

Chapter 2

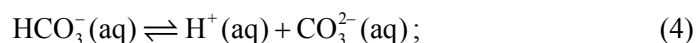
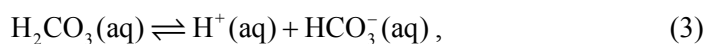
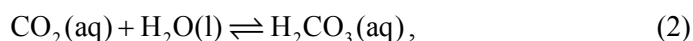
Solution chemistry of carbon dioxide in sea water

1. Introduction

This chapter outlines the chemistry of carbon dioxide in sea water so as to provide a coherent background for the rest of this Guide. The following sections lay out the thermodynamic framework required for an understanding of the solution chemistry; the thermodynamic data needed to interpret field and laboratory results are presented in Chapter 5.

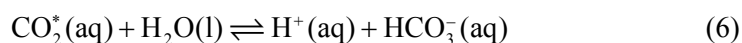
2. Reactions in solution

The reactions that take place when carbon dioxide dissolves in water can be represented by the following series of equilibria:



the notations (g), (l), (aq) refer to the state of the species, *i.e.*, a gas, a liquid or in aqueous solution respectively. It is difficult to analytically distinguish between the species $\text{CO}_2(\text{aq})$ and $\text{H}_2\text{CO}_3(\text{aq})$. It is usual to combine the concentrations of $\text{CO}_2(\text{aq})$ and $\text{H}_2\text{CO}_3(\text{aq})$ and to express this sum as the concentration of a hypothetical species, $\text{CO}_2^*(\text{aq})$.

Redefining (1), (2), and (3) in terms of this species gives



The equilibrium relationships between the concentrations of these various species can then be written as

$$K_0 = [\text{CO}_2^*] / f(\text{CO}_2), \quad (7)$$

$$K_1 = [\text{H}^+][\text{HCO}_3^-] / [\text{CO}_2^*], \quad (8)$$

$$K_2 = [\text{H}^+][\text{CO}_3^{2-}] / [\text{HCO}_3^-]. \quad (9)$$

In these equations, $f(\text{CO}_2)$ is the fugacity of carbon dioxide in the gas phase and brackets represent total stoichiometric concentrations¹ of the particular chemical species enclosed. These equilibrium constants are functions of the temperature, pressure and salinity of the solution (*e.g.*, sea water) and have been measured in a variety of studies (see Chapter 5).

3. Fugacity

The fugacity of carbon dioxide is not the same as its partial pressure—the product of mole fraction and total pressure, $x(\text{CO}_2) \cdot p$ —but rather takes account of the non-ideal nature of the gas phase. The fugacity of a gas such as CO_2 can be determined from knowledge of its equation of state:

$$f(\text{CO}_2) = x(\text{CO}_2) \cdot p \cdot \exp\left(\frac{1}{RT} \int_0^p (V(\text{CO}_2) - RT/p') dp'\right). \quad (10)$$

The equation of state of a real gas such as CO_2 , either alone or in a mixture, can be represented by a virial expression:

$$\frac{pV(\text{CO}_2)}{RT} = 1 + \frac{B(x, T)}{V(\text{CO}_2)} + \frac{C(x, T)}{V(\text{CO}_2)^2} + \dots \quad (11)$$

This equation, truncated after the second term, is usually adequate to represent p - V - T properties at pressures up to a few atmospheres (Dymond and Smith, 1980).

It is known from statistical mechanics that the virial coefficients $B(x, T)$, $C(x, T)$, *etc.* relate to pair-wise interactions in the gas phase (Guggenheim, 1967). This property can be used to estimate $B(x, T)$ for particular gas mixtures, such as CO_2 in air, from measurements on binary mixtures or from a model of the intermolecular potential energy function for the molecules concerned. The magnitude of the fugacity coefficient (the ratio of fugacity to partial pressure) is a function both of temperature and of gas phase composition (Fig. 1).

