9 CHEMISTRY OF CARBONIC ACID IN WATER

9.1 INTRODUCTION

Studying the carbon isotopic composition of water, whether it concerns freshwater or seawater, a complication arises from the fact that the dissolved inorganic carbon always consists of more than one compound, while also the presence of gaseous CO_2 and solid calcium carbonate may be relevant. In fact we are dealing with the following compounds and concentrations:

gaseous CO_2 (occasionally denoted by CO_2g) with a partial pressure P_{CO2}
dissolved CO_2 (denoted by CO_2aq)
dissolved carbonic acid, H_2CO_3 with $a = [H_2CO_3] + [CO_2aq]$
dissolved bicarbonate, HCO_3^- with $b = [HCO_3^-]$
dissolved carbonate, CO_3^{2-} with $c = [CO_3^{2-}]$
total dissolved inorganic carbon, DIC, with $C_T = a + b + c$
solid carbonate, $CaCO_3$ (occasionally denoted by s)

The ambiguity in using carbon isotopes now consists of two observations:

1) On the one hand, only the isotopic composition of a single compound in relation to that of another compound is geochemically or hydrologically meaningful. We have seen an example of this statement while discussing the carbon isotopic composition of groundwater, for ^{13}C as well as ^{14}C (Figs.7.7 and 8.4). In other words: an isotopic fractionation factor is a fundamental, physico/chemical quantity only if it is the ratio between two isotopic ratios of single compounds. For instance:

$$^{13}\alpha_{a/b} = {}^{13}R_a/{}^{13}R_b \qquad \text{and} \qquad {}^{13}\alpha_{c/b} = {}^{13}R_c/{}^{13}R_b$$

2) **a)** On the other hand, in mass balance considerations the carbon isotopic composition of a mixture of compounds is relevant. For instance, if CO_2 or $CaCO_3$ are being removed from a dissolved carbon solution, of for estuarine mixing of fresh- and seawater, the total ^{13}C mass balance has to be taken into account. In this chapter some examples are given.

b) Measuring the carbon isotopic composition of a solution comes to extracting the total CO_2 from the sample after acidification, instead of single compounds.

For the essential translation of $^{13}\delta$ of total dissolved carbon to $^{13}\delta$ of single compounds, and conversely, the inorganic carbon chemistry, i.e. of the dissolved inorganic carbon is required.

Once the various concentrations of the dissolved species -to be deduced in the next sections are known, the ^{13}C mass balance:

$$\begin{aligned}&\left([CO_2aq]+[H_2CO_3]+[HCO_3^-]+[CO_3^{2-}]\right)^{13}R_{DIC} = \\ &= [CO_2aq]^{13}R_{CO_2aq} + [H_2CO_3]^{13}R_{H_2CO_3} + [HCO_3^-]^{13}R_{HCO_3} + [CO_3^{2-}]^{13}R_{CO_3}\end{aligned} \quad \textbf{(9.1)}$$

or, inserting the previously mentioned symbols for the various concentrations and combining the concentration of CO_2aq and the carbonic acid, H_2CO_3, the latter being a negligibly small fraction, the isotopic composition of the total dissolved carbon ($C_T = a + b + c$) is:

$$^{13}R_{C_T} = \frac{a \cdot R_a + b \cdot R_b + c \cdot R_c}{C_T} \quad \textbf{(9.2)}$$

and conversely, inserting the proper fractionation factors as mentioned before:

$$^{13}R_b = \frac{C_T \cdot {}^{13}R_{C_T}}{a \cdot \alpha_{a/b} + b + c \cdot \alpha_{c/b}} b \quad \textbf{(9.3)}$$

The next sections will be devoted to analysing the chemical composition of carbonate waters.

9.2 CARBONIC ACID EQUILIBRIA

In the presence of gaseous CO_2, dissolved CO_2 exchanges with CO_2 gas:

$$CO_2(g) + H_2O \Leftrightarrow CO_2(aq) + H_2O \quad \textbf{(9.4)}$$

$$CO_2(aq) + H_2O \Leftrightarrow H_2CO_3 \quad \textbf{(9.5)}$$

where g and aq refer to the gaseous and dissolved phase, respectively. Although the concentration of $CO_2(aq)$ far exceeds that of dissolved H_2CO_3 (in the order of 10^3) we denote the concentration of all dissolved CO_2 by $[H_2CO_3]$. The equilibrium condition between the phases is quantified by the *molar solubility* K_o (Henry's law):

$$K_0 = \frac{[H_2CO_3]}{P_{CO_2}} \quad \textbf{(9.6)}$$

where the atmospheric CO_2 partial pressure, P_{CO2}, is in atm, K_o is the solubility in mol L^{-1} atm^{-1} and $[H_2CO_3]$ is the dissolved CO_2 concentration in mol/kg of water.

