

5

Physical and thermodynamic data

Table of Contents

1	Values for various fundamental constants	2
2	Atomic Weights	2
3	Vapor pressure of water	5
3.1	Pure water	5
3.2	Sea water	5
4	Densities of various substances	6
4.1	Air-saturated water	6
4.2	Sea water	6
4.3	Sodium chloride solutions	7
4.4	A mixture of NaCl and HCl at 25 °C.	8
4.5	Mercury	8
4.6	Various solids	9
5	Virial coefficients for carbon dioxide	9
5.1	Pure carbon dioxide gas	9
5.2	Carbon dioxide in air	9
6	Salinity and the composition of sea water	10
6.1	The major ion composition of sea water	10
6.2	A simplified synthetic sea water recipe	12
7	Equilibrium constants	12
7.1	Solubility of carbon dioxide in sea water	12
7.2	Acid-base reactions in sea water	13
	Bisulfate ion	13
	Boric acid	14
	Carbonic acid	14
	Hydrogen fluoride	15
	Phosphoric acid	16
	Silicic acid	17
	Water	18
7.3	Acid-base reactions in sodium chloride media	18
	Carbonic acid	18
	2-amino-2-hydroxymethyl-1,3-propanediol	19
	Water	19
8	References	19

1. Values for various fundamental constants

$$R = 8.314510(70) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$F = 96485.309(29) \text{ C}\cdot\text{mol}^{-1}$$

$$0 \text{ }^\circ\text{C} = 273.15 \text{ K (defined)}$$

$$1 \text{ atm} = 101325 \text{ Pa (defined)}$$

(Cohen & Taylor, 1986). For each constant, the standard deviation uncertainty in the least significant digits is given in parentheses.

2. Atomic Weights

Atomic weights are quoted here (Table 2.1) to five significant figures unless the dependable accuracy is more limited by either the combined uncertainties of the best published atomic weight determinations, or by the variability of isotopic composition in normal terrestrial occurrences (the latter applied to elements **annotated r**). The last significant figure of each tabulated value is considered reliable to ± 1 except when a larger single-digit uncertainty is inserted in parentheses following the atomic weight. Neither the highest or the lowest actual atomic weight of any normal sample is thought likely to differ from the tabulated value by more than the assigned uncertainty. However, the tabulated values do not apply either to samples of highly exceptional isotopic composition arising from most geological occurrences (for elements **annotated g**) or to those whose isotopic composition has been artificially altered. Such might even be found in commerce without disclosure of that modification (for elements **annotated m**). Elements annotated by an asterisk (*) have no stable isotope and are generally represented in this Table by just one of the element's commonly known radioisotopes, with a corresponding relative atomic mass in the atomic weight column. However, three such elements (Th, Pa and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated. For more detail, see the complete table (cited in IUPAC, 1993). Some atomic weights have been revised to reflect more recent determinations (IUPAC, 1994).

Table 2.1: IUPAC Table of standard atomic weights abridged to five significant figures. Scaled to the relative atomic mass $A(^{12}\text{C}) = 12$.

	Name	Symbol	Atomic weight	Annotations
1	Hydrogen	H	1.0079	g m
2	Helium	He	4.0026	
3	Lithium	Li	6.941(2)	g m r
4	Beryllium	Be	9.0122	
5	Boron	B	10.811(5)	g m r
6	Carbon	C	12.011	g r
7	Nitrogen	N	14.007	
8	Oxygen	O	15.999	
9	Fluorine	F	18.998	
10	Neon	Ne	20.180	m
11	Sodium (Natrium)	Na	22.990	
12	Magnesium	Mg	24.305	
13	Aluminium	Al	26.982	
14	Silicon	Si	28.086	
15	Phosphorus	P	30.974	
16	Sulfur	S	32.066(6)	g r
17	Chlorine	Cl	35.453	m
18	Argon	Ar	39.948	g r
19	Potassium (Kalium)	K	39.098	g
20	Calcium	Ca	40.078(4)	g
21	Scandium	Sc	44.956	
22	Titanium	Ti	47.867	
23	Vanadium	V	50.942	
24	Chromium	Cr	51.996	
25	Manganese	Mn	54.938	
26	Iron	Fe	55.845(2)	
27	Cobalt	Co	58.933	
28	Nickel	Ni	58.693	
29	Copper	Cu	63.546(3)	r
30	Zinc	Zn	65.39(2)	
31	Gallium	Ga	69.723	
32	Germanium	Ge	72.61(2)	
33	Arsenic	As	74.922	
34	Selenium	Se	78.96(3)	
35	Bromine	Br	79.904	
36	Krypton	Kr	83.80	g m
37	Rubidium	Rb	85.468	
38	Strontium	Sr	87.62	
39	Yttrium	Y	88.906	
40	Zirconium	Zr	91.224(2)	g
41	Niobium	Nb	92.906	
42	Molybdenum	Mo	95.94	g
43	Technetium*	⁹⁹ Tc	98.906	
44	Ruthenium	Ru	101.07(2)	g
45	Rhodium	Rh	102.91	
46	Palladium	Pd	106.42	g
47	Silver	Ag	107.87	
48	Cadmium	Cd	112.41	
49	Indium	In	114.82	
50	Tin	Sn	118.71	
51	Antimony (Stibium)	Sb	121.76	g
52	Tellurium	Te	127.60	g

Table 2.1: IUPAC Table of standard atomic weights abridged to five significant figures. Scaled to the relative atomic mass $A(^{12}\text{C}) = 12$.