¹ Strictly, equations (7) to (9) should be expressed in terms of activities rather than concentrations. However, as the activity coefficients are approximately constant for small amounts of reacting species in a background medium, these expressions are valid and correspond to “ionic medium” equilibrium constants based on a sea water medium.

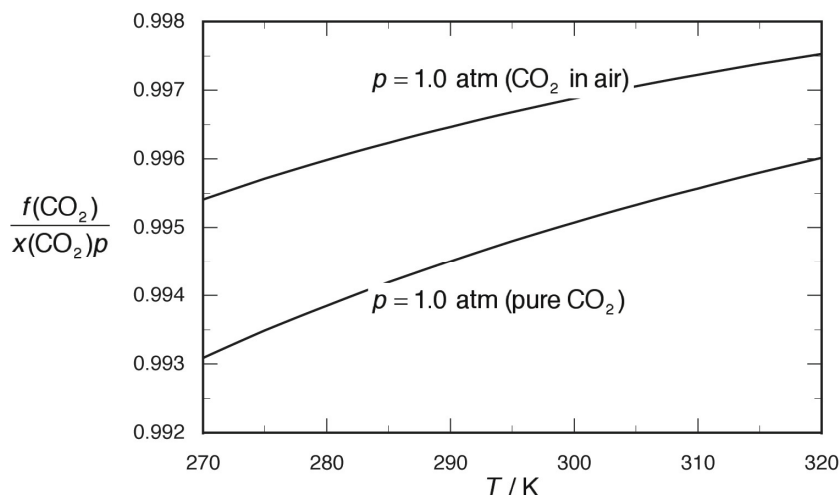


Fig. 1 Variation of the fugacity coefficient with temperature at 1 atm total pressure for pure CO₂ gas and for CO₂ in air: $x(\text{CO}_2) = 350 \times 10^{-6}$ (calculated using the procedure described in SOP 24 of this Guide).

4. Analytical parameters of the CO₂ system

Unfortunately, the concentrations of the individual species of the carbon dioxide system in solution can not be measured directly. There are, however, four parameters that can be measured. These are used together with ancillary information to obtain a complete description of the carbon dioxide system in sea water. Methods for determining each of these parameters are detailed in Chapter 4.

4.1 Total dissolved inorganic carbon

The total dissolved inorganic carbon in a sea water sample:

$$C_T = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (12)$$

can be measured directly by acidifying the sample, extracting the CO₂ gas that is produced and measuring its amount.

4.2 Total alkalinity

The total alkalinity of a sample of sea water is a form of mass-conservation relationship for hydrogen ion. It is rigorously defined (Dickson, 1981) as “. . . the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ at 25°C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in 1 kilogram of sample.” Thus

$$\begin{aligned} A_T = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] \\ & + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] + [\text{NH}_3] + [\text{HS}^-] + \dots \\ & - [\text{H}^+]_F - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] - \dots \end{aligned} \quad (13)$$

where the ellipses stand for additional minor acid or base species that are either unidentified or present in such small amounts that they can be safely neglected. $[H^+]_F$ is the *free* concentration of hydrogen ion—see equation (15).

4.3 Fugacity of CO₂ in equilibrium with a sea water sample

This measurement typically requires a gas phase that is in equilibrium with a sea water sample at a known pressure and temperature. The concentration of CO₂ is then determined in the gas phase and the corresponding value of $f(\text{CO}_2)$ —for that temperature—estimated from equation (10).

