

Chapter 5

Physical and thermodynamic data

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1. Values for various fundamental constants

$$R = 8.314472(15) \text{ J K}^{-1} \text{ mol}^{-1},$$

$$F = 96485.3399(24) \text{ C mol}^{-1},$$

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

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

(from <http://physics.nist.gov/cuu/Constants/index.html>). For each constant, the standard uncertainty in the least significant digits is given in parentheses.

2. Atomic weights

Atomic weights are quoted here (Table 1) to 5 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 (elements **annotated r**). The last significant figure of each tabulated value is considered reliable to at least ± 1 except when a larger single-digit uncertainty is inserted in parentheses following the atomic weight. In many cases the “official” values (IUPAC, 2006) have more than five significant figures and the precision is considerably better than ± 1 at the precision shown here. In a few cases the truncation to five significant figures will mean that the true confidence interval is strongly asymmetric relative to the values shown here. Neither the highest nor 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 (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 (elements **annotated m**). Elements that have no stable isotope are excluded from this table except for Th, Pa, and U which do have a characteristic terrestrial isotope composition.

Table 1 IUPAC (2006) table of standard atomic weights abridged to five significant figures. Scaled to the relative atomic mass $A(^{12}\text{C}) = 12$ (includes 2007 revisions).

	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(7)	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	

Table 1 Continued.

	Name	Symbol	Atomic weight	Annotations
13	Aluminium	Al	26.982	
14	Silicon	Si	28.086	
15	Phosphorus	P	30.974	
16	Sulfur	S	32.065(5)	g r
17	Chlorine	Cl	35.453(2)	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	65.38(2)	
31	Gallium	Ga	69.723	
32	Germanium	Ge	72.64	
33	Arsenic	As	74.922	
34	Selenium	Se	78.96(3)	
35	Bromine	Br	79.904	
36	Krypton	Kr	83.798(2)	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	95.96(2)	g
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(3)	g
53	Iodine	I	126.90	
54	Xenon	Xe	131.29	g m
55	Caesium	Cs	132.91	
56	Barium	Ba	137.33	
57	Lanthanum	La	138.91	

Table 1 Continued.

	Name	Symbol	Atomic weight	Annotations
58	Cerium	Ce	140.12	g
59	Praesodymium	Pr	140.91	
60	Neodymium	Nd	144.24	g
62	Samarium	Sm	150.36(2)	g
63	Europium	Eu	151.96	g
64	Gadolinium	Gd	157.25(3)	g
65	Terbium	Tb	158.93	
66	Dysprosium	Dy	162.50	g
67	Holmium	Ho	164.93	
68	Erbium	Er	167.26	g
69	Thulium	Tm	168.93	
70	Ytterbium	Yb	173.05	
71	Lutetium	Lu	174.97	g
72	Hafnium	Hf	178.49(2)	
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	
79	Gold	Au	196.97	
80	Mercury	Hg	200.59(2)	
81	Thallium	Tl	204.38	
82	Lead	Pb	207.2	g r
83	Bismuth	Bi	208.98	
90	Thorium*	Th	232.04	g
91	Protoactinium*	Pa	231.04	
92	Uranium*	U	238.03	g m

* These elements have no stable isotope.

3. Vapor pressure of water

3.1 Pure water

The vapor pressure of pure water (p_σ) over the temperature range 273 to 647 K (*i.e.*, from the triple point to the critical point of water) is represented by the polynomial (Wagner and Pruß, 2002)

$$\ln\left(\frac{p_\sigma}{p_c}\right) = \frac{T_c}{T} \left(a_1 \vartheta + a_2 \vartheta^{1.5} + a_3 \vartheta^3 + a_4 \vartheta^{3.5} + a_5 \vartheta^4 + a_6 \vartheta^{7.5} \right) \quad (1)$$

where $\vartheta = (1 - T/T_c)$, $T_c = 647.096$ K and $p_c = 22.064$ MPa. The coefficients are:

$$\begin{aligned} a_1 &= -7.859\,517\,83, & a_4 &= 22.680\,741\,1, \\ a_2 &= 1.844\,082\,59, & a_5 &= -15.961\,871\,9, \\ a_3 &= -11.786\,649\,7, & a_6 &= 1.801\,225\,02. \end{aligned}$$

At 25°C (298.15 K), $p_\sigma = 3.1698$ kPa.

