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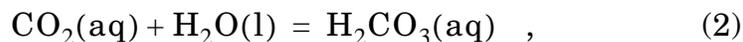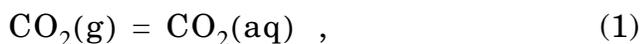
Solution chemistry of carbon dioxide in sea water

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 Handbook. 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 of this handbook.

2. Reactions in solution

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

$$CO_2(g) \; = \; CO_2(aq) \quad , \tag{1}$$

$$CO_2(aq) + H_2O(l) \; = \; H_2CO_3(aq) \quad , \tag{2}$$

$$H_2CO_3(aq) \; = \; H^+(aq) + HCO_3^-(aq) \quad , \tag{3}$$

$$HCO_3^-(aq) \; = \; H^+(aq) + CO_3^{2-}(aq) \quad ; \tag{4}$$

the notations (g), (l), (aq) refer to the state of the species, *i. e.* a gas, a liquid or in aqueous solution respectively. Unfortunately, it is difficult to distinguish between the species $CO_2(aq)$ and $H_2CO_3(aq)$ by analytical means. It is thus usual to lump the concentrations of $CO_2(aq)$ and $H_2CO_3(aq)$ together and to express this sum as the concentration of a hypothetical species, $CO_2^*(aq)$.

Reactions (1), (2) and (3) are redefined in terms of this species:

$$CO_2(g) \; = \; CO_2^*(aq) \quad , \tag{5}$$

$$CO_2^*(aq) + H_2O(l) \; = \; H^+(aq) + HCO_3^-(aq) \quad . \tag{6}$$
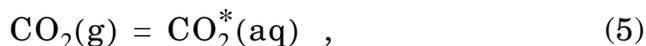
The equilibrium relationships between the concentrations of

these various species can then be written as:

$$K_0 = [CO_2^*] / f(CO_2) \quad , \tag{7}$$

$$K_1 = [H^+][HCO_3^-] / [CO_2^*] \quad , \tag{8}$$

$$K_2 = [H^+][CO_3^{2-}] / [HCO_3^-] \quad . \tag{9}$$

In these equations, $f(CO_2)$ is the fugacity of carbon dioxide in the gas phase and brackets represent total stoichiometric concentrations[*] of the particular chemical species enclosed. These equilibrium constants are functions of the temperature, pressure and composition (salinity) of the solution (sea water) and have been measured on a variety of occasions (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, $x(CO_2)p$ —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 a knowledge of its equation of state:

$$f(CO_2) = x(CO_2)p \; \exp\left(\int_0^p \frac{(V(CO_2) - RT/p')\mathrm{d}p'}{RT} \right) \; . \tag{10}$$

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:

$$\frac{pV(CO_2)}{RT} = 1 + \frac{B(x, T)}{V(CO_2)} + \frac{C(x, T)}{V(CO_2)^2} + \; .... \tag{11}$$

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

It is known from statistical mechanics that the virial coefficient $B(x, T)$ results from pair-wise interactions in the gas phase (Guggenheim, 1967); this property can be used to

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[*]   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.