4.4 Total hydrogen ion concentration

The hydrogen ion concentration in sea water is usually reported as pH:

$$\text{pH} = -\log[H^+]. \quad (14)$$

Although the concept of a total hydrogen ion concentration is somewhat confusing², it is needed to define acid dissociation constants accurately in sea water (Dickson, 1990). Total hydrogen ion concentration is defined as

$$[H^+] = [H^+]_F \cdot (1 + S_T / K_S). \quad (15)$$

$[H^+]_F$ is the *free* hydrogen ion concentration, S_T is the total sulfate concentration ($[\text{SO}_4^{2-}] + [\text{HSO}_4^-]$) and K_S is the acid dissociation constant for HSO_4^- . At pH values above 4, equation (15) can be approximated as

$$[H^+] = [H^+]_F + [\text{HSO}_4^-]. \quad (16)$$

The various equilibrium constants required to describe acid–base chemistry in sea water have been measured in the laboratory (see Chapter 5 for recommended constants). In addition to knowing the carbon parameters, the total concentrations of the various other (non-CO₂) acid–base systems in the sample of interest are needed to fully constrain the carbon dioxide system in sea water. The total concentrations of conservative constituents, such as borate, sulfate, and fluoride, can be estimated from salinity. Those of non-conservative constituents, such as phosphate, silicate, ammonia or hydrogen sulfide, must be measured but approximate “reference” concentrations are adequate for most purposes. Because of the relative consistency of the chemical constituents of sea water, it is generally accepted that only two of the four measurable carbon parameters are needed together with the equilibrium constants, temperature, pressure, and salinity, to have a complete description of the system (see Park (1969), Skirrow (1975), and the Annexe to this chapter).

This practice assumes that our present knowledge of the nature, total concentrations, and thermodynamic properties of all the possible acid–base species in sea water is complete. It is probably better at this stage to overdetermine the system whenever possible, *i.e.*, to measure more than two of these parameters on any given sample and to use the redundancy to confirm that the measurements fit with our understanding of the thermodynamics of acid–base processes in sea water.

² See Dickson (1984, 1993) for a detailed discussion of the various pH scales that have been used in sea water.

5. Bibliography

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Annexe

Equations that describe the CO₂ system in sea water

It is possible, in theory, to obtain a *complete* description of the carbon dioxide system in a sample of sea water at a particular temperature and pressure provided that the following information is known³:

- the solubility constant for CO₂ in sea water, K_0 ,
- the equilibrium constants for each of the acid–base pairs that are assumed to exist in the solution,
- the total concentrations of all the non-CO₂ acid–base pairs,
- the values of at least two of the CO₂ related parameters: $C_T, A_T, f(\text{CO}_2), [\text{H}^+]$.

The optimal choice of experimental variables is dictated by the nature of the problem being studied and remains at the discretion of the investigator. Although each of the CO₂ related parameters is linearly independent, they are not orthogonal. For certain combinations there are limits to the accuracy with which the other parameters can be predicted from the measured data. These errors end up being propagated through the equations presented here. Such errors result from all the experimentally derived information, including the various equilibrium constants. As a consequence it is usually better to *measure* a particular parameter directly using one of the methods detailed in Chapter 4 than to calculate it from other measurements.

When more than two of the CO₂-related parameters have been measured on a single sea water sample, it is possible to use the various possible pairs of parameters to compute the other redundant parameters and thus to assess the internal consistency of our knowledge of the system. Again, it is necessary to take all the sources of error into account when doing this. Alternately, one can describe the system independently of one or more of the dissociation constants for carbonic acid. Equations that allow each of these possibilities to be realized are derived here.

³ The rank of the system of equilibrium equations that describes the acid–base chemistry of sea water—*i.e.*, the number of linearly independent variables—is equal to the number of independent mass-conservation relationships plus the number of acid–base pairs considered (the number of dissociation constants).

Table 1 Equations for the sea water acid–base system.**Mass-conservation equations⁴**

$$C_T = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (17)$$

$$\begin{aligned} A_T = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] \\ & + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] + [\text{NH}_3] + [\text{HS}^-] + \dots \\ & - [\text{H}^+]_F - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] - \dots \end{aligned} \quad (18)$$