3.2 Sea water

For sea water, the vapor pressure is related to that of pure water,

$$p_\sigma(\text{s/w}) \approx p_\sigma \exp\left(-0.018\phi \sum_B m_B/m^\circ\right) \quad (2)$$

where

- p_σ is the vapor pressure of pure water (1),
- $\sum_B m_B$ is the total molality of dissolved species (3),
- ϕ is the osmotic coefficient of sea water (4),
- $m^\circ = 1$ mol kg-H₂O⁻¹.

For sea water (of the composition detailed in section 6.1),

$$\sum_B m_B/m^\circ = \frac{31.998S}{10^3 - 1.005S} \quad (3)$$

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

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

for $I = 0.3 - 0.8$ mol kg-H₂O⁻¹ ($S = 16-40$). (Although strictly speaking, 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 $S = 35$, $p_\sigma(\text{s/w}) = 3.1106$ 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 and Harris, 1992)

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

At 25°C, $\rho_w = 997.041$ kg m⁻³ = 0.997041 g cm⁻³.

4.2 Sea water

The density of sea water in the temperature range 0 to 40°C (IPTS 68¹) and the salinity range 0 to 42 is given by the expression (Millero and Poisson, 1981)

$$\rho_{\text{SW}}/(\text{kg m}^{-3}) = \rho_{\text{SMOW}}/(\text{kg m}^{-3}) + AS + BS^{1.5} + CS^2 \quad (6)$$

where²

$$\begin{aligned} \rho_{\text{SMOW}}/(\text{kg m}^{-3}) = & 999.842594 + 6.793952 \times 10^{-2}(t/^\circ\text{C}) \\ & - 9.095290 \times 10^{-3}(t/^\circ\text{C})^2 + 1.001685 \times 10^{-4}(t/^\circ\text{C})^3 \\ & - 1.120083 \times 10^{-6}(t/^\circ\text{C})^4 + 6.536332 \times 10^{-9}(t/^\circ\text{C})^5, \quad (7) \end{aligned}$$

$$\begin{aligned} A = & 8.24493 \times 10^{-1} - 4.0899 \times 10^{-3}(t/^\circ\text{C}) \\ & + 7.6438 \times 10^{-5}(t/^\circ\text{C})^2 - 8.2467 \times 10^{-7}(t/^\circ\text{C})^3 + 5.3875 \times 10^{-9}(t/^\circ\text{C})^4, \quad (8) \end{aligned}$$

$$B = -5.72466 \times 10^{-3} + 1.0227 \times 10^{-4}(t/^\circ\text{C}) - 1.6546 \times 10^{-6}(t/^\circ\text{C})^2, \quad (9)$$

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

t is on IPTS 68 and S is the salinity.

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

4.3 Sodium chloride solutions

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

$$\begin{aligned} \frac{10^3(\rho(\text{NaCl}) - \rho_{\text{SMOW}})}{\text{g cm}^{-3}} = & \left(\frac{m}{m^\circ}\right) \left[45.5655 - 0.2341 \left(\frac{t}{^\circ\text{C}}\right) \right. \\ & \left. + 3.4128 \times 10^{-3} \left(\frac{t}{^\circ\text{C}}\right)^2 - 2.7030 \times 10^{-5} \left(\frac{t}{^\circ\text{C}}\right)^3 + 1.4037 \times 10^{-7} \left(\frac{t}{^\circ\text{C}}\right)^4 \right] \\ & + \left(\frac{m}{m^\circ}\right)^{3/2} \left[-1.8527 + 5.3956 \times 10^{-2} \left(\frac{t}{^\circ\text{C}}\right) - 6.2635 \times 10^{-4} \left(\frac{t}{^\circ\text{C}}\right)^2 \right] \\ & + \left(\frac{m}{m^\circ}\right)^2 \left[-1.6368 - 9.5653 \times 10^{-4} \left(\frac{t}{^\circ\text{C}}\right) + 5.2829 \times 10^{-5} \left(\frac{t}{^\circ\text{C}}\right)^2 \right] \\ & + 0.2274 \left(\frac{m}{m^\circ}\right)^{5/2} \quad (11) \end{aligned}$$

¹ The International Practical Temperature Scale of 1968 (IPTS 68) has 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 and Harris, 1992):