	Name	Symbol	Atomic weight	Annotations
53	Iodine	I	126.90	
54	Xenon	Xe	131.29(2)	g m
55	Caesium	Cs	132.91	
56	Barium	Ba	137.33	
57	Lanthanum	La	138.91	
58	Cerium	Ce	140.12	g
59	Praesodymium	Pr	140.91	
60	Neodymium	Nd	144.24(3)	g
61	Promethium*	^{147}Pm	146.92	
62	Samarium	Sm	150.36	g
63	Europium	Eu	151.96	g
64	Gadolinium	Gd	157.25(3)	g
65	Terbium	Tb	158.93	
66	Dysprosium	Dy	162.50(3)	g
67	Holmium	Ho	164.93	
68	Erbium	Er	167.26	g
69	Thulium	Tm	168.93	
70	Ytterbium	Yb	173.04	
71	Lutetium	Lu	174.97	g
72	Hafnium	Hf	178.49	
73	Tantalum	Ta	180.95	
74	Tungsten(Wolfram)	W	183.84	
75	Rhenium	Re	186.21	
76	Osmium	Os	190.23(3)	g
77	Iridium	Ir	192.22	
78	Platinum	Pt	195.08(3)	
79	Gold	Au	196.97	
80	Mercury	Hg	200.59	
81	Thallium	Tl	204.38	
82	Lead	Pb	207.2	g r
83	Bismuth	Bi	208.98	
84	Polonium*	^{210}Po	209.98	
85	Astatine*	^{210}At	209.99	
86	Radon*	^{222}Rn	222.02	
87	Francium*	^{223}Fr	223.02	
88	Radium*	^{226}Ra	226.03	
89	Actinium*	^{227}Ac	227.03	
90	Thorium*	Th	232.04	g
91	Protoactinium*	Pa	231.04	
92	Uranium*	U	238.03	g m
93	Neptunium*	^{237}Np	237.05	
94	Plutonium*	^{239}Pu	239.05	
95	Americium*	^{241}Am	241.06	
96	Curium*	^{244}Cm	244.06	
97	Berkelium*	^{249}Bk	249.08	
98	Californium*	^{252}Cf	252.08	
99	Einsteinium*	^{252}Es	252.08	
100	Fermium*	^{257}Fm	257.10	
101	Mendelevium*	^{258}Md	258.10	
102	Nobelium*	^{259}No	259.10	
103	Lawrencium*	^{262}Lr	262.11	

3. Vapor pressure of water

3.1 Pure water

The vapor pressure of pure water over the temperature range 273–648 K is represented by the Chebyshev polynomial (Ambrose and Lawrenson, 1972):

$$\left(\frac{T}{\text{K}}\right) \log\left(\frac{VP(\text{H}_2\text{O})}{\text{kPa}}\right) = \frac{1}{2}a_0 + \left[\sum_{k=1}^{11} a_k E_k(x) \right], \quad (3.1.1)$$

where $x = (2(T/\text{K}) - 921)/375$ and T is measured on the International Practical Temperature Scale of 1968 (Note 1). The Chebyshev coefficients are

$$\begin{array}{ll} a_0 = 2794.0144 & a_6 = 0.1371 \\ a_1 = 1430.6181 & a_7 = 0.0629 \\ a_2 = -18.2465 & a_8 = 0.0261 \\ a_3 = 7.6875 & a_9 = 0.0200 \\ a_4 = -0.0328 & a_{10} = 0.0117 \\ a_5 = 0.2728 & a_{11} = 0.0067. \end{array}$$

At 25 °C (298.15 K), $VP(\text{H}_2\text{O}) = 3.1686$ kPa.

3.2 Sea water

The vapor pressure of water in sea water is related to that of pure water:

$$VP(\text{H}_2\text{O}, \text{s/w}) \approx VP(\text{H}_2\text{O}) \exp\left(-0.018 \phi \sum_{\text{B}} m_{\text{B}}/m^\circ\right), \quad (3.2.1)$$

where

$VP(\text{H}_2\text{O})$ is the vapor pressure of pure water (3.1.1),

$\sum_{\text{B}} m_{\text{B}}$ is the total molality of dissolved species (3.2.2),

ϕ is the osmotic coefficient of sea water (3.2.3),

$m^\circ = 1 \text{ mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{-1}$.

For sea water (of the composition detailed in § 6.1)

$$\sum_{\text{B}} m_{\text{B}}/m^\circ = \frac{31.998 S}{10^3 - 1.005 S}, \quad (3.2.2)$$

¹ The International Practical Temperature Scale of 1968 (IPTS 68) has recently been superseded by the International Temperature Scale of 1990 (ITS 90). A simple equation can be used to relate the two over the oceanographic temperature range 0 to 40 °C (Jones & Harris, 1992):

$$t_{90}/^\circ\text{C} = 0.0002 + 0.99975 t_{68}/^\circ\text{C}.$$

and the osmotic coefficient at 25 °C is given by (Millero, 1974):

$$\begin{aligned} \phi = & 0.90799 - 0.08992 \left(\frac{\frac{1}{2} \sum_B m_B}{m^\circ} \right) + 0.18458 \left(\frac{\frac{1}{2} \sum_B m_B}{m^\circ} \right)^2 \\ & - 0.07395 \left(\frac{\frac{1}{2} \sum_B m_B}{m^\circ} \right)^3 - 0.00221 \left(\frac{\frac{1}{2} \sum_B m_B}{m^\circ} \right)^4, \end{aligned} \quad (3.2.3)$$

for $I = 0.3 - 0.8 \text{ mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{-1}$ ($S = 16-40$). (Although strictly ϕ is a function of temperature as well as of I , the change between 0 and 40 °C is typically about 1% and can be ignored here.)

At 25 °C and $S = 35$, $VP(\text{H}_2\text{O}, \text{s/w}) = 3.1094 \text{ kPa}$.

4. Densities of various substances

4.1 Air-saturated water

The density of air-saturated water in the temperature range 5 to 40 °C—*i.e.* avoiding the temperature of maximum density—is given by the expression (Jones & Harris, 1992):

$$\begin{aligned} \rho_W / (\text{kg}\cdot\text{m}^{-3}) = & 999.84847 + 6.337563 \times 10^{-2} (t/^\circ\text{C}) \\ & - 8.523829 \times 10^{-3} (t/^\circ\text{C})^2 + 6.943248 \times 10^{-5} (t/^\circ\text{C})^3 \\ & - 3.821216 \times 10^{-7} (t/^\circ\text{C})^4, \end{aligned} \quad (4.1.1)$$

where t is the temperature on ITS 90 (see Note 1).

At 25 °C, $\rho_W = 997.041 \text{ kg}\cdot\text{m}^{-3} = 0.997041 \text{ g}\cdot\text{cm}^{-3}$.