estimate $B(x, T)$ for particular gas mixtures—such as CO_2 in air—from measurements on binary mixtures or from a model expression for the intermolecular potential energy function for the molecules concerned. The magnitude of the fugacity coefficient—the ratio between fugacity and partial pressure—is a function both of temperature and of gas phase composition (figure 1).
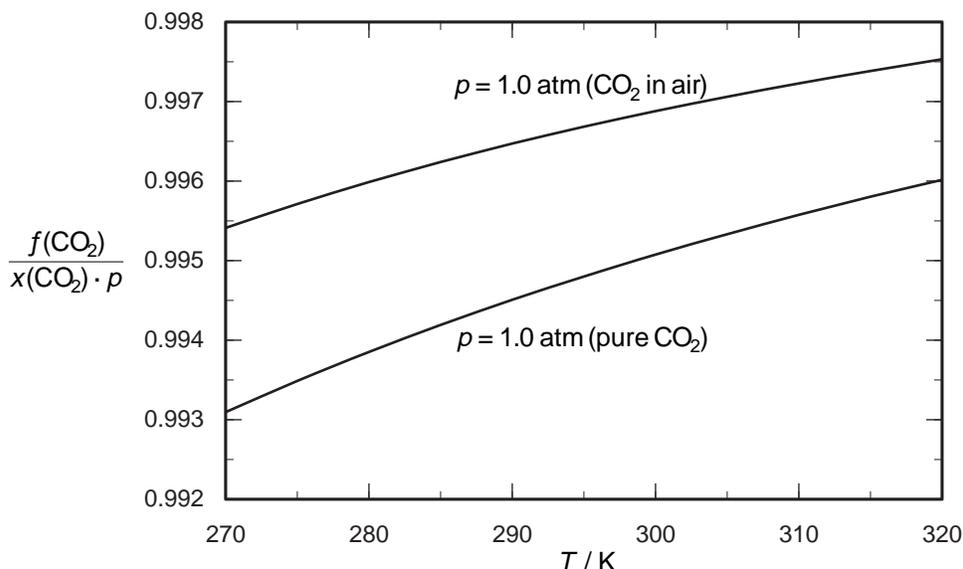

Figure 1. Variation of fugacity coefficient with temperature at 1 atm total pressure for pure CO_2 gas and for CO_2 in air: $x(CO_2) = 350 \times 10^{-6}$ (calculated using the procedure described in SOP 24 of this Handbook).

4. Analytical parameters of the CO_2 system

Unfortunately, the concentrations of the individual species of the carbon dioxide system in solution cannot 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.

Total dissolved inorganic carbon. The total dissolved inorganic carbon in a sea water sample:

$$C_T \ = \ [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \quad , \qquad (12)$$

can be measured directly by acidifying the sample, extracting the CO_2 gas that is produced and measuring its amount.

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 one kilogram of sample." Thus

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}]$$
$$+ 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + \ldots$$
$$- [H^+]_F - [HSO_4^-] - [HF] - [H_3PO_4] - \ldots, \quad (13)$$

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 (14).

Fugacity of CO_2 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—measured— pressure and temperature. The concentration of CO_2 is then determined in that gas phase and the corresponding value of $f(CO_2)$—for that temperature—estimated from equation (10).

Total hydrogen ion concentration. Although the concept of a total hydrogen ion concentration is somewhat confusing—see Dickson (1984; 1993) for a detailed discussion of the various pH scales that have been used in sea water—it is needed to define acid dissociation constants accurately in sea water media (Dickson, 1990). Total hydrogen ion concentration is defined as

$$[H^+] = [H^+]_F (1 + S_T / K_S) \ ; \quad (14)$$

$[H^+]_F$ is the *free* concentration of hydrogen ion in sea water, S_T is the total sulfate concentration ($[HSO_4^-] + [SO_4^{2-}]$) and K_S is the acid dissociation constant for HSO_4^-. The approximation

$$[H^+] \approx [H^+]_F + [HSO_4^-] \quad (15)$$

only holds well at pH values above 4. (Note: pH = $-\log [H^+]$.)

Typically, the various equilibrium constants required to describe acid–base chemistry in sea water are measured in the laboratory (see Chapter 5 of this handbook for recommended values). In

addition, the total amounts of the various other (non-CO_2) acid/base systems in the sample of interest are usually known; either from the salinity—for conservative constituents such as borate, sulfate and fluoride—or from measurements—for constituents such as phosphate, silicate, ammonia or hydrogen sulfide. As a result, it is only necessary to know two parameters from the four above 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 about 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 over-determine 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.

5. References

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Annexe

Equations that describe the CO_2 system in sea water

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). It is therefore possible 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 known:

- the solubility constant for CO_2 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-CO_2 acid/base pairs,
- the values for at least two of the CO_2 related parameters: C_T, A_T, $f(CO_2)$, $[H^+]$.