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

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

where t is the temperature (IPTS 68), m the molality of the sodium chloride solution, and $m^\circ = 1 \text{ mol kg-H}_2\text{O}^{-1}$. ρ_{SMOW} is calculated using equation (7)—see Footnote 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

$$\frac{m(\text{NaCl})}{m^\circ} = \frac{10^3 C(\text{NaCl})}{10^3 - 58.443 C(\text{NaCl})}. \quad (12)$$

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

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°C⁴ (Millero, personal communication):

$$\rho_{\text{mix}}(25^\circ\text{C}) = \frac{\rho_{\text{W}}(25^\circ\text{C})[10^3 + m_{\text{T}}(m(\text{HCl}) + m(\text{NaCl}))]}{10^3 + \varphi_{\text{mix}}(m(\text{HCl}) + m(\text{NaCl}))(\rho_{\text{W}}(25^\circ\text{C}))} \quad (13)$$

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

$$m_{\text{T}} = \frac{36.46m(\text{HCl}) + 58.44m(\text{NaCl})}{m(\text{HCl}) + m(\text{NaCl})}, \quad (14)$$

$$\varphi_{\text{mix}} = \frac{m(\text{HCl})\varphi_{\text{HCl}} + m(\text{NaCl})\varphi_{\text{NaCl}}}{m(\text{HCl}) + m(\text{NaCl})}, \quad (15)$$

and the apparent molar volumes at 25°C,

$$\varphi_{\text{HCl}} = 17.854 + 1.460\sqrt{m} - 0.307m, \quad (16)$$

$$\varphi_{\text{NaCl}} = 16.613 + 1.811\sqrt{m} + 0.094m \quad (17)$$

where $m = m(\text{HCl}) + m(\text{NaCl})$. The concentrations $m(\text{HCl})$ and $m(\text{NaCl})$ are in mol kg-H₂O⁻¹.

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

4.5 Various solids

From data of Weast (1975),

$$\text{Potassium chloride: } \rho(\text{KCl}) = 1.984 \text{ g cm}^{-3} \quad (18)$$

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 $< 10^{-5}$ over the temperature range 0–50°C.

⁴ At temperatures other than 25°C, equation (13) is not reliable.

$$\text{Sodium chloride: } \rho(\text{NaCl}) = 2.165 \text{ g cm}^{-3} \quad (19)$$

$$\text{Sodium carbonate: } \rho(\text{Na}_2\text{CO}_3) = 2.532 \text{ g cm}^{-3} \quad (20)$$

$$\text{Sodium sulfate: } \rho(\text{Na}_2\text{SO}_4) = 2.68 \text{ g cm}^{-3} \quad (21)$$

Sodium tetraborate decahydrate (borax):

$$\rho(\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}) = 1.73 \text{ g cm}^{-3} \quad (22)$$

2-amino-2-hydroxymethyl-1,3-propanediol (“TRIS”):

$$\rho(\text{H}_2\text{NC}(\text{CH}_2\text{OH})_3) = 1.35 \text{ g cm}^{-3} \quad (23)$$

$$\text{2-aminopyridine: } \rho(\text{C}_5\text{H}_6\text{N}_2) = 1.24 \text{ g cm}^{-3} \quad (24)$$

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)

$$\begin{aligned} \frac{B(\text{CO}_2, T)}{\text{cm}^3 \text{ mol}^{-1}} = & -1636.75 + 12.0408 \left(\frac{T}{\text{K}} \right) - 3.27957 \times 10^{-2} \left(\frac{T}{\text{K}} \right)^2 \\ & + 3.16528 \times 10^{-5} \left(\frac{T}{\text{K}} \right)^3 \end{aligned} \quad (25)$$

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

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

5.2 Carbon dioxide in air

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

$$\delta_{\text{B-C}} = B_{\text{BC}} - \frac{1}{2}(B_{\text{BB}} + B_{\text{CC}}) \quad (26)$$

Weiss (1974) used the Lennard–Jones (6–12) potential to calculate values for the cross-virial coefficient δ for the binary mixture: CO_2 –air (see also SOP 24). He found that the temperature dependence of this parameter could be represented by the equation

$$\frac{\delta(\text{CO}_2 - \text{air})}{\text{cm}^3 \text{ mol}^{-1}} = 57.7 - 0.118 \left(\frac{T}{\text{K}} \right) \quad (27)$$

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

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

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 g 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 sections 3.2 and 4.2).

