are broken and subtract from this total the bond energies of the bonds formed in the reaction. Unfortunately, few values for the heats of formation and bond dissociation energies of sulfur- and halogen-containing molecules have been reported in standard reference tables (*1*, *5*, *10*, *11*, *13*). These data (Table I) were therefore derived by making use of eq 2 and information found in the literature. As an

$$D_0^\circ(\text{X-Y}) = \Delta H_{f0}^\circ(\text{X}) + \Delta H_{f0}^\circ(\text{Y}) - \Delta H_{f0}^\circ(\text{XY}) \qquad (2)$$

example of the use of Table I the exothermicities of four chemical reactions involving sulfur- and chlorine-containing species are listed below:

$$\text{S(g)} + \text{Cl(g)} + \text{M(g)} \rightarrow \text{SCl(g)} + \text{M(g)} \quad \Delta H_0^\circ = -76 \text{ kcal/mol} \qquad (3)$$

M in reaction 3 refers to the third body involved in this termolecular reaction.

$$\text{S(g)} + \text{ClO(g)} \rightarrow \text{SCl(g)} + \text{O(g)} \quad \Delta H_0^\circ = -12 \text{ kcal/mol} \qquad (4)$$

$$\text{SCl(g)} + \text{O}_3\text{(g)} \rightarrow \text{OSCl(g)} + \text{O}_2\text{(g)} \quad \Delta H_0^\circ = -75 \text{ kcal/mol} \qquad (5)$$

$$\text{OSCl(g)} + \text{O}_3\text{(g)} \rightarrow \text{O}_2\text{SCl(g)} + \text{O}_2\text{(g)} \quad \Delta H_0^\circ = -80 \text{ kcal/mol} \qquad (6)$$

It is also interesting to note that abstraction of a Cl atom from $CFCl_3$ or CF_2Cl_2 by an S atom is slightly exothermic since the C–Cl bond energies in these molecules are approximately 70–75 kcal/mol (*17*).

$$\text{S(g)} + \text{CF}_x\text{Cl}_{4-x}\text{(g)} \rightarrow \text{SCl(g)} + \text{CF}_x\text{Cl}_{3-x}\text{(g)} \qquad (7)$$

The corresponding reactions of $S(^1D_2)$ and $S(^1S_0)$, which are formed from photolysis of SCO in the stratosphere (*4*), are 26.4 and 63.4 kcal/mol, respectively, more exothermic than reactions involving ground-state S atoms.

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Thermodynamic Quantities for the Ionization of Water in Sodium Chloride Media to 300 °C

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The thermodynamic quantities at the saturation pressure for the dissociation of water at rounded temperatures from 0 to 300 °C and ionic strengths to 5 *m* in NaCl media are presented in tabular form. The thermodynamic parameters were derived by computer from analytical expressions representing $Q_w = [H^+][OH^-]$ presented in an earlier paper. The small difference in the effect of NaCl over KCl on the ionization of water is briefly discussed.

Data have been previously reported (*1*, *3*) which precisely define the ionization behavior of water, $H_2O(l) = H^+ + OH^-$, in both NaCl and KCl media at the saturation vapor pressure of water to 300 °C. In the study of aqueous equilibria involving hydrogen ion or hydroxide ion dissociation it is often desirable to examine the thermodynamic quantities for the processes. However, the analytical expressions representing $Q_w \equiv [H^+][OH^-]$ as a function of temperature, pressure, and ionic strength are sufficiently complex to require the use of computers for routine derivation of the thermodynamic parameters. These calculations have already been reported for the KCl media but not for the NaCl media (*3*).

In this brief paper we have employed the results from ref 3 to fix the parameters describing the infinite dilution and the

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Table I. Thermodynamic Quantities for the Dissociation of Water at Rounded Temperatures and Ionic Strengths at the Saturation Pressure in NaCl Media