Although the rank is determined by the chemical description of the system, the optimal choice of experimental variables is dictated by the nature of the problem being studied and remains at the discretion of the investigator.

Note that although each of the CO_2 related parameters are linearly independent, they are not orthogonal. For certain combinations there are limitations to the accuracy with which the other parameters can be predicted from the measured data. This results from error propagation 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 rather than to calculate it from other measurements, particularly if accurate value is needed for geochemical purposes.

When more than two of the CO_2 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.

Table 1: Equations for the sea water acid/base system

Mass-conservation equations:

$$C_T = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \tag{A.1}$$

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-]$$
$$+ [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3]$$
$$+ [HS^-] - [H^+]_F - [HSO_4^-] - [HF] - [H_3PO_4] \tag{A.2}$$

$$B_T = [B(OH)_3] + [B(OH)_4^-] \tag{A.3}$$

$$S_T = [HSO_4^-] + [SO_4^{2-}] \tag{A.4}$$

$$F_T = [HF] + [F^-] \tag{A.5}$$

$$P_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \tag{A.6}$$

$$Si_T = [Si(OH)_4] + [SiO(OH)_3^-] \tag{A.7}$$

$$NH_{3\,T} = [NH_4^+] + [NH_3] \tag{A.8}$$

$$H_2S_T = [H_2S] + [HS^-] \tag{A.9}$$

Equilibrium constants:

$$K_0 = [CO_2^*]/f(CO_2) \tag{A.10}$$

$$K_1 = [H^+][HCO_3^-]/[CO_2^*] \tag{A.11}$$

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] \tag{A.12}$$

$$K_W = [H^+][OH^-] \tag{A.13}$$

$$K_B = [H^+][B(OH)_4^-]/[B(OH)_3] \tag{A.14}$$

$$K_S = [H^+]_F [SO_4^{2-}]/[HSO_4^-] \tag{A.15}$$

$$K_F = [H^+][F^-]/[HF] \tag{A.16}$$

$$K_{1P} = [H^+][H_2PO_4^-]/[H_3PO_4] \tag{A.17}$$

$$K_{2P} = [H^+][HPO_4^{2-}]/[H_2PO_4^-] \tag{A.18}$$

$$K_{3P} = [H^+][PO_4^{3-}]/[HPO_4^{2-}] \tag{A.19}$$

$$K_{Si} = [H^+][SiO(OH)_3^-]/[Si(OH)_4] \tag{A.20}$$

$$K_{NH3} = [H^+][NH_3]/[NH_4^+] \tag{A.21}$$

$$K_{H2S} = [H^+][HS^-]/[H_2S] \tag{A.22}$$

Table 2: Expression for the concentrations of the various
species in equation (A.2).

$$[HCO_3^-] = \frac{C_T K_1 [H^+]}{[H^+]^2 + K_1 [H^+] + K_1 K_2} \tag{A.23}$$

$$[CO_3^{2-}] = \frac{C_T K_1 K_2}{[H^+]^2 + K_1 [H^+] + K_1 K_2} \tag{A.24}$$

$$[B(OH)_4^-] = B_T / (1 + [H^+]/K_B) \tag{A.25}$$

$$[OH^-] = K_W / [H^+] \tag{A.26}$$

$$[H_3PO_4] = \frac{P_T [H^+]^3}{[H^+]^3 + K_{1P}[H^+]^2 + K_{1P}K_{2P}[H^+] + K_{1P}K_{2P}K_{3P}} \tag{A.27}$$

$$[H_2PO_4^-] = \frac{P_T K_{1P}[H^+]^2}{[H^+]^3 + K_{1P}[H^+]^2 + K_{1P}K_{2P}[H^+] + K_{1P}K_{2P}K_{3P}} \tag{A.28}$$