Another is the treatment of sea water as a constant ionic medium in which the thermodynamics of various chemical processes 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 2) and a standard mean chemical composition of sea water (Table 3) can be calculated using the equilibrium constants for the dissociation of water, carbonic and boric acids.

Table 2 Standard mean analytical composition of sea water with $S = 35$ and 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 and Riley (1966)
Bromide	0.003473	0.00084	Morris and Riley (1966)
Fluoride	0.000067	0.00007	Riley (1965)
Sodium	0.55661	0.46906	from charge balance
Magnesium	0.06626	0.05282	Carpenter and Manella (1973)
Calcium	0.02127	0.01028	Riley and Tongudai (1967)
Potassium	0.0206	0.01021	Riley and Tongudai (1967)
Strontium	0.00041	0.00009	Riley and 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

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

Table 3 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 synthetic sea water recipe can be obtained from the recipe in Table 2 as follows: replace bromide, fluoride, and total alkalinity with chloride and replace strontium with calcium. The resultant composition (Table 4) 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.*, 1993a, b).

Table 4 Simplified synthetic 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.* (1993a, b). 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.,

$$K_0 = [\text{CO}_2^*] / f(\text{CO}_2), \quad (29)$$

is given by the expression (Weiss, 1974)

$$\begin{aligned} \ln(K/k^\circ) = & 93.4517 \left(\frac{100}{T/K} \right) - 60.2409 + 23.3585 \ln \left(\frac{T/K}{100} \right) \\ & + S \left[0.023517 - 0.023656 \left(\frac{T/K}{100} \right) + 0.0047036 \left(\frac{T/K}{100} \right)^2 \right]. \end{aligned} \quad (30)$$

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

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

7.2.1 Bisulfate ion

The equilibrium constant for the reaction



i.e.,

$$K_S = [\text{H}^+]_F [\text{SO}_4^{2-}] / [\text{HSO}_4^-], \quad (32)$$

is given by the expression (Dickson, 1990a)

$$\begin{aligned} \ln(K_S/k^\circ) = & \frac{-4276.1}{(T/K)} + 141.328 - 23.093 \ln(T/K) \\ & + \left(\frac{-13856}{(T/K)} + 324.57 - 47.986 \ln(T/K) \right) \times \left(\frac{I}{m^\circ} \right)^{1/2} \\ & + \left(\frac{35474}{(T/K)} - 771.54 + 114.723 \ln(T/K) \right) \times \left(\frac{I}{m^\circ} \right) \\ & - \frac{2698}{(T/K)} \left(\frac{I}{m^\circ} \right)^{3/2} + \frac{1776}{(T/K)} \left(\frac{I}{m^\circ} \right)^2 + \ln(1 - 0.001005S) \end{aligned} \quad (33)$$

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

$$I/m^\circ = \frac{19.924S}{1000 - 1.005S}. \quad (34)$$

The term $\ln(1 - 0.001005S)$ converts the value of K_S from $\text{mol kg-H}_2\text{O}^{-1}$ (used in Dickson, 1990a) to mol kg-soln^{-1} .

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

7.2.2 Boric acid

The equilibrium constant for the reaction



i.e.,

$$K_B = [\text{H}^+][\text{B(OH)}_4^-]/[\text{B(OH)}_3] \quad (36)$$

is given by the expression (Dickson, 1990b)

$$\begin{aligned} \ln\left(\frac{K_B}{k^\circ}\right) = & \frac{-8966.90 - 2890.53S^{1/2} - 77.942S + 1.728S^{3/2} - 0.0996S^2}{(T/K)} \\ & + (148.0248 + 137.1942S^{1/2} + 1.62142S) \\ & + (-24.4344 - 25.085S^{1/2} - 0.2474S)\ln(T/K) \\ & + 0.053105S^{1/2}(T/K) \end{aligned} \quad (37)$$

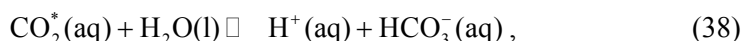
where $k^\circ = 1 \text{ mol kg-soln}^{-1}$. This equation is in excellent agreement with the measurements made by Roy *et al.* (1993a); it is also in reasonable agreement with the results of Hansson (1973a).