t, °C	log Q_w	ΔH, cal mole^{-1}	ΔS, cal mole^{-1} deg^{-1}	ΔC_p, cal mole^{-1} deg^{-1}	ΔV_w, cm^3 mole^{-1}
I = 0.0					
0	−14.941 ± 0.009	14954 ± 63	−13.62 ± 0.21	−75.7 ± 4.2	−24.1 ± 2.2
25	−13.993 ± 0.009	13340 ± 24	−19.28 ± 0.09	−55.3 ± 1.5	−23.0 ± 1.9
50	−13.272 ± 0.006	12111 ± 33	−23.25 ± 0.12	−44.4 ± 1.2	−22.8 ± 1.7
75	−12.709 ± 0.006	11063 ± 57	−26.37 ± 0.18	−40.4 ± 1.2	−23.7 ± 1.6
100	−12.264 ± 0.009	10045 ± 84	−29.20 ± 0.24	−41.7 ± 1.2	−25.8 ± 1.6
125	−11.914 ± 0.009	8943 ± 89	−32.05 ± 0.24	−47.0 ± 1.2	−29.2 ± 1.6
150	−11.642 ± 0.012	7666 ± 96	−35.15 ± 0.24	−55.6 ± 3.0	−34.0 ± 1.7
175	−11.441 ± 0.012	6140 ± 100	−38.65 ± 0.24	−67.1 ± 3.6	−40.3 ± 1.8
200	−11.302 ± 0.012	4290 ± 190	−42.65 ± 0.39	−81.4 ± 7.2	−48.5 ± 2.3
225	−11.222 ± 0.012	2040 ± 360	−47.25 ± 0.72	−99.1 ± 9.3	−59.6 ± 3.3
250	−11.196 ± 0.015	−710 ± 600	−52.59 ± 1.20	−122.2 ± 10.8	−76.4 ± 5.1
275	−11.224 ± 0.027	−4170 ± 930	−58.97 ± 1.80	−158.1 ± 14.1	−105.9 ± 9.2
300	−11.301 ± 0.045	−8910 ± 1350	−67.30 ± 2.60	−230.3 ± 22.2	−166.1 ± 18.3
I = 0.1					
0	−14.738 ± 0.006	15080 ± 63	−12.23 ± 0.21	−74.2 ± 4.2	−23.20 ± 1.8
25	−13.780 ± 0.006	13520 ± 24	−17.70 ± 0.09	−52.4 ± 1.5	−22.00 ± 1.4
50	−13.046 ± 0.006	12378 ± 32	−21.39 ± 0.12	−40.3 ± 1.2	−21.68 ± 1.4
75	−12.467 ± 0.006	11445 ± 54	−24.17 ± 0.18	−35.4 ± 1.2	−22.38 ± 1.3
100	−12.004 ± 0.006	10567 ± 84	−26.61 ± 0.24	−35.7 ± 0.9	−24.20 ± 1.2
125	−11.631 ± 0.009	9630 ± 99	−29.03 ± 0.27	−39.9 ± 1.2	−27.19 ± 1.2
150	−11.335 ± 0.012	8552 ± 100	−31.65 ± 0.30	−46.6 ± 3.0	−31.38 ± 1.2
175	−11.104 ± 0.012	7285 ± 100	−34.55 ± 0.30	−54.9 ± 3.3	−36.86 ± 1.4
200	−10.932 ± 0.012	5810 ± 170	−37.75 ± 0.36	−63.4 ± 6.9	−43.90 ± 1.8
225	−10.811 ± 0.012	4120 ± 330	−41.19 ± 0.66	−71.0 ± 9.0	−53.33 ± 2.6
250	−10.735 ± 0.015	2260 ± 560	−44.80 ± 0.80	−77.8 ± 9.9	−67.42 ± 4.1
275	−10.695 ± 0.024	210 ± 860	−48.50 ± 1.70	−88.0 ± 13.0	−92.03 ± 7.0
300	−10.683 ± 0.042	−2260 ± 1240	−52.80 ± 2.30	−116.0 ± 20.0	−141.70 ± 19.0
I = 0.5					
0	−14.665 ± 0.009	15142 ± 69	−11.67 ± 0.24	−72.0 ± 4.2	−22.1 ± 1.5
25	−13.701 ± 0.006	13652 ± 45	−16.90 ± 0.15	−49.0 ± 1.5	−20.8 ± 1.2
50	−12.957 ± 0.006	12609 ± 51	−20.27 ± 0.18	−35.8 ± 1.2	−20.3 ± 1.2
75	−12.365 ± 0.009	11801 ± 66	−22.68 ± 0.21	−29.8 ± 1.2	−20.8 ± 1.1
100	−11.883 ± 0.009	11073 ± 90	−24.70 ± 0.27	−29.2 ± 1.2	−22.2 ± 1.1
125	−11.489 ± 0.012	10311 ± 105	−26.67 ± 0.30	−32.3 ± 1.2	−24.7 ± 1.1
150	−11.167 ± 0.015	9443 ± 105	−28.78 ± 0.30	−37.4 ± 2.7	−28.2 ± 1.2
175	−10.907 ± 0.015	8438 ± 105	−31.08 ± 0.30	−42.9 ± 3.0	−32.6 ± 1.3
200	−10.701 ± 0.018	7310 ± 170	−33.51 ± 0.39	−46.6 ± 6.6	−38.2 ± 1.6
225	−10.540 ± 0.018	6140 ± 320	−35.90 ± 0.66	−46.4 ± 8.7	−45.6 ± 2.2
250	−10.416 ± 0.021	5040 ± 550	−38.02 ± 0.81	−40.4 ± 10.5	−56.4 ± 3.5
275	−10.316 ± 0.030	4170 ± 880	−39.60 ± 1.70	−29.0 ± 15.9	−74.9 ± 6.4
300	−10.226 ± 0.045	3570 ± 1370	−40.60 ± 2.60	−20.9 ± 28.8	−111.6 ± 13.2
I = 1.0					
0	−14.684 ± 0.009	15146 ± 67	−11.74 ± 0.23	−69.9 ± 0.5	−21.2 ± 1.5
25	−13.718 ± 0.008	13718 ± 56	−16.76 ± 0.19	−46.1 ± 0.6	−19.8 ± 1.4
50	−12.969 ± 0.009	12757 ± 45	−19.86 ± 0.16	−32.1 ± 0.7	−19.3 ± 1.3
75	−12.366 ± 0.009	12051 ± 35	−21.97 ± 0.13	−25.4 ± 0.8	−19.6 ± 1.3
100	−11.872 ± 0.010	11442 ± 33	−23.66 ± 0.11	−24.0 ± 0.9	−20.8 ± 1.3
125	−11.462 ± 0.010	10819 ± 45	−25.27 ± 0.13	−26.3 ± 1.0	−22.9 ± 1.4
150	−11.121 ± 0.010	10113 ± 67	−26.99 ± 0.17	−30.3 ± 1.1	−25.8 ± 1.5
175	−10.839 ± 0.011	9305 ± 95	−28.83 ± 0.23	−34.1 ± 1.3	−29.5 ± 1.5
200	−10.608 ± 0.012	8430 ± 130	−30.72 ± 0.30	−35.1 ± 1.5	−34.0 ± 1.8
225	−10.418 ± 0.014	7600 ± 160	−32.42 ± 0.37	−30.5 ± 1.6	−39.8 ± 2.4
250	−10.259 ± 0.016	6970 ± 200	−33.61 ± 0.45	−17.4 ± 1.7	−48.1 ± 4.0
275	−10.117 ± 0.019	6810 ± 250	−33.87 ± 0.53	5.8 ± 1.9	−62.1 ± 7.7
300	−9.976 ± 0.023	7320 ± 300	−32.87 ± 0.62	35.6 ± 2.1	−89.1 ± 17.0
I = 3.0					
0	−14.931 ± 0.017	15040 ± 200	−13.25 ± 0.69	−62.4 ± 1.4	−19.1 ± 2.3
25	−13.966 ± 0.011	13830 ± 170	−17.53 ± 0.57	−36.6 ± 1.7	−17.5 ± 2.3
50	−13.203 ± 0.014	13130 ± 130	−19.79 ± 0.45	−20.6 ± 2.0	−16.7 ± 2.3
75	−12.576 ± 0.017	12740 ± 110	−20.95 ± 0.36	−11.8 ± 2.3	−16.6 ± 2.3
100	−12.044 ± 0.019	12500 ± 100	−21.62 ± 0.32	−8.2 ± 2.7	−17.1 ± 2.4
125	−11.587 ± 0.021	12300 ± 140	−22.13 ± 0.37	−8.1 ± 3.0	−18.2 ± 2.6
150	−11.190 ± 0.021	12080 ± 200	−22.64 ± 0.50	−9.1 ± 3.4	−19.8 ± 2.7
175	−10.842 ± 0.023	11850 ± 280	−23.17 ± 0.68	−9.0 ± 3.8	−21.6 ± 2.9
200	−10.536 ± 0.027	11670 ± 380	−23.54 ± 0.88	−4.2 ± 4.3	−23.4 ± 3.2
225	−10.261 ± 0.033	11710 ± 490	−23.40 ± 1.10	9.1 ± 4.8	−25.3 ± 4.2
250	−10.005 ± 0.042	12240 ± 610	−22.40 ± 1.30	35.8 ± 5.2	−27.4 ± 7.1
275	−9.753 ± 0.053	13660 ± 750	−19.70 ± 1.60	81.7 ± 5.8	−30.0 ± 14.0
300	−9.482 ± 0.066	16550 ± 900	−14.50 ± 1.90	155.6 ± 6.3	−32.7 ± 32.0
I = 5.0					
0	−15.254 ± 0.033	14890 ± 340	−15.27 ± 1.15	−55.3 ± 2.4	−17.6
25	−14.291 ± 0.026	13880 ± 280	−18.85 ± 0.95	−27.9 ± 2.8	−15.9
50	−13.518 ± 0.029	13420 ± 220	−20.33 ± 0.76	−10.1 ± 3.3	−14.9
75	−12.869 ± 0.034	13310 ± 170	−20.65 ± 0.60	0.4 ± 3.9	−14.5
100	−12.306 ± 0.037	13400 ± 170	20.40 ± 0.53	5.9 ± 4.4	−14.6
125	−11.807 ± 0.038	13580 ± 230	−19.92 ± 0.62	8.1 ± 5.1	−15.1
150	−11.360 ± 0.039	13790 ± 340	−19.38 ± 0.84	9.4 ± 5.7	−15.7
175	−10.954 ± 0.042	14060 ± 470	−18.75 ± 1.13	12.5 ± 6.4	−16.1
200	−10.582 ± 0.048	14460 ± 640	−17.90 ± 1.50	21.0 ± 7.1	−16.1
225	−10.234 ± 0.058	15200 ± 820	−16.30 ± 1.80	39.6 ± 7.9	−15.3
250	−9.896 ± 0.072	16580 ± 1020	−13.60 ± 2.20	74.2 ± 8.7	−13.1
275	−9.551 ± 0.089	19110 ± 1250	−8.90 ± 2.60	133.2 ± 9.6	−7.9
300	−9.177 ± 0.110	23600 ± 1500	−0.90 ± 3.10	233.3 ± 10.5	6.1