4.2 Sea water

The density of sea water in the temperature range 0 to 40 °C (IPTS 68—see Note 1) and the salinity range 0 to 42 is given by the expression (Millero & Poisson, 1981):

$$\rho_{\text{SW}} / (\text{kg}\cdot\text{m}^{-3}) = \rho_{\text{SMOW}} / (\text{kg}\cdot\text{m}^{-3}) + A S + B S^{1.5} + C S^2 \quad (4.2.1)$$

where (Note 2)

$$\begin{aligned} \rho_{\text{SMOW}} / (\text{kg}\cdot\text{m}^{-3}) = & 999.842594 + 6.793952 \times 10^{-2} (t/^\circ\text{C}) \\ & - 9.095290 \times 10^{-3} (t/^\circ\text{C})^2 + 1.001685 \times 10^{-4} (t/^\circ\text{C})^3 \\ & - 1.120083 \times 10^{-6} (t/^\circ\text{C})^4 + 6.536332 \times 10^{-9} (t/^\circ\text{C})^5, \end{aligned} \quad (4.2.2)$$

² SMOW — Standard Mean Ocean Water (Craig, 1961)—is pure water with a specified isotopic composition and free of dissolved gases.

$$\begin{aligned}
 A = & 8.24493 \times 10^{-1} - 4.0899 \times 10^{-3} (t/^{\circ}\text{C}) \\
 & + 7.6438 \times 10^{-5} (t/^{\circ}\text{C})^2 - 8.2467 \times 10^{-7} (t/^{\circ}\text{C})^3 \\
 & + 5.3875 \times 10^{-9} (t/^{\circ}\text{C})^4, \quad (4.2.3)
 \end{aligned}$$

$$\begin{aligned}
 B = & -5.72466 \times 10^{-3} + 1.0227 \times 10^{-4} (t/^{\circ}\text{C}) \\
 & - 1.6546 \times 10^{-6} (t/^{\circ}\text{C})^2, \quad (4.2.4)
 \end{aligned}$$

$$C = 4.8314 \times 10^{-4}; \quad (4.2.5)$$

t is on IPTS 68 and S is the salinity.

At 25 °C (IPTS 68) and $S = 35$, $\rho_{\text{SW}} = 1023.343 \text{ kg}\cdot\text{m}^{-3}$.

4.3 Sodium chloride solutions

The density of a solution of sodium chloride in water in the temperature range 0 to 50 °C (IPTS 68—see Note 1) and the concentration range 0.1 mol·kg-H₂O⁻¹ to saturation can be calculated from the expression (Lo Surdo *et al.*, 1982):

$$\begin{aligned}
 \frac{10^3(\rho(\text{NaCl}) - \rho_{\text{SMOW}})}{\text{g}\cdot\text{cm}^{-3}} = & \left(\frac{m}{m^{\circ}}\right) \left(45.5655 - 0.2341\left(\frac{t}{^{\circ}\text{C}}\right)\right) \\
 & + 3.4128 \times 10^{-3} \left(\frac{t}{^{\circ}\text{C}}\right)^2 - 2.7030 \times 10^{-5} \left(\frac{t}{^{\circ}\text{C}}\right)^3 + 1.4037 \times 10^{-7} \left(\frac{t}{^{\circ}\text{C}}\right)^4 \\
 & + \left(\frac{m}{m^{\circ}}\right)^{3/2} \left(-1.8527 + 5.3956 \times 10^{-2} \left(\frac{t}{^{\circ}\text{C}}\right) - 6.2635 \times 10^{-4} \left(\frac{t}{^{\circ}\text{C}}\right)^2\right) \\
 & + \left(\frac{m}{m^{\circ}}\right)^2 \left(-1.6368 - 9.5653 \times 10^{-4} \left(\frac{t}{^{\circ}\text{C}}\right) + 5.2829 \times 10^{-5} \left(\frac{t}{^{\circ}\text{C}}\right)^2\right) \\
 & + 0.2274 \left(\frac{m}{m^{\circ}}\right)^{5/2} \quad (4.3.1)
 \end{aligned}$$

where t is the temperature (IPTS 68), m the molality of the sodium chloride solution and $m^{\circ} = 1 \text{ mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{-1}$. ρ_{SMOW} is calculated using equation (4.2.2)—see Note 3.

To convert the concentration of sodium chloride expressed in mol·kg-soln⁻¹— $C(\text{NaCl})$ —to mol·kg-H₂O⁻¹ use the expression:

$$\frac{m(\text{NaCl})}{m^{\circ}} = \frac{10^3 C(\text{NaCl})}{10^3 - 58.443 C(\text{NaCl})}. \quad (4.3.2)$$

At 25 °C and $m = 0.725 \text{ mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{-1}$, $\rho(\text{NaCl}) = 1.02581 \text{ g}\cdot\text{cm}^{-3}$.

³ In the original paper of Lo Surdo *et al.* (1982) an alternate formulation based on the work of Kell (1975) was used for the density of pure water. The difference is <10 ppm over the temperature range 0 to 50 °C.

4.4 A mixture of NaCl and HCl at 25 °C

An expression based on Young's rule has been developed for the density of a mixture of NaCl and HCl at a temperature of 25 °C (Millero, *personal communication*):

$$\rho_{\text{mix}}(25\text{ °C}) = \frac{\rho_{\text{W}}(25\text{ °C})(10^3 + m_{\text{T}}\{m(\text{HCl}) + m(\text{NaCl})\})}{10^3 + \phi_{\text{mix}}\{m(\text{HCl}) + m(\text{NaCl})\}(\rho_{\text{W}}(25\text{ °C}))}, \quad (4.4.1)$$

where $\rho_{\text{W}}(25\text{ °C}) = 0.99704\text{ g}\cdot\text{cm}^{-3}$ (Note 4),

$$m_{\text{T}} = \frac{36.46\ m(\text{HCl}) + 58.44\ m(\text{NaCl})}{m(\text{HCl}) + m(\text{NaCl})}, \quad (4.4.2)$$

$$\phi_{\text{mix}} = \frac{m(\text{HCl})\ \phi_{\text{HCl}} + m(\text{NaCl})\ \phi_{\text{NaCl}}}{m(\text{HCl}) + m(\text{NaCl})}, \quad (4.4.3)$$

and the apparent molar volumes at 25 °C:

$$\phi_{\text{HCl}} = 17.854 + 1.460\sqrt{m} - 0.307\ m, \quad (4.4.4)$$

$$\phi_{\text{NaCl}} = 16.613 + 1.811\sqrt{m} + 0.094\ m, \quad (4.4.5)$$

where $m = m(\text{HCl}) + m(\text{NaCl})$. The concentrations $m(\text{HCl})$ and $m(\text{NaCl})$ are in $\text{mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{-1}$.

At $m(\text{HCl}) = 0.2\ \text{mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{-1}$ and $m(\text{NaCl}) = 0.5\ \text{mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{-1}$, $\rho_{\text{mix}}(25\text{ °C}) = 1.02056\ \text{g}\cdot\text{cm}^{-3}$.

4.5 Mercury

The density of mercury in the temperature range 0 to 50 °C is given by Weast (1975):

$$\rho(\text{Hg}) = 13.5955 \left(1 - \alpha_{\text{V}}(\text{Hg}) \left(\frac{t}{\text{°C}} \right) \right) \text{ g} \cdot \text{cm}^{-3}; \quad (4.5.1)$$

where t is the temperature (presumably on IPTS 68). The volumetric coefficient of expansion

$$\alpha_{\text{V}}(\text{Hg}) = \left(181792 + 0.175 \left(\frac{t}{\text{°C}} \right) + 0.035116 \left(\frac{t}{\text{°C}} \right)^2 \right) \times 10^{-9}. \quad (4.5.2)$$

At 25 °C, $\rho(\text{Hg}) = 13.5337\ \text{g}\cdot\text{cm}^{-3}$.