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

7.2.3 Carbonic acid

The equilibrium constants used here are based on the measurements of Mehrbach *et al.* (1973) and have been converted to the total hydrogen ion pH scale by Lueker *et al.* (2000) who also showed them to be in good agreement with direct measurements of $p(\text{CO}_2)$, C_T , and A_T . These constants are in reasonable agreement with those measured by Roy *et al.* (1993b), Goyet and Poisson (1989), and Hansson (1973b).

The equilibrium constant for the reaction



i.e.,

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2^*] \quad (39)$$

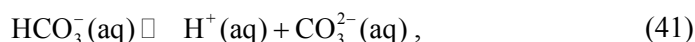
is given by the expression (Lueker *et al.*, 2000)

$$\log_{10}(K_1/k^\circ) = \frac{-3633.86}{(T/\text{K})} + 61.2172 - 9.67770 \ln(T/\text{K}) + 0.011555S - 0.0001152S^2 \quad (40)$$

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

At $S = 35$ and $t = 25^\circ\text{C}$ (298.15 K), $\log_{10}(K_1/k^\circ) = -5.8472$.

The equilibrium constant for the reaction



i.e.,

$$K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-], \quad (42)$$

is given by the expression (Lueker *et al.*, 2000)

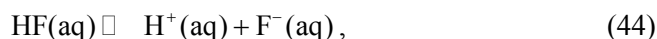
$$\log_{10}(K_2/k^\circ) = \frac{-471.78}{(T/\text{K})} - 25.9290 + 3.16967 \ln(T/\text{K}) + 0.01781S - 0.0001122S^2 \quad (43)$$

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

At $S = 35$ and $t = 25^\circ\text{C}$ (298.15 K), $\log_{10}(K_2/k^\circ) = -8.9660$.

7.2.4 Hydrogen fluoride

The equilibrium constant for the reaction



i.e.,

$$K_F = [\text{H}^+][\text{F}^-]/[\text{HF}], \quad (45)$$

is given by the expression (Perez and Fraga, 1987)

$$\ln(K_F/k^\circ) = \frac{874}{(T/\text{K})} - 9.68 + 0.111S^{1/2} \quad (46)$$

where $k^\circ = 1 \text{ mol kg-soln}^{-1}$. This equation gives values that are in reasonable agreement with those suggested by Dickson and Riley (1979a).

At $S = 35$ and $t = 25^\circ\text{C}$ (298.15K), $\ln(K_F/k^\circ) = -6.09$.

7.2.5 Phosphoric acid

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

⁵ 0.015 has been subtracted from the constant term in each of these expressions: (49), (52), (55) 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.,

$$K_{1p} = [\text{H}^+][\text{H}_2\text{PO}_4^-]/[\text{H}_3\text{PO}_4], \quad (48)$$

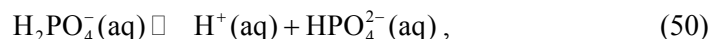
is given by the expression

$$\begin{aligned} \ln(K_{1p}/k^\circ) = & \frac{-4576.752}{T/K} + 115.525 - 18.453 \ln(T/K) \\ & + \left(\frac{-106.736}{(T/K)} + 0.69171 \right) S^{1/2} + \left(-\frac{0.65643}{(T/K)} - 0.01844 \right) S \end{aligned} \quad (49)$$

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

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

The equilibrium constant for the reaction



i.e.,

$$K_{2p} = [\text{H}^+][\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-], \quad (51)$$

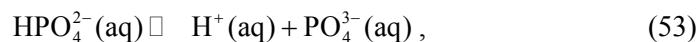
is given by the expression

$$\begin{aligned} \ln(K_{2p}/k^\circ) = & \frac{-8814.715}{T/K} + 172.0883 - 27.927 \ln(T/K) \\ & + \left(\frac{-160.340}{(T/K)} + 1.3566 \right) S^{1/2} + \left(\frac{0.37335}{(T/K)} - 0.05778 \right) S \end{aligned} \quad (52)$$

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

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

The equilibrium constant for the reaction



i.e.,

$$K_{3p} = [\text{H}^+][\text{PO}_4^{3-}]/[\text{HPO}_4^{2-}], \quad (54)$$

is given by the expression

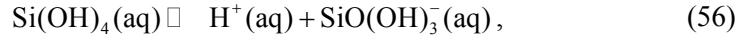
$$\begin{aligned} \ln(K_{3p}/k^\circ) = & \frac{-3070.75}{(T/K)} - 18.141 + \left(\frac{17.27039}{(T/K)} + 2.81197 \right) S^{1/2} \\ & + \left(\frac{-44.99486}{(T/K)} - 0.09984 \right) S \end{aligned} \quad (55)$$