H_2CO_3 dissociates in water according to

$$H_2CO_3 + \Leftrightarrow H^+ + HCO_3^- \quad \textbf{(9.7)}$$

and

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \qquad \textbf{(9.8)}$$

where the equilibrium conditions are quantified by the *dissociation* or *acidity constants*:

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \qquad \textbf{(9.9)}$$

and

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \qquad \textbf{(9.10)}$$

Finally the dissociation of water obeys the equilibrium condition

$$K_w = [H^+][OH^-] \qquad \textbf{(9.11)}$$

Here we have to emphasise that, although the hydrogen ion, H^+, is commonly hydrated to form H_3O^+ or even to multiple hydrated ions, we will write the hydrated hydrogen ion as H^+ as the hydrated structure does not enter the chemical models.

The $[H^+]$ concentration is generally given as a pH value, defined as the negative logarithm:

$$pH = -{}^{10}\log[H^+] \qquad \textbf{(9.12)}$$

The total concentration of dissolved inorganic carbon (= total carbon, also denoted by ΣCO_2 or ΣC or DIC) is defined by:

$$C_T = [CO_2aq] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = a + b + c \qquad \textbf{(9.13)}$$

The *alkalinity* is a practical quantity, following from the conservation of electroneutrality in solutions where the metal-ion concentrations (Na, Ca, Mg) and pH are constant:

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + [\text{other weak acid anions}] \qquad \textbf{(9.14)}$$

in which concentrations of other weak acids may be included in the interest of high precision, such as humic acids in freshwater or borate, $[B(OH)_4^-]$, in seawater.

Under natural conditions $[H^+]$ and $[OH^-]$ are negligibly small compared to the carbonate species concentrations. The sum of the weak acid and alkali-ion concentrations, determined by an acid titration, referred to as the total alkalinity, thus about equals the *carbonate alkalinity* defined as:

$$A_C = [HCO_3^-] + 2[CO_3^{2-}] = b + 2c \qquad \textbf{(9.15)}$$

If the water contains Ca^{2+} (or Mg^{2+}) and carbonate or is in contact with calcite also the dissociation equilibrium of calcite affects the carbon chemistry:

$$CaCO_3 \Leftrightarrow Ca^{2+} + CO_3{}^{2-} \qquad \textbf{(9.16)}$$

where the concentrations are limited by the solubility product:

$$K_{CaCO3} = [Ca^{2+}][CO_3{}^{2-}] \qquad \textbf{(9.17)}$$

9.3 THE EQUILIBRIUM CONSTANTS

Basically all values of the solubilities and dissociation constants are temperature dependent. However, the K values also depend on the solute concentrations, because the formation of ion complexes between the carbonic ions and molecules and ions in the solution hinder the dissolved carbonic molecules and ions to take part in the thermodynamic equilibrium reactions. Therefore, in the thermodynamic equation, the concentrations have to be replaced by their *activities*, that are smaller than the concentrations. The *thermodynamic solubility constant* is:

$$K_0 = \frac{a_{H_2CO_3}}{P_{CO_2}} = \frac{\gamma_a[H_2CO_3]}{P_{CO_2}} \qquad \textbf{(9.18a)}$$

where in general the *activity coefficients* $\gamma < 1$ ($\gamma = 1$ for an *ideal solution*, i.e. with zero solute concentrations or zero *ionic strength*).