⁴ At temperatures other than 25 °C, equation (4.4.1) is not reliable.

4.6 Various solids

Data from Weast (1975).

Potassium chloride

$$\rho(\text{KCl}) = 1.984 \text{ g}\cdot\text{cm}^{-3} \quad (4.6.1)$$

Sodium chloride

$$\rho(\text{NaCl}) = 2.165 \text{ g}\cdot\text{cm}^{-3} \quad (4.6.2)$$

Sodium carbonate

$$\rho(\text{Na}_2\text{CO}_3) = 2.532 \text{ g}\cdot\text{cm}^{-3} \quad (4.6.3)$$

Sodium sulfate

$$\rho(\text{Na}_2\text{SO}_4) = 2.68 \text{ g}\cdot\text{cm}^{-3} \quad (4.6.4)$$

Sodium tetraborate decahydrate (borax)

$$\rho(\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}) = 1.73 \text{ g}\cdot\text{cm}^{-3} \quad (4.6.5)$$

2-amino-2-hydroxymethyl-1,3-propanediol ("tris")

$$\rho(\text{H}_2\text{NC}(\text{CH}_2\text{OH})_3) = 1.35 \text{ g}\cdot\text{cm}^{-3} \quad (4.6.6)$$

2-aminopyridine

$$\rho(\text{C}_5\text{H}_6\text{N}_2) = 1.24 \text{ g}\cdot\text{cm}^{-3} \quad (4.6.7)$$

5. Virial coefficients for carbon dioxide

5.1 Pure carbon dioxide gas

The first virial coefficient of CO_2 is given by the expression (Weiss, 1974)

$$\frac{B(\text{CO}_2, T)}{\text{cm}^3 \cdot \text{mol}^{-1}} = -1636.75 + 12.0408 \left(\frac{T}{\text{K}}\right) - 3.27957 \times 10^{-2} \left(\frac{T}{\text{K}}\right)^2 + 3.16528 \times 10^{-5} \left(\frac{T}{\text{K}}\right)^3, \quad (5.1.1)$$

where $265 < (T/\text{K}) < 320$.

At 25°C (298.15 K), $B(\text{CO}_2, 298.15 \text{ K}) = -123.2 \text{ cm}^3\cdot\text{mol}^{-1}$.

5.2 Carbon dioxide in air

For a binary mixture (B-C), it is possible to define a cross virial coefficient:

$$\delta_{\text{B-C}} = B_{\text{BC}} - \frac{1}{2}(B_{\text{BB}} - B_{\text{CC}}) \quad (5.2.1)$$

Weiss (1974) used the Lennard-Jones (6–12) potential to calculate values for the cross-virial coefficient δ for the binary mixture: CO₂–air (see also SOP 24). He found that the temperature dependence of this parameter could be represented by the equation

$$\frac{\delta(\text{CO}_2 - \text{air})}{\text{cm}^3 \cdot \text{mol}^{-1}} = 57.7 - 0.118 \left(\frac{T}{\text{K}} \right), \quad (5.2.2)$$

where $273 < (T/\text{K}) < 313$.

At 25 °C (298.15 K), $\delta(\text{CO}_2\text{--air}) = 22.5 \text{ cm}^3 \cdot \text{mol}^{-1}$.

6. Salinity and the composition of sea water

6.1 The major ion composition of sea water

Traditionally the parameter salinity, S , has been used to give a measure of the total dissolved solids in sea water. Originally this was intended to be an analytical parameter with the units $\text{g} \cdot \text{kg}^{-1}$, but this direct approach was quickly superseded by the practice of estimating salinity from alternative, simpler procedures (*e.g.* the measurement of chlorinity or conductivity ratio). The concept of a “constant composition of sea water” is then invoked to relate these parameters to salinity (UNESCO, 1966).

Although the idea of “constant composition of sea water” is recognized as being not strictly accurate, it is a useful device in simplifying the study of the various physicochemical properties of sea water. One example of this is the treatment of sea water as a two component system—water and sea-salt—to represent its thermodynamic properties (*e. g.* osmotic coefficient or density, see § 3.2 and § 4.2). Another is the treatment of sea water as a constant ionic medium in which the thermodynamics of various chemical process involving minor constituents can be studied (*e. g.* gas solubility or acid–base equilibria).

Analytical results for the other major components of sea water are usually expressed relative to chlorinity (Table 6.1) and a standard mean chemical composition of sea water (Table 6.2) can be calculated using the equilibrium constants for the dissociation of water, carbonic and boric acids.

Table 6.1: Standard mean analytical composition of sea water with $S = 35$, chlorinity = 19.374.

Component	Relative Concentration ^a	mol·kg-soln ⁻¹	Reference
Chloride	0.99889	0.54586	calculated from chlorinity
Sulfate	0.1400	0.02824	Morris & Riley (1966)
Bromide	0.003473	0.00084	Morris & Riley (1966)
Fluoride	0.000067	0.00007	Riley (1965)
Sodium	0.55661	0.46906	from charge balance
Magnesium	0.06626	0.05282	Carpenter & Manella (1973)
Calcium	0.02127	0.01028	Riley & Tongudai (1967)
Potassium	0.0206	0.01021	Riley & Tongudai (1967)
Strontium	0.00041	0.00009	Riley & Tongudai (1967)
Boron	0.000232	0.000416	Uppström (1974)
Total alkalinity		0.002400	average surface water
pH = 8.1		10 ^{-8.1}	average surface water

a. Expressed relative to the chlorinity (= $S/1.80655$). Thus the total sulfate (molar mass 96.062 g) at a salinity S is given by:

$$S_T = \left(\frac{0.1400}{96.062}\right) \times \left(\frac{S}{1.80655}\right) \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}.$$

Table 6.2: Standard mean chemical composition of sea water ($S = 35$)