$$[HPO_4^{2-}] = \frac{P_T K_{1P}K_{2P}[H^+]}{[H^+]^3 + K_{1P}[H^+]^2 + K_{1P}K_{2P}[H^+] + K_{1P}K_{2P}K_{3P}} \tag{A.29}$$

$$[PO_4^{3-}] = \frac{P_T K_{1P}K_{2P}K_{3P}}{[H^+]^3 + K_{1P}[H^+]^2 + K_{1P}K_{2P}[H^+] + K_{1P}K_{2P}K_{3P}} \tag{A.30}$$

$$[SiO(OH)_3^-] = Si_T / (1 + [H^+]/K_{Si}) \tag{A.31}$$

$$[NH_3] = NH_{3\,T} / (1 + [H^+]/K_{NH3}) \tag{A.32}$$

$$[HS^-] = H_2S_T / (1 + [H^+]/K_{H2S}) \tag{A.33}$$

$$[H^+]_F = [H^+] / (1 + S_T/K_S) \tag{A.34}$$

$$[HSO_4^-] = S_T / (1 + K_S/[H^+]_F) \tag{A.35}$$

$$[HF] = F_T / (1 + K_F/[H^+]) \tag{A.36}$$

[H+] and A_T

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

$$A_C = [HCO_3^-] + 2[CO_3^{2-}] \quad . \tag{A.37}$$

The concentrations of the non-CO_2 species that contribute to A_T are calculated using the expressions given in table 2, thus

$$A_C = A_T - [B(OH)_4^-] - [OH^-] - [HPO_4^{2-}]$$
$$-2[PO_4^{3-}] - [SiO(OH)_3^-] - [NH_3] - [HS^-]$$
$$+ [H^+]_F + [HSO_4^-] + [HF] + [H_3PO_4] \, . \tag{A.38}$$

Then from (A.11),

$$[HCO_3^-] = \frac{[CO_2^*]K_1}{[H^+]} \quad , \tag{A.39}$$

and from (A.12)

$$[CO_3^{2-}] = \left(\frac{[CO_2^*]K_1}{[H^+]}\right)\frac{K_2}{[H^+]} \quad . \tag{A.40}$$

Substituting into (A.37) and rearranging

$$[CO_2^*] = \frac{A_C[H^+]^2}{K_1([H^+] + 2K_2)} \quad , \tag{A.41}$$

and hence

$$[HCO_3^-] = \frac{A_C[H^+]}{[H^+] + 2K_2} \quad , \tag{A.42}$$

$$[CO_3^{2-}] = \frac{A_C K_2}{[H^+] + 2K_2} \quad . \tag{A.43}$$

C_T is calculated from (A.1) and $f(CO_2)$ from (A.10):

$$f(CO_2) = [CO_2^*]/K_0 \ .$$
(A.44)

[H⁺] and $f(CO_2)$

$[CO_2^*]$ is calculated from (A.10):

$$[CO_2^*] = K_0 f(CO_2) \quad .$$
(A.45)

Thus, from (A.11) and (A.12),

$$[HCO_3^-] = \frac{K_0 K_1 f(CO_2)}{[H^+]} \quad ,$$
(A.46)

$$[CO_3^{2-}] = \frac{K_0 K_1 K_2 f(CO_2)}{[H^+]^2} \quad .$$
(A.47)

C_T is calculated from (A.1) and A_T from (A.2); $[HCO_3^-]$ and $[CO_3^{2-}]$ are given by (A.46) and (A.47), the remaining terms are calculated from the expressions given in table 2.

[H⁺] and C_T

Equations (A.11) and (A.12) are rearranged and substituted into (A.1) to give

$$C_T = [CO_2^*]\left(1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}\right) \quad .$$
(A.48)

Thus

$$[CO_2^*] = \frac{C_T[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1 K_2} \quad ,$$
(A.49)

$$[HCO_3^-] = \frac{C_T K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1 K_2} \quad ,$$
(A.50)

$$[CO_3^{2-}] = \frac{C_T K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1 K_2} \quad .$$
(A.51)

$f(CO_2)$ is calculated from (A.44) and A_T from (A.2); 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 (A.2)—the expression for A_T—in terms of total concentrations and $[H^+]$ (see table 2). The resulting equation is solved for $[H^+]$ using either a Newton-Raphson technique or a simple iterative approach; a suitable initial estimate for calculations involving ocean water is $[H^+] = 10^{-8}$.