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

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

7.2.6 Silicic acid

The equilibrium constant for the reaction



i.e.,

$$K_{\text{Si}} = [\text{H}^+][\text{SiO(OH)}_3^-]/[\text{Si(OH)}_4], \quad (57)$$

is given by the expression (Millero, 1995)

$$\begin{aligned} \ln(K_{\text{Si}}/k^\circ) = & \frac{-8904.2}{(T/\text{K})} + 117.385 - 19.334 \ln(T/\text{K}) \\ & + \left(\frac{-458.79}{(T/\text{K})} + 3.5913 \right) (I/m^\circ)^{1/2} + \left(\frac{188.74}{(T/\text{K})} - 1.5998 \right) (I/m^\circ) \\ & + \left(\frac{-12.1652}{(T/\text{K})} + 0.07871 \right) (I/m^\circ)^2 + \ln(1 - 0.001005S) \end{aligned} \quad (58)$$

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

The ionic strength is calculated from the expression

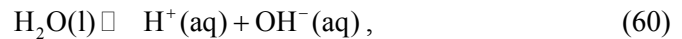
$$I/m^\circ = \frac{19.924S}{1000 - 1.005S} \approx 0.02S. \quad (59)$$

The term $\ln(1 - 0.001005S)$ converts the value of K_{Si} from mol kg-H₂O⁻¹ to mol kg-soln⁻¹; m° is as in equation (11).

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

7.2.7 Water

The equilibrium constant for the reaction



i.e.,

$$K_{\text{w}} = [\text{H}^+][\text{OH}^-], \quad (61)$$

is given by the expression (Millero, 1995)

$$\begin{aligned} \ln(K_{\text{w}}/(k^\circ)^2) = & \frac{-13847.26}{(T/\text{K})} + 148.9652 - 23.6521 \ln(T/\text{K}) \\ & + \left(\frac{118.67}{(T/\text{K})} - 5.977 + 1.0495 \ln(T/\text{K}) \right) S^{1/2} - 0.01615S \end{aligned} \quad (62)$$

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

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

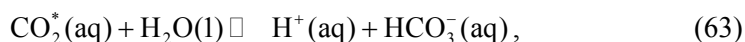
7.3 Acid–base reactions in sodium chloride media

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

7.3.1 Carbonic acid

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

The equilibrium constant for the reaction



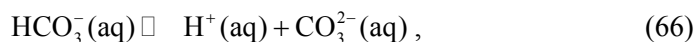
i.e.,

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2^*], \quad (64)$$

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

$$\ln(K_1/k^\circ) = -13.82. \quad (65)$$

The equilibrium constant for the reaction



i.e.,

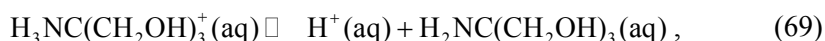
$$K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-], \quad (67)$$

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

$$\ln(K_2/k^\circ) = -21.97. \quad (68)$$

7.3.2 2-amino-2-hydroxymethyl-1,3-propanediol (“TRIS”)

The equilibrium constant for the reaction



i.e.,

$$K_{\text{tris}} = [\text{H}^+][\text{H}_2\text{NC}(\text{CH}_2\text{OH})_3]/[\text{H}_3\text{NC}(\text{CH}_2\text{OH})_3^+], \quad (70)$$

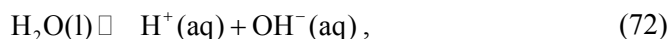
at $C(\text{NaCl}) = 0.7 \text{ mol kg-soln}^{-1}$ and $t = 25^\circ\text{C}$ is

$$\ln(K_{\text{TRIS}}/k^\circ) = -18.90 \quad (71)$$

(Millero *et al.*, 1987).

7.3.3 Water

The equilibrium constant for the reaction



i.e.,

$$K_{\text{w}} = [\text{H}^+][\text{OH}^-], \quad (73)$$

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

$$\ln(K_w/(k^\circ)^2) = -31.71 \quad (74)$$

(Dyrssen and Hansson, 1973).

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