Species	mol·kg-soln ⁻¹	g·kg-soln ⁻¹	mol·kg-H ₂ O ⁻¹	g·kg-H ₂ O ⁻¹
Cl ⁻	0.54586	19.3524	0.56576	20.0579
SO ₄ ²⁻	0.02824	2.7123	0.02927	2.8117
Br ⁻	0.00084	0.0673	0.00087	0.0695
F ⁻	0.00007	0.0013	0.00007	0.0013
Na ⁺	0.46906	10.7837	0.48616	11.1768
Mg ²⁺	0.05282	1.2837	0.05475	1.3307
Ca ²⁺	0.01028	0.4121	0.01065	0.4268
K ⁺	0.01021	0.3991	0.01058	0.4137
Sr ²⁺	0.00009	0.0079	0.00009	0.0079
B(OH) ₃	0.00032	0.0198	0.00033	0.0204
B(OH) ₄ ⁻	0.00010	0.0079	0.00010	0.0079
CO ₂ [*]	0.00001	0.0004	0.00001	0.0004
HCO ₃ ⁻	0.00177	0.1080	0.00183	0.1117
CO ₃ ²⁻	0.00026	0.0156	0.00027	0.0162
OH ⁻	0.00001	0.0002	0.00001	0.0002
sum of column	1.11994	35.1717	1.16075	36.4531
ionic strength	0.69734		0.72275	

6.2 A simplified synthetic sea water recipe

A simplified artificial sea water recipe can be obtained from the recipe in Table 6.2 as follows: replace bromide, fluoride, and total alkalinity with chloride and replace strontium with calcium. The resultant composition (Table 6.3) is the basis of the synthetic sea water that has been used to determine a variety of equilibrium constants for use in sea water (*e. g.* Dickson, 1990; Roy *et al.*, 1993):

Table 6.3: Simplified artificial sea water composition ($S = 35$)^a

Species	mol·kg-soln ⁻¹	g·kg-soln ⁻¹	mol·kg-H ₂ O ⁻¹	g·kg-H ₂ O ⁻¹
Cl ⁻	0.54922	19.4715	0.56918	20.1791
SO ₄ ²⁻	0.02824	2.7128	0.02927	2.8117
Na ⁺	0.46911	10.7848	0.48616	11.1768
Mg ²⁺	0.05283	1.2840	0.05475	1.3307
Ca ²⁺	0.01036	0.4152	0.01074	0.4304
K ⁺	0.01021	0.3992	0.01058	0.4137
sum of column	1.11997	35.0675	1.16068	36.3424
ionic strength	0.69713		0.72248	

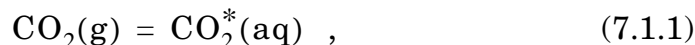
- a. The composition here is very slightly different from that used by Dickson (1990) or Roy *et al.*, (1993). This is the result of minor changes in the molar masses used to compute the various concentrations.

7. Equilibrium constants

All the equations for the equilibrium constants presented here use concentrations expressed in moles per kilogram of solution. In addition, with the exception of that for bisulfate ion, all acid dissociation constants are expressed in terms of “total” hydrogen ion concentration (see Chapter 2).

7.1 Solubility of carbon dioxide in sea water

The equilibrium constant for the process



i. e.

$$K_0 = [\text{CO}_2^*] / f(\text{CO}_2) \quad , \quad (7.1.2)$$

is given by the expression (Weiss, 1974):

$$\begin{aligned} \ln(K_0/k^\circ) = & 93.4517\left(\frac{100}{T/K}\right) - 60.2409 + 23.3585 \ln\left(\frac{T/K}{100}\right) \\ & + S\left(0.023517 - 0.023656\left(\frac{T/K}{100}\right) + 0.0047036\left(\frac{T/K}{100}\right)^2\right), \end{aligned} \quad (7.1.3)$$

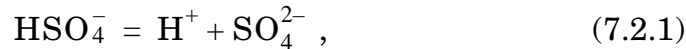
The fugacity of CO₂ gas (see Chapter 2) is expressed in atm;
 $k^\circ = 1 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$.

At $S = 35$ and $t = 25^\circ\text{C}$ (298.15 K), $\ln(K_0/k^\circ) = -3.5617$.

7.2 Acid-base reactions in sea water

BISULFATE ION

The equilibrium constant for the reaction



i. e.

$$K_S = [\text{H}^+]_{\text{F}}[\text{SO}_4^{2-}]/[\text{HSO}_4^-], \quad (7.2.2)$$

is given by the expression (Dickson, 1990a):

$$\begin{aligned} \ln(K_S/k^\circ) = & \frac{-4276.1}{(T/K)} + 141.328 - 23.093 \ln(T/K) \\ & + \left(\frac{-13856}{(T/K)} + 324.57 - 47.986 \ln(T/K)\right) \times \left(\frac{I}{m^\circ}\right)^{1/2} \\ & + \left(\frac{35474}{(T/K)} - 771.54 + 114.723 \ln(T/K)\right) \times \left(\frac{I}{m^\circ}\right) \\ & - \frac{2698}{(T/K)}\left(\frac{I}{m^\circ}\right)^{3/2} + \frac{1776}{(T/K)}\left(\frac{I}{m^\circ}\right)^2 + \ln(1 - 0.001005 S). \end{aligned} \quad (7.2.3)$$

$k^\circ = 1 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$ and hydrogen ion concentration is expressed on the “free” scale. The ionic strength is calculated from the expression

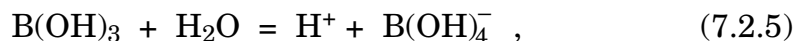
$$I/m^\circ = \frac{19.924S}{1000 - 1.005S}; \quad (7.2.4)$$

The term $\ln(1 - 0.001005S)$ converts the value of K_S from $\text{mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{-1}$ (used in the paper of Dickson) to $\text{mol}\cdot\text{kg}\cdot\text{soln}^{-1}$.

At $S = 35$ and $t = 25^\circ\text{C}$ (298.15K), $\ln(K_S/k^\circ) = -2.30$.

BORIC ACID

The equilibrium constant for the reaction



i. e.

$$K_B = [\text{H}^+][\text{B(OH)}_4^-]/[\text{B(OH)}_3] , \quad (7.2.6)$$

is given by the expression (Dickson,1990b):

$$\begin{aligned} \ln\left(\frac{K_B}{k^\circ}\right) = & \frac{-8966.90 - 2890.53 S^{1/2} - 77.942 S + 1.728 S^{3/2} - 0.0996 S^2}{(T/\text{K})} \\ & + (148.0248 + 137.1942 S^{1/2} + 1.62142 S) \\ & + (-24.4344 - 25.085 S^{1/2} - 0.2474 S) \ln(T/\text{K}) \\ & + 0.053105 S^{1/2} (T/\text{K}) ; \end{aligned} \quad (7.2.7)$$

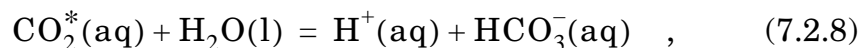
$k^\circ = 1 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$. This equation is in excellent agreement with the measurements made by Roy *et al.* (1993a); it is also in reasonable agreement with the results of Hansson (1973a).