Once $[H^+]$ has been calculated,

$$[HCO_3^-] = \frac{C_T K_1 [H^+]}{[H^+]^2 + K_1 [H^+] + K_1 K_2} \quad , \tag{A.52}$$

$$[CO_3^{2-}] = \frac{C_T K_1 K_2}{[H^+]^2 + K_1 [H^+] + K_1 K_2} \quad . \tag{A.53}$$

Hence

$$[CO_2^*] = [H^+][HCO_3^-]/K_1 \quad ; \tag{A.54}$$

$f(CO_2)$ is calculated from (A.44).

A_T and $f(CO_2)$

$[CO_2^*]$ is calculated from (A.10):

$$[CO_2^*] = K_0 f(CO_2) \quad . \tag{A.55}$$

Equations (A.11) and (A.12) are then rewritten as:

$$[HCO_3^-] = \frac{K_0 K_1 f(CO_2)}{[H^+]} \quad , \tag{A.56}$$

$$[CO_3^{2-}] = \frac{K_0 K_1 K_2 f(CO_2)}{[H^+]^2} \quad . \tag{A.57}$$

These terms are substituted into (A.2) 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 $[H^+] = 10^{-8}$. Once $[H^+]$ has been calculated, C_T is calculated from (A.1) using the final values obtained for $[HCO_3^-]$ and $[CO_3^{2-}]$.

C_T and $f(CO_2)$

For this calculation, it is convenient to define the constant

$$K = K_1/K_2 = \frac{[HCO_3^-]^2}{[CO_2^*][CO_3^{2-}]} \quad . \tag{A.58}$$

for the equilibrium process

$$CO_2^*(aq) + CO_3^{2-}(aq) + H_2O(l) = 2HCO_3^-(aq) \quad . \tag{A.59}$$

$[CO_2^*]$ is calculated from (A.10):

$$[CO_2^*] = K_0 f(CO_2) \, , \tag{A.60}$$

(A.45) is then combined with (A.58) and (A.1) to give

$$C_T = K_0 f(CO_2) + [HCO_3^-] + \frac{[HCO_3^-]^2}{K K_0 f(CO_2)} \quad . \tag{A.61}$$

Rearranging,

$$[HCO_3^-]^2 + K K_0 f(CO_2)[HCO_3^-]$$
$$+ K K_0 f(CO_2)(K_0 f(CO_2) - C_T) = 0 \, . \tag{A.62}$$

The solution is[*]

$$[HCO_3^-] = \frac{-K K_0 f(CO_2)}{2}$$
$$+ \frac{\sqrt{(K K_0 f(CO_2))^2 - 4(K K_0 f(CO_2))(K_0 f(CO_2) - C_T)}}{2}$$
$$\tag{A.63}$$

and

$$[CO_3^{2-}] = C_T - [CO_2^*] - [HCO_3^-] \quad . \tag{A.64}$$

$[H^+]$ is calculated from (A.11)

$$[H^+] = \frac{K_1 [CO_2^*]}{[HCO_3^-]} \; ; \tag{A.65}$$

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

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[*] The alternate solution implies that $[HCO_3^-] < 0$.