$$B_T = [\text{B}(\text{OH})_3] + [\text{B}(\text{OH})_4^-] \quad (19)$$

$$S_T = [\text{HSO}_4^-] + [\text{SO}_4^{2-}] \quad (20)$$

$$F_T = [\text{HF}] + [\text{F}^-] \quad (21)$$

$$P_T = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \quad (22)$$

$$Si_T = [\text{Si}(\text{OH})_4] + [\text{SiO}(\text{OH})_3^-] \quad (23)$$

$$NH_{3T} = [\text{NH}_4^+] + [\text{NH}_3] \quad (24)$$

$$H_2S_T = [\text{H}_2\text{S}] + [\text{HS}^-] \quad (25)$$

Equilibrium constants

$$K_0 = [\text{CO}_2^*]/f(\text{CO}_2) \quad (26)$$

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2^*] \quad (27)$$

$$K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (28)$$

$$K_B = [\text{H}^+][\text{B}(\text{OH})_4^-]/[\text{B}(\text{OH})_3] \quad (29)$$

$$K_w = [\text{H}^+][\text{OH}^-] \quad (30)$$

$$K_S = [\text{H}^+][\text{SO}_4^{2-}]/[\text{HSO}_4^-] \quad (31)$$

$$K_F = [\text{H}^+][\text{F}^-]/[\text{HF}] \quad (32)$$

$$K_{1P} = [\text{H}^+][\text{H}_2\text{PO}_4^-]/[\text{H}_3\text{PO}_4] \quad (33)$$

$$K_{2P} = [\text{H}^+][\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-] \quad (34)$$

$$K_{3P} = [\text{H}^+][\text{PO}_4^{3-}]/[\text{HPO}_4^{2-}] \quad (35)$$

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

$$K_{\text{NH}_3} = [\text{H}^+][\text{NH}_3]/[\text{NH}_4^+] \quad (37)$$

$$K_{\text{H}_2\text{S}} = [\text{H}^+][\text{HS}^-]/[\text{H}_2\text{S}] \quad (38)$$

⁴ The aqueous chemistry of Si is rather complex, and encompasses more species than are considered here. This approximation is adequate for the present purpose of estimating the silicate contribution to alkalinity.

Table 2 Expressions for the concentrations of the various species in equation (18).

$$[\text{HCO}_3^-] = \frac{C_T K_1 [\text{H}^+]}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2} \quad (39)$$

$$[\text{CO}_3^{2-}] = \frac{C_T K_1 K_2}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2} \quad (40)$$

$$[\text{B}(\text{OH})_4^-] = B_T / (1 + [\text{H}^+] / K_B) \quad (41)$$

$$[\text{OH}^-] = K_w / [\text{H}^+] \quad (42)$$

$$[\text{H}_3\text{PO}_4] = \frac{P_T [\text{H}^+]^3}{[\text{H}^+]^3 + K_{1P} [\text{H}^+]^2 + K_{1P} K_{2P} [\text{H}^+] + K_{1P} K_{2P} K_{3P}} \quad (43)$$

$$[\text{H}_2\text{PO}_4^-] = \frac{P_T K_{1P} [\text{H}^+]^2}{[\text{H}^+]^3 + K_{1P} [\text{H}^+]^2 + K_{1P} K_{2P} [\text{H}^+] + K_{1P} K_{2P} K_{3P}} \quad (44)$$

$$[\text{HPO}_4^{2-}] = \frac{P_T K_{1P} K_{2P} [\text{H}^+]}{[\text{H}^+]^3 + K_{1P} [\text{H}^+]^2 + K_{1P} K_{2P} [\text{H}^+] + K_{1P} K_{2P} K_{3P}} \quad (45)$$

$$[\text{PO}_4^{3-}] = \frac{P_T K_{1P} K_{2P} K_{3P}}{[\text{H}^+]^3 + K_{1P} [\text{H}^+]^2 + K_{1P} K_{2P} [\text{H}^+] + K_{1P} K_{2P} K_{3P}} \quad (46)$$

$$[\text{SiO}(\text{OH})_3^-] = S_{iT} / (1 + [\text{H}^+] / K_{Si}) \quad (47)$$