At $S = 35$ and $t = 25 \text{ }^\circ\text{C}$ (298.15 K), $\ln(K_B/k^\circ) = -19.7964$.

CARBONIC ACID

The equilibrium constants used here are from Roy *et al.* (1993b). These constants are in excellent agreement with those measured by Goyet & Poisson (1989), and in reasonable agreement with those of Hansson (1973b) and Mehrbach *et al.*(1973).

The equilibrium constant for the reaction



i. e.

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2^*] \quad (7.2.9)$$

is given by the expression (Roy *et al.*, 1993):

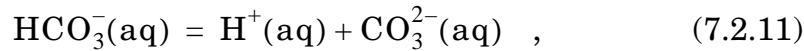
$$\begin{aligned} \ln(K_1/k^\circ) = & \frac{-2307.1266}{(T/\text{K})} + 2.83655 - 1.5529413 \ln(T/\text{K}) \\ & + \left(\frac{-4.0484}{(T/\text{K})} - 0.20760841\right) S^{1/2} + 0.08468345 S \\ & - 0.00654208 S^{3/2} + \ln(1 - 0.001005 S) ; \end{aligned} \quad (7.2.10)$$

where $k^\circ = 1 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$.

The term $\ln(1 - 0.001005S)$ converts the value of K_1 from mol·kg-H₂O⁻¹ (in the original paper of Roy *et al.*) to mol·kg-soln⁻¹.

At $S = 35$ and $t = 25$ °C (298.15 K), $\ln(K_1/k^\circ) = -13.4847$.

The equilibrium constant for the reaction



i. e.

$$K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (7.2.12)$$

is given by the expression (Roy *et al.*, 1993):

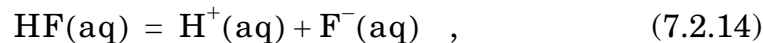
$$\begin{aligned} \ln(K_2/k^\circ) = & \frac{-3351.6106}{(T/\text{K})} - 9.226508 - 0.2005743 \ln(T/\text{K}) \\ & + \left(\frac{-23.9722}{(T/\text{K})} - 0.106901773 \right) S^{1/2} + 0.1130822 S \\ & - 0.00846934 S^{3/2} + \ln(1 - 0.001005 S) ; \quad (7.2.13) \end{aligned}$$

where $k^\circ = 1$ mol·kg-soln⁻¹. The term $\ln(1 - 0.001005 S)$ converts the value of K_1 from mol·kg-H₂O⁻¹ (in the paper of Roy *et al.*) to mol·kg-soln⁻¹.

At $S = 35$ and $t = 25$ °C (298.15 K), $\ln(K_2/k^\circ) = -20.5504$.

HYDROGEN FLUORIDE

The equilibrium constant for the reaction



i. e.

$$K_{\text{F}} = [\text{H}^+][\text{F}^-]/[\text{HF}] \quad , \quad (7.2.15)$$

is given by the expression (Dickson & Riley, 1979a)

$$\begin{aligned} \ln(K_{\text{F}}/k^\circ) = & \frac{1590.2}{(T/\text{K})} - 12.641 + 1.525(I/m^\circ)^{1/2} \\ & + \ln(1 - 0.001005 S) + \ln(1 + S_{\text{T}}/K_{\text{S}}) ; \quad (7.2.16) \end{aligned}$$

where $k^\circ = 1$ mol·kg-soln⁻¹. The ionic strength is calculated from

$$I/m^\circ = \frac{19.924S}{1000 - 1.005S} ; \quad (7.2.17)$$

The term $\ln(1 - 0.001005S)$ converts the value of K_{F} from mol·kg-H₂O⁻¹ (in the paper of Dickson & Riley) to mol·kg-soln⁻¹;

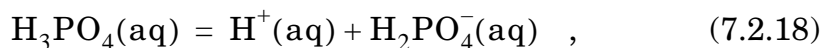
and the term $\ln(1 + S_T/K_S)$ converts from the “free” hydrogen ion concentration scale to the “total” scale—see Table 6.1 for S_T .

At $S = 35$ and $t = 25$ °C (289.15K), $\ln(K_F/k^\circ) = -5.80$.

PHOSPHORIC ACID

The expressions below are from Millero (1995)—Note 5—and are a composite of measurements by Kester & Pytkowicz (1967), by Dickson & Riley (1979b) and by Johansson & Wedborg (1979).

The equilibrium constant for the reaction



i. e.

$$K_{1P} = [\text{H}^+][\text{H}_2\text{PO}_4^-]/[\text{H}_3\text{PO}_4] \quad , \quad (7.2.19)$$

is given by the expression

$$\begin{aligned} \ln(K_{1P}/k^\circ) = & \frac{-4576.752}{T/\text{K}} + 115.525 - 18.453 \ln(T/\text{K}) + \\ & \left(\frac{-106.736}{(T/\text{K})} + 0.69171 \right) S^{1/2} + \left(-\frac{0.65643}{(T/\text{K})} - 0.01844 \right) S \quad ; \end{aligned} \quad (7.2.20)$$

where $k^\circ = 1 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$.

At $S = 35$ and $t = 25$ °C (298.15 K), $\ln(K_{1P}/k^\circ) = -3.71$.

The equilibrium constant for the reaction



i. e.

$$K_{2P} = [\text{H}^+][\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-] \quad , \quad (7.2.22)$$

is given by the expression

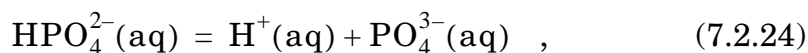
$$\begin{aligned} \ln(K_{2P}/k^\circ) = & \frac{-8814.715}{T/\text{K}} + 172.0883 - 27.927 \ln(T/\text{K}) + \\ & \left(\frac{-160.340}{(T/\text{K})} + 1.3566 \right) S^{1/2} + \left(\frac{0.37335}{(T/\text{K})} - 0.05778 \right) S \quad ; \end{aligned} \quad (7.2.23)$$

where $k^\circ = 1 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$.

At $S = 35$ and $t = 25$ °C (298.15 K), $\ln(K_{2P}/k^\circ) = -13.727$.

⁵ 0.015 has been subtracted from the constant term in each of these expressions: (7.2.20), (7.2.23), (7.2.26) to convert—approximately—from the SWS pH scale (including HF) used by Millero (1995) to the “total” hydrogen ion scale used here.