pressure-dependent behavior. The needed derivatives were obtained by numerical differentiation of eq 1 below. Table I lists the values for ΔH, ΔS, ΔC_p, and ΔV which best describe the ionization process in NaCl at the saturation pressure of water at six ionic strength values and at 25 °C intervals from 0 to 300 °C. The errors given (three times the standard error) for the quantities at ionic strengths of 0.5 or less are taken from ref 3 and at higher ionic strength values they were obtained by propagation of the errors assigned to the data in ref 1. The difference in the effect of NaCl over KCl on the ionization of water is relatively small. Below unit ionic strength log Q_w values in the two media agree within less than 0.05 units, at higher ionic strengths and at the higher temperatures log Q_w for NaCl are more positive than the values in KCl solution by larger amounts, reaching a maximum of 0.151 difference at 250 °C and I = 3.0. There is a small but regular trend toward reduced ΔH values for NaCl over KCl media at the higher temperatures as the ionic strength increases, e.g., 7320 ± 300 vs. 10 950 ± 1820 cal mol^{-1} for NaCl and KCl media, respectively, at 300 °C and I = 1.0, and 16 500 ± 900 vs. 21 380 ± 3500 cal mol^{-1}, respectively, at 300 °C and I = 3.0. Similarly, more negative ΔS values at the higher salt concentrations are shown for NaCl media, −14.50 ± 1.90 vs. −6.50 ± 6.60 cal mol^{-1} deg^{-1} for NaCl and KCl solutions, respectively, at 300 °C and I = 3.0.