$$[\text{NH}_3] = N H_{3T} / (1 + [\text{H}^+] / K_{\text{NH}_3}) \quad (48)$$

$$[\text{HS}^-] = H_2 S_T / (1 + [\text{H}^+] / K_{\text{H}_2\text{S}}) \quad (49)$$

$$[\text{H}^+]_F = [\text{H}^+] / (1 + S_T / K_S) \quad (50)$$

$$[\text{HSO}_4^-] = S_T / (1 + K_S / [\text{H}^+]_F) \quad (51)$$

$$[\text{HF}] = F_T / (1 + K_F / [\text{H}^+]) \quad (52)$$

$[\text{H}^+]$ and A_T

The carbonate alkalinity (*i.e.*, the contribution of carbonate species to the total alkalinity) is defined as

$$A_C = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (53)$$

The concentrations of the non-CO₂ species that contribute to A_T are calculated using the expressions given in Table 2, thus

$$\begin{aligned} A_C = A_T - & ([\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] \\ & + [\text{SiO}(\text{OH})_3^-] + [\text{NH}_3] + [\text{HS}^-] + \dots \\ & - [\text{H}^+]_F - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] - \dots) \end{aligned} \quad (54)$$

Then from (27),

$$[\text{HCO}_3^-] = \frac{[\text{CO}_2^*]K_1}{[\text{H}^+]}, \quad (55)$$

and from (28),

$$[\text{CO}_3^{2-}] = \left(\frac{[\text{CO}_2^*]K_1}{[\text{H}^+]} \right) \frac{K_2}{[\text{H}^+]}. \quad (56)$$

Substituting into (53) and rearranging,

$$[\text{CO}_2^*] = \frac{A_c[\text{H}^+]^2}{K_1([\text{H}^+] + 2K_2)}, \quad (57)$$

and hence

$$[\text{HCO}_3^-] = \frac{A_c[\text{H}^+]}{[\text{H}^+] + 2K_2}, \quad (58)$$

$$[\text{CO}_3^{2-}] = \frac{A_c K_2}{[\text{H}^+] + 2K_2}. \quad (59)$$

C_T is calculated from (17) and $f(\text{CO}_2)$ from (26):

$$f(\text{CO}_2) = \frac{[\text{CO}_2^*]}{K_0}. \quad (60)$$

$[\text{H}^+]$ and $f(\text{CO}_2)$

$[\text{CO}_2^*]$ is given by (26):

$$[\text{CO}_2^*] = K_0 f(\text{CO}_2). \quad (61)$$

Thus, from (27) and (28),

$$[\text{HCO}_3^-] = \frac{K_0 K_1 f(\text{CO}_2)}{[\text{H}^+]}, \quad (62)$$

$$[\text{CO}_3^{2-}] = \frac{K_0 K_1 K_2 f(\text{CO}_2)}{[\text{H}^+]^2}. \quad (63)$$

C_T is calculated from (17) and A_T from (18); $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ are given by (62) and (63), the remaining terms are calculated from the expressions given in Table 2.

$[\text{H}^+]$ and C_T

Equations (27) and (28) are rearranged and substituted into (17) to give

$$C_T = [\text{CO}_2^*] \left(1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2} \right). \quad (64)$$

Thus

$$[\text{CO}_2^*] = \frac{C_T [\text{H}^+]^2}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2}, \quad (65)$$

$$[\text{HCO}_3^-] = \frac{C_T K_1 [\text{H}^+]}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2}, \quad (66)$$

$$[\text{CO}_3^{2-}] = \frac{C_T K_1 K_2}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2}. \quad (67)$$

$f(\text{CO}_2)$ is calculated from (60) and A_T from (18); the various terms needed are calculated from the expressions given in Table 2.

A_T and C_T

The easiest approach to using this pair of parameters is to rewrite (18), the expression for A_T , in terms of total concentrations and $[\text{H}^+]$ (see Table 2). The resulting equation is solved for $[\text{H}^+]$ using either a Newton–Raphson technique or a simple iterative approach; a suitable initial estimate for calculations involving sea water is: $[\text{H}^+] = 10^{-8} \text{ mol kg}^{-1}$.