The equilibrium constant for the reaction



i. e.

$$K_{3\text{P}} = [\text{H}^+][\text{PO}_4^{3-}]/[\text{HPO}_4^{2-}] \quad , \quad (7.2.25)$$

is given by the expression

$$\begin{aligned} \ln(K_{3\text{P}}/k^\circ) = & \frac{-3070.75}{T/\text{K}} - 18.141 + \\ & \left(\frac{17.27039}{T/\text{K}} + 2.81197 \right) S^{1/2} + \left(\frac{-44.99486}{T/\text{K}} - 0.09984 \right) S \quad ; \end{aligned} \quad (7.2.26)$$

where $k^\circ = 1 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$.

At $S = 35$ and $t = 25^\circ\text{C}$ (298.15 K), $\ln(K_{3\text{P}}/k^\circ) = -20.24$.

SILICIC ACID

The equilibrium constant for the reaction



i. e.

$$K_{\text{Si}} = [\text{H}^+][\text{SiO}(\text{OH})_3^-]/[\text{Si}(\text{OH})_4] \quad , \quad (7.2.28)$$

is given by the expression (Millero, 1995):

$$\begin{aligned} \ln(K_{\text{Si}}/k^\circ) = & \frac{-8904.2}{(T/\text{K})} + 117.385 - 19.334 \ln(T/\text{K}) + \\ & + \left(\frac{-458.79}{(T/\text{K})} + 3.5913 \right) (I/m^\circ)^{1/2} + \left(\frac{188.74}{(T/\text{K})} - 1.5998 \right) (I/m^\circ) \\ & + \left(\frac{-12.1652}{(T/\text{K})} + 0.07871 \right) (I/m^\circ)^2 + \ln(1 - 0.001005S); \end{aligned} \quad (7.2.29)$$

where $k^\circ = 1 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$. This expression is based on the results of Sjöberg *et al.* (1981) and the review by Baes & Mesmer (1976); 0.015 has been subtracted from the constant (see Note 5). The ionic strength is calculated from the expression

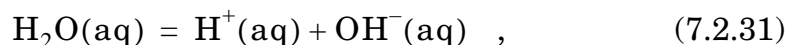
$$I/m^\circ = \frac{19.924S}{1000 - 1.005S} \approx 0.02S \quad ; \quad (7.2.30)$$

The term $\ln(1 - 0.001005S)$ converts the value of K_{Si} from $\text{mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{-1}$ to $\text{mol}\cdot\text{kg}\cdot\text{soln}^{-1}$.

At $S = 35$ and $t = 25^\circ\text{C}$ (298.15 K), $\ln(K_{\text{Si}}/k^\circ) = -21.61$.

WATER

The equilibrium constant for the reaction



i. e.

$$K_{\text{W}} = [\text{H}^+][\text{OH}^-] \quad , \quad (7.2.32)$$

is given by the expression (Millero, 1995):

$$\begin{aligned} \ln(K_{\text{W}}/(k^\circ)^2) = & \frac{-13847.26}{(T/\text{K})} + 148.9652 - 23.6521 \ln(T/\text{K}), \\ & + \left(\frac{118.67}{(T/\text{K})} - 5.977 + 1.0495 \ln(T/\text{K}) \right) S^{1/2} - 0.01615S \quad ; \end{aligned} \quad (7.2.33)$$

where $k^\circ = 1 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$. This expression is based on results published by Hansson (1973a), by Culberson & Pytkowicz (1973) and by Dickson & Riley (1979a). Note that 0.015 has been subtracted from the constant term (see Note 5).

At $S = 35$ and $t = 25 \text{ }^\circ\text{C}$ (298.15 K), $\ln(K_{\text{W}}/(k^\circ)^2) = -30.434$.

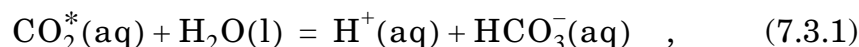
7.3 Acid-base reactions in sodium chloride media

The values given here are appropriate to a background medium with $C(\text{NaCl}) = 0.7 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$ and at a temperature of $25 \text{ }^\circ\text{C}$.

CARBONIC ACID

The values given here are from Dyrssen & Hansson (1973).

The equilibrium constant for the reaction



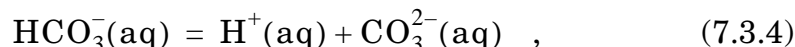
i. e.

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2^*] \quad (7.3.2)$$

at $C(\text{NaCl}) = 0.7 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$ and $t = 25 \text{ }^\circ\text{C}$ is

$$\ln(K_1/k^\circ) = -13.82 \quad . \quad (7.3.3)$$

The equilibrium constant for the reaction



i. e.

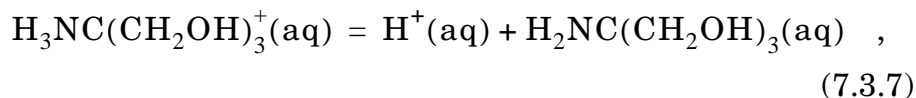
$$K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (7.3.5)$$

at $C(\text{NaCl}) = 0.7 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$ and $t = 25 \text{ }^\circ\text{C}$ is

$$\ln(K_2/k^\circ) = -21.97 \quad . \quad (7.3.6)$$

2-AMINO-2-HYDROXYMETHYL-1,3-PROPANEDIOL

The equilibrium constant for the reaction



i. e.

$$K_{\text{tris}} = [\text{H}^+][\text{H}_2\text{NC}(\text{CH}_2\text{OH})_3]/[\text{H}_3\text{NC}(\text{CH}_2\text{OH})_3^+] \quad (7.3.8)$$

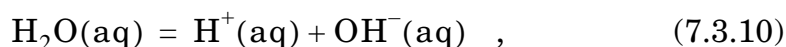
at $C(\text{NaCl}) = C(\text{NaCl}) = 0.7 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$ and $t = 25 \text{ }^\circ\text{C}$ is

$$\ln(K_{\text{tris}}/k^\circ) = -18.90 \quad , \quad (7.3.9)$$

(Millero *et al.*, 1987).

WATER

The equilibrium constant for the reaction



i. e.

$$K_{\text{W}} = [\text{H}^+][\text{OH}^-] \quad , \quad (7.3.11)$$

at $C(\text{NaCl}) = 0.7 \text{ mol}\cdot\text{kg}\cdot\text{soln}^{-1}$ and $t = 25 \text{ }^\circ\text{C}$ is

$$\ln(K_{\text{W}}/(k^\circ)^2) = -31.71 \quad , \quad (7.3.12)$$

(Dyrssen & Hansson, 1973).