In the non-ideal solutions of seawater and brackish water it is more practical to describe the relation between the real, *measurable* concentrations by the *apparent solubility constant*:

$$K_0' = \frac{[H_2CO_3]}{P_{CO_2}} = \frac{K_0}{\gamma_a} \qquad \textbf{(9.18b)}$$

The *thermodynamic* and the *apparent acidity (dissociation) constants* of the first and second dissociation of carbonic acid (Eqs.9.6, 9.9 and 9.10) are now related by:

$$K_1 = \frac{a_H \cdot a_{HCO3}}{a_{H_2CO_3}} = \frac{\gamma_H[H^+]\cdot\gamma_b[HCO_3^-]}{\gamma_a[H_2CO_3]} \qquad \textbf{(9.19a)}$$

and

$$K_1' = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{\gamma_a}{\gamma_H \cdot \gamma_b} K_1 \qquad \textbf{(9.19b)}$$

and with respect to the second dissociation constant:

$$K_2 = \frac{a_H \cdot a_{CO_3}}{a_{HCO_3}} = \frac{\gamma_H[H^+] \cdot \gamma_c[CO_3^{2-}]}{\gamma_b[HCO_3^-]} \qquad \textbf{(9.20a)}$$

and

$$K_2' = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{\gamma_b}{\gamma_H \cdot \gamma_c} K_2 \qquad \textbf{(9.20b)}$$

The definition also takes into account that in reality instead of $[H^+]$ the pH is being measured based on a series of buffer solutions. Therefore, in these equations $[H^+]$ is to be replaced by 10^{-pH}.

Comparing fresh and seawater, the differences in the first and second dissociation constants of carbonic acid -K_1 and K_2 for freshwater, and K_1' and K_2' for seawater- and the consequences thereoff will appear spectacular.

For practical reasons the values of the dissociation constants are generally given as:

$$pK = - {}^{10}\log K \qquad \text{or} \qquad K = 10^{-pK} \qquad \textbf{(9.21)}$$

The K_0, K_1 and K_2 values for freshwater (ideal solution) and seawater as a function of the water temperature and the water salinity are discussed in the next section and shown in Figs.9.1 - 9.4.

9.3.1 IDEAL SOLUTIONS

Most freshwaters can be considered as ideal solutions (extrapolated to zero ionic strength). Values for the temperature range of 0 to 40 °C and the salinity range of 0 to 40 ‰ are shown in Figs.9.1 to 9.4 and in Table 9.1 (left-hand shaded column). The classic data of Harned and co-authors are practically equal to those reported by Millero and Roy (1997) for freshwater (at S = 0‰):

$$pK_0 = -2622.38/T - 0.0178471T + 15.5873 \text{ (Harned and Davis, 1943)} \qquad \textbf{(9.22)}$$

$$pK_1 = 3404.71/T + 0.032786T - 14.8435 \text{ (Harned and Davis, 1943)} \qquad \textbf{(9.23)}$$

$$pK_2 = 2902.39/T + 0.02379T - 6.4980 \text{ (Harned and Scholes, 1941)} \qquad \textbf{(9.24)}$$

$$\ln K_w = 148.9802 - 13847.26/T - 23.6521 \ln T \text{ (Dickson and Riley, 1979)} \qquad \textbf{(9.25)}$$

where the *absolute temperature* T = t(°C) + 273.15 K.

9.3.2 SEAWATER

The salt concentration of seawater is defined by the *salinity*, given in g/kg of seawater, or in ‰. Probably the best data have been reported by Millero and Roy (1997); these values for the temperature range of 0 to 40°C and the salinity range of 0 to 40‰ are shown in Figs.9.1 to 9.4 and in Table 9.1 (right-hand shaded column). The seawater values (at S = 35‰) are practically equal to the values published by Weiss (1974) and by Mehrbach et al. (1973), as reported by Dickson and Millero (1987):

$$\ln K_o' = -60.2409 + 9345.17 / T + 23.3585 \ln(0.01T) + \\ + S\,[0.023517 - 0.023656\,(0.01T) + 0.0047036\,(0.01T)^2 \qquad \textbf{(9.26)}$$

$$pK_1' = 3670.7 / T - 62.008 + 9.7944 \ln T - 0.0118\,S + 0.000116\,S^2 \qquad \textbf{(9.27)}$$

$$pK_2' = 1394.7 / T + 4.777 - 0.0184\,S + 0.000118\,S^2 \qquad \textbf{(9.28)}$$

(K_0': Weiss, 1974), (K_1', K_2': Mehrbach et al. (1973), reported by Dickson and Millero (1987).

The *salinity* values S are related to the originally used *chlorinity*, i.e. the concentration of chloride (+bromide and iodide, also given in g/kg or ‰), by:

$$S = 1.80655\,Cl \qquad \textbf{(9.29)}$$

The solubility product of calcium carbonate differs for the two different crystalline types, calcite and aragonite. Figs.9.5 and 9.6 show values at specific temperatures and salinities.