Once $[\text{H}^+]$ has been calculated,

$$[\text{HCO}_3^-] = \frac{C_T K_1 [\text{H}^+]}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2}, \quad (68)$$

$$[\text{CO}_3^{2-}] = \frac{C_T K_1 K_2}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2}. \quad (69)$$

$[\text{CO}_2^*]$ is then calculated from

$$[\text{CO}_2^*] = \frac{[\text{H}^+][\text{HCO}_3^-]}{K_1} \quad (70)$$

and $f(\text{CO}_2)$ is calculated from (60).

A_T and $f(\text{CO}_2)$

$[\text{CO}_2^*]$ is given by (26):

$$[\text{CO}_2^*] = K_0 f(\text{CO}_2). \quad (71)$$

Equations (27) and (28) are then rewritten as

$$[\text{HCO}_3^-] = \frac{K_0 K_1 f(\text{CO}_2)}{[\text{H}^+]}, \quad (72)$$

$$[\text{CO}_3^{2-}] = \frac{K_0 K_1 K_2 f(\text{CO}_2)}{[\text{H}^+]^2}. \quad (73)$$

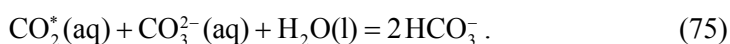
These terms are substituted into (18) together with the remaining terms from Table 2. The resulting expression is solved for $[H^+]$ using either a Newton–Raphson technique or a simple iterative approach; a suitable initial estimate for ocean water is: $[H^+] = 10^{-8} \text{ mol kg}^{-1}$. Once $[H^+]$ has been calculated, C_T is calculated from (17) using the final values obtained for $[HCO_3^-]$ and $[CO_3^{2-}]$.

C_T and $f(\text{CO}_2)$

For this calculation, it is convenient to define the constant

$$K = K_1/K_2 = \frac{[HCO_3^-]^2}{[CO_2^*][CO_3^{2-}]} \quad (74)$$

For the equilibrium process,



$[CO_2^*]$ is given by (26):

$$[CO_2^*] = K_0 f(\text{CO}_2) \quad (76)$$

and combining (17) and (74) gives

$$C_T = K_0 f(\text{CO}_2) + [HCO_3^-] + \frac{[HCO_3^-]^2}{KK_0 f(\text{CO}_2)} \quad (77)$$

Rearranging,

$$\begin{aligned} [HCO_3^-]^2 + KK_0 f(\text{CO}_2)[HCO_3^-] \\ + KK_0 f(\text{CO}_2)(K_0 f(\text{CO}_2) - C_T) = 0. \end{aligned} \quad (78)$$

The solution is

$$\begin{aligned} [HCO_3^-] = \frac{1}{2} \left[-KK_0 f(\text{CO}_2) + \left((KK_0 f(\text{CO}_2))^2 \right. \right. \\ \left. \left. - 4(KK_0 f(\text{CO}_2))(K_0 f(\text{CO}_2) - C_T) \right)^{1/2} \right] \end{aligned} \quad (79)$$

and

$$[CO_3^{2-}] = C_T - [CO_2^*] - [HCO_3^-] \quad (80)$$

$[H^+]$ is calculated from (27):

$$[H^+] = \frac{K_1 [CO_2^*]}{[HCO_3^-]} \quad (81)$$

A_T from (18): the various terms needed are calculated from the expressions given in Table 2.