The basis for the thermodynamic data are the expressions (*1*, *3*)

$$\log Q_w = (3.1286 \times 10^4/T) + 94.9734 \ln T - 0.097611T - (2.17087 \times 10^6/T^2) - 606.522 + 2A(I^{1/2})/(1 + (I^{1/2})) - [0.61139 - (87.645/T) - 1.6698 \times 10^{-6}T^2 + 0.24456F(I)]I - 0.0157\phi m_{\mathrm{NaCl}} + \beta(12.99535 - 0.014449T - 4.219071 \times 10^{-3}(I^{1/2})T + 7.05620 \times 10^{-7}(I^{1/2})T^2)(P - P_s) \tag{1}$$

where

$$F(I) = [1 - (1 + 2(I^{1/2}) - 2I) \exp(-2(I^{1/2}))]/4I \tag{2}$$

$$A = -2.97627 + 4.80688 \times 10^{-2}T - 2.69280 \times 10^{-4}T^2 + 7.49524 \times 10^{-7}T^3 - 1.02352 \times 10^{-9}T^4 + 5.58004 \times 10^{-13}T^5 \tag{3}$$

$$\beta = [50.9929 - 0.233581t + 1.9750 \times 10^{-3}t^2 + 1.78505 \times 10^{-3} \exp(0.0380606)t] \times 10^{-6}\ \mathrm{bar}^{-1} \tag{4}$$

(ϕ = osmotic coefficient of the NaCl solution (*2*), P_s is the vapor pressure of water at T(K), t is in °C, and I is the ionic strength.)

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