8. References

- Ambrose D. & I. J. Lawrenson (1972) The vapour pressure of water. *Journal of Chemical Thermodynamics* **4**, 755–761.
- Baes C. F. Jr. & R. E. Mesmer (1976) *The hydrolysis of cations*. John Wiley & Sons, Inc., 489 pp.
- Carpenter J. H. & M. E. Manella (1973) Magnesium to Chlorinity ratios in sea water. *Journal of Geophysical Research* **78**, 3621–3626.
- Cohen E. R. & B. N. Taylor (1986) The 1986 adjustments of the fundamental physical constants. *CODATA Bulletin* **63**, 1–49.

- Craig H. (1961) Standards for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science* **133**, 1833–1834.
- Culberson C. H. & R. M. Pytkowicz (1973) Ionization of water in seawater. *Marine Chemistry* **1**, 309–316.
- Dickson A. G. & J. P. Riley (1979a) The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. I. The ionic product of water (K_W). *Marine Chemistry* **7**, 89–99.
- Dickson A. G. & J. P. Riley (1979b) The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. II. The dissociation of phosphoric acid. *Marine Chemistry* **7**, 101–109.
- Dickson A. G. (1990a) Standard potential of the reaction: $\text{AgCl(s)} + \frac{1}{2}\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO_4 in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* **22**, 113–127.
- Dickson A. G. (1990b) Thermodynamics of the dissociation of boric acid in synthetic sea water from 273.15 to 298.15 K. *Deep-Sea Research* **37**, 755–766.
- Dyrssen D. & I. Hansson (1973) Ionic medium effects in sea water — a comparison of acidity constants of carbonic acid and boric acid in sodium chloride and synthetic sea water. *Marine Chemistry* **1**, 137–149.
- Goyet C. & A. Poisson (1989) New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity. *Deep-Sea Research* **36**, 1635–1654.
- Hansson I. (1973a) Determination of the acidity constant of boric acid in synthetic sea water media. *Acta Chemica Scandinavica* **27**, 924–930.
- Hansson I. (1973b) The determination of the dissociation constants of carbonic acid in synthetic sea water in the salinity range of 20 – 40‰ and temperature range of 5 – 30 °C. *Acta Chemica Scandinavica* **27**, 931–944.
- IUPAC (1993) 1991 Table of atomic weights abridged to five significant figures. *Chemistry International* **15**, 128–129. (Based upon the 1991 table published in *Pure & Applied Chemistry* 1992, **64**, 1519–1534.)
- IUPAC (1994) Atomic weights of the elements. *Pure & Applied Chemistry* **66**, 2423–2444.

- Jones F. E. & G. L. Harris (1992) ITS-90 density of water formulation for volumetric standards calibration. *Journal of Research of the National Institute of Standards and Technology* **97**, 335–340.
- Kell G. S. (1975) Density, thermal expansivity, and compressibility of water from 0 to 150 °C: correlations and tables for atmospheric pressure and saturation reviewed and expressed on 1968 temperature scale. *Journal of Chemical and Engineering Data* **20**, 97
- Kester D. R. & R. M. Pytkowicz (1967) Determination of the apparent dissociation constants of phosphoric acid in sea water. *Limnology and Oceanography* **12**, 243–252.
- Khoo K. H., R. W. Ramette, C. H. Culberson & R. G. Bates (1977) Determination of hydrogen ion concentrations in seawater from 5 to 40 °C: standard potentials at salinities from 20 to 45‰. *Analytical Chemistry* **49**, 29–34.
- Lo Surdo A., E. M. Alzola & F. J. Millero (1982) The (p, V, T) properties of concentrated aqueous electrolytes. I. Densities and apparent molar volumes of NaCl, Na₂SO₄, MgCl₂, and MgSO₄ solutions from .1 mol·kg⁻¹ to saturation and from 273.15 to 323.15 K. *Journal of Chemical Thermodynamics* **14**, 649–662.
- Mehrbach C., C. H. Culberson, J. E. Hawley & R. M. Pytkowicz (1973) Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnology and Oceanography* **18**, 897–907.
- Millero F. J. (1974) Seawater as a multicomponent electrolyte solution. In: *The Sea*, Vol. 5, E. D. Goldberg (editor), pp. 3–80.
- Millero F. J. (1995) Thermodynamics of the carbon dioxide system in the oceans. *Geochimica et Cosmochimica Acta* **59**, 661–677.
- Millero F. J. & Poisson, A. (1981) International one-atmosphere equation of state for sea water. *Deep-Sea Research* **28**, 625–629.
- Millero F. J., J. P. Hershey & M. Fernandez (1987) The pK^* of TRISH⁺ in Na-K-Mg-Ca-Cl-SO₄ Brines – pH scales. *Geochimica et Cosmochimica Acta* **51**, 707–711.
- Morris A. W. & J. P. Riley (1966) The bromide/chlorinity and sulphate/chlorinity ratio in sea water. *Deep-Sea Research* **13**, 699–705.

- Riley J. P. (1965) The occurrence of anomalously high fluoride concentrations in the North Atlantic. *Deep-Sea Research* **12**, 219–220.
- Riley J. P. & M. Tongudai (1967) The major cation / chlorinity ratios in sea water. *Chemical Geology* **2**, 263–269.
- Roy R. N., L. N. Roy, M. Lawson, K. M. Vogel, C. Porter-Moore, W. Davis & F. J. Millero (1993a) Thermodynamics of the dissociation of boric acid in seawater at $S = 35$ from 0 to 55 °C. *Marine Chemistry* **44**, 243–248.
- Roy R. N., L. N. Roy, K. M. Vogel, C. Porter-Moore, T. Pearson, C. E. Good, F. J. Millero & D. J. Cambell (1993b) Determination of the ionization constants of carbonic acid in seawater in salinities 5 to 45 and temperatures 0 to 45 °C. *Marine Chemistry* **44**, 249–267.
- Saunders, P. M. (1990) The International Temperature Scale of 1990, ITS-90. *WOCE Notes*, **2**(3), 7.
- Sjöberg S., A. Nordin & N. Ingri (1981) Equilibrium and structural studies of silicon(IV) and aluminium(III) in aqueous solution. II. Formation constants for the monosilicate ions $\text{SiO}(\text{OH})_3^-$ and $\text{SiO}_2(\text{OH})_2^{2-}$. A precision study at 25°C in a simplified seawater medium. *Marine Chemistry* **10**, 521–532.
- UNESCO (1966) Second report of the Joint Panel on Oceanographic Tables and Standards. *UNESCO Technical Papers in Marine Science* No. 4.
- Uppström L. R. (1974) Boron/chlorinity ratio of deep-sea water from the Pacific Ocean. *Deep-Sea Research* **21**, 161–162.
- Weast, R. F. (1975) *CRC Handbook of chemistry and physics*, 56th edition, Chemical Rubber Company.
- Weiss R. F. (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chemistry* **2**, 203–215.