$[H^+]$, A_T and C_T

The concentrations of the non-CO₂ species that contribute to A_T are calculated using the expressions given in Table 2. The carbonate alkalinity, A_C , is then calculated from (54). Equations (17), (27), and (53) can then be combined to give

$$2C_T - A_C = [CO_2^*] \left(2 + \frac{K_1}{[H^+]} \right). \quad (82)$$

Hence

$$[CO_2^*] = \frac{[H^+](2C_T - A_C)}{2[H^+] + K_1}, \quad (83)$$

$$[HCO_3^-] = \frac{K_1(2C_T - A_C)}{2[H^+] + K_1}, \quad (84)$$

$$\begin{aligned} [CO_3^{2-}] &= A_C - C_T + [CO_2^*] \\ &= \frac{[H^+]A_C + K_1(A_C - C_T)}{2[H^+] + K_1}. \end{aligned} \quad (85)$$

An expression for $[CO_2^*]$ can also be derived in terms of K_2 :

$$[CO_2^*] = C_T - [HCO_3^-] - [CO_3^{2-}] \quad (86)$$

and $[HCO_3^-]$ and $[CO_3^{2-}]$ are given by (58) and (59), thus

$$[CO_2^*] = C_T - \frac{A_C([H^+] + K_2)}{[H^+] + 2K_2}. \quad (87)$$

$f(CO_2)$ is then calculated from (60).

$[H^+]$, A_T and $f(CO_2)$

The concentrations of the contributions of the various non-CO₂ species to A_T are calculated using the expressions given in Table 2. A_C is calculated from (54). Then, from (26),

$$[CO_2^*] = K_0 f(CO_2) \quad (88)$$

and from (27),

$$[HCO_3^-] = \frac{K_0 K_1 f(CO_2)}{[H^+]}, \quad (89)$$

Then, from (28) and (53),

$$[CO_3^{2-}] = \frac{A_C [H^+] - K_0 K_1 f(CO_2)}{2[H^+]}. \quad (90)$$

There are no equations that can be used to calculate these independently of K_1 . C_T is calculated from (17).

[H⁺], C_T and f(CO₂)

From (26),

$$[\text{CO}_2^*] = K_0 f(\text{CO}_2). \quad (91)$$

[HCO₃⁻] is given either by

$$[\text{HCO}_3^-] = \frac{K_0 K_1 f(\text{CO}_2)}{[\text{H}^+]}, \quad (92)$$

or can be obtained from (17) and (28):

$$\begin{aligned} [\text{HCO}_3^-] &= C_T - [\text{CO}_2^*] - \frac{[\text{HCO}_3^-] K_2}{[\text{H}^+]} \\ &= \frac{[\text{H}^+](C_T - K_0 f(\text{CO}_2))}{[\text{H}^+] + K_2}. \end{aligned} \quad (93)$$

[CO₃²⁻] can be obtained either from [H⁺] and f(CO₂):

$$\begin{aligned} [\text{CO}_3^{2-}] &= C_T - [\text{CO}_2^*] - [\text{HCO}_3^-] \\ &= C_T - K_0 f(\text{CO}_2) (1 + K_1/[\text{H}^+]) \end{aligned} \quad (94)$$

or from the equation for [HCO₃⁻] above, (93):

$$[\text{CO}_3^{2-}] = \frac{(C_T - K_0 f(\text{CO}_2)) K_2}{[\text{H}^+] + K_2}. \quad (95)$$

A_T is then calculated from (18), the terms for [HCO₃⁻] and [CO₃²⁻] are given by either (92) and (94), in terms of K₁, or (93) and (95), in terms of K₂. The remaining terms are calculated from the expressions given in Table 2.

[H⁺], A_T, C_T and f(CO₂)

The following sets of equations have the property that they do not embody directly either of the dissociation constants functions K₁ or K₂. The carbonate alkalinity, A_C, is first calculated from A_T and [H⁺] using (54) and the expressions in Table 2.

[CO₂^{*}] is calculated from (26):

$$[\text{CO}_2^*] = K_0 f(\text{CO}_2) \quad (96)$$

and then

$$[\text{HCO}_3^-] = 2C_T - A_C - 2K_0 f(\text{CO}_2), \quad (97)$$

$$[\text{CO}_3^{2-}] = A_C - C_T + K_0 f(\text{CO}_2). \quad (98)$$

The dissociation constants for carbonic acid can then be calculated from (27) and (28).