$[H^+]$, A_T and C_T

The concentrations of the non-CO_2 species that contribute to A_T are calculated using the expressions given in table 2. The carbonate alkalinity, A_C, is then calculated from (A.38). Equations (A.1), (A.11) and (A.37) can then be combined to give

$$2C_T - A_C = [CO_2^*]\left(2 + \frac{K_1}{[H^+]}\right) \quad .$$ (A.66)

Hence

$$[CO_2^*] = \frac{[H^+](2C_T - A_C)}{2[H^+] + K_1} \quad ,$$ (A.67)

$$[HCO_3^-] = \frac{K_1(2C_T - A_C)}{2[H^+] + K_1} \quad ,$$ (A.68)

$$[CO_3^{2-}] = A_C - C_T + [CO_2^*]$$

$$= \frac{[H^+]A_C + K_1(A_C - C_T)}{2[H^+] + K_1} \quad .$$ (A.69)

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

$$[CO_2^*] = C_T - [HCO_3^-] - [CO_3^{2-}] \quad .$$ (A.70)

$[HCO_3^-]$ and $[CO_3^{2-}]$ are given by (A.42) and (A.43), thus

$$[CO_2^*] = C_T - \frac{A_C([H^+] + K_2)}{[H^+] + 2K_2} \quad .$$ (A.71)

In both of these cases $f(CO_2)$ is calculated from (A.10).

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

The concentrations of the contributions of the various non-CO_2 species to A_T are calculated using the expressions given in table 2. A_C is calculated from (A.38). Then, from (A.10)

$$[CO_2^*] = K_0 f(CO_2) \quad .$$ (A.72)

and from (A.11)

$$[HCO_3^-] = \frac{K_0 K_1 f(CO_2)}{[H^+]} \quad . \tag{A.73}$$

Then, from (A.12) and (A.37),

$$[CO_3^{2-}] = \frac{A_C[H^+] - K_0 K_1 f(CO_2)}{2[H^+]} \quad . \tag{A.74}$$

There are no equations that can be used to calculate these independently of K_1. C_T is calculated from (A.1).

[H$^+$], C_T and f(CO$_2$)

From (A.10)

$$[CO_2^*] = K_0 f(CO_2) \quad . \tag{A.75}$$

$[HCO_3^-]$ is given either by

$$[HCO_3^-] = \frac{K_0 K_1 f(CO_2)}{[H^+]} \quad , \tag{A.76}$$

or can be obtained from (A.1) and (A.12):

$$[HCO_3^-] = C_T - [CO_2^*] - \frac{[HCO_3^-]K_2}{[H^+]}$$

$$= \frac{[H^+](C_T - K_0 f(CO_2))}{[H^+] + K_2} \quad . \tag{A.77}$$

$[CO_3^{2-}]$ can be obtained either from [H$^+$] and f(CO$_2$):

$$[CO_3^{2-}] = C_T - [CO_2^*] - [HCO_3^-]$$

$$= C_T - K_0 f(CO_2)(1 + K_1/[H^+]) \quad , \tag{A.78}$$

or from the equation for $[HCO_3^-]$ above, (A.77),

$$[CO_3^{2-}] = \frac{(C_T - K_0 f(CO_2))K_2}{[H^+] + K_2} \quad . \tag{A.79}$$

A_T is then calculated from (A.2), the terms for $[HCO_3^-]$ and $[CO_3^{2-}]$ are given by either (A.76) and (A.78)—in terms of K_1—

or (A.77) and (A.79)—in terms of K_2. The remaining terms are calculated from the expressions given in table 2.

[H$^+$], A_T, C_T and f(CO$_2$)

The following set of equations have the property that they do not embody directly either of the ionization functions K_1 or K_2. The carbonate alkalinity, A_C, is first calculated from A_T and [H$^+$] using (A.38) and the expressions in Table 2.

$[CO_2^*]$ is calculated from

$$[CO_2^*] = K_0 f(CO_2) \quad , \tag{A.80}$$

and then

$$[HCO_3^-] = 2C_T - A_C - 2K_0 f(CO_2) \quad , \tag{A.81}$$

$$[CO_3^{2-}] = A_C - C_T + K_0 f(CO_2) \quad . \tag{A.82}$$

The ionization constants for carbonic acid can then be calculated from (A.11) and (A.12).