9.3.3 BRACKISH WATER

The large differences between K and K', i.e. the large effect of salt concentrations on the acidity constants (Fig.9.4), result in an entirely different chemical character of freshwater and seawater, as will be illustrated in the next sections. The acidity constants for freshwater with zero salinity and for seawater have extensively been studied experimentally. The problem remains the proper treatment of waters with varying low salt concentrations. In order to obtain the proper K' values, the K values must be corrected with the help of the Debye-Hückel theory applicable at low concentrations. The treatment of non-ideal solutions is illustrated here by considering freshwaters with less dissolved salts than about 400mg/L (Stumm and Morgan, 1970).

A measure for the salt concentration is the *ionic strength* (I) of the water. This can be approximated by:

$$I \cong 2.5\times10^{-5}\,S \qquad \textbf{(9.30)}$$

where S is the salt concentration in mg/l. The approximate values for the two acidity constants then are:

$$pK_1' = pK_1 - \frac{0.5\sqrt{I}}{1+1.4\sqrt{I}} \qquad \text{and} \qquad pK_2' = pK_2 - \frac{2\sqrt{I}}{1+1.4\sqrt{I}} \qquad \textbf{(9.31)}$$

Table 9.1 Apparent solubility and acidity (dissociation) constants of carbonic acid for various temperatures and salinities. The values are according to Millero and Roy (1997).

$K_0.10^2$	**S (‰)**								
t (°C)	**0**	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**
0	**7.691**	7.499	7.295	7.112	6.934	6.761	6.592	**6.412**	6.252
5	**6.383**	6.223	6.067	5.916	5.754	5.610	5.470	**5.321**	5.188
10	**5.370**	5.236	5.105	4.977	4.842	4.721	4.603	**4.477**	4.365
15	**4.571**	4.457	4.345	4.236	4.121	4.018	3.917	**3.811**	3.715
20	**3.936**	3.837	3.741	3.648	3.556	3.459	3.373	**3.289**	3.199
25	**3.428**	3.342	3.258	3.177	3.090	3.013	2.938	**2.858**	2.786
30	**3.013**	2.938	2.864	2.793	2.723	2.655	2.582	**2.518**	2.449
35	**2.679**	2.612	2.547	2.483	2.415	2.355	2.296	**2.234**	2.178
40	**2.404**	2.344	2.286	2.223	2.168	2.113	2.061	**2.004**	1.954

$K_1.10^7$									
t (°C)	**0**	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**
0	**2.667**	4.667	5.433	5.984	6.412	6.761	7.047	**7.278**	7.464
5	**3.069**	5.420	6.353	7.015	7.534	7.962	8.299	**8.610**	8.851
10	**3.467**	6.194	7.295	8.072	8.690	9.204	9.638	**10.00**	10.30
15	**3.846**	6.966	8.241	9.162	9.908	10.52	11.04	**11.48**	11.86
20	**4.188**	7.727	9.183	10.26	11.12	11.83	12.45	**13.00**	13.46
25	**4.498**	8.433	10.09	11.32	12.33	13.18	13.90	**14.52**	15.07
30	**4.753**	9.099	10.96	12.36	13.52	14.49	15.35	**16.11**	16.75
35	**4.966**	9.705	11.80	13.37	14.69	15.81	16.79	**17.66**	18.41
40	**5.105**	10.26	12.56	14.32	15.81	17.06	18.20	**19.19**	20.09

$K_2.10^{10}$									
t (°C)	**0**	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**
0	**0.240**	1.291	1.879	2.355	2.773	3.155	3.508	**3.837**	4.150
5	**0.284**	1.600	2.339	2.951	3.491	3.981	4.436	**4.864**	5.272
10	**0.331**	1.950	2.877	3.639	4.325	4.943	5.534	**6.095**	6.607
15	**0.380**	2.350	3.491	4.436	5.284	6.081	6.823	**7.516**	8.185
20	**0.430**	2.793	4.188	5.346	6.397	7.379	8.299	**9.183**	10.05
25	**0.479**	3.289	4.966	6.383	7.656	8.872	10.02	**11.12**	12.19
30	**0.527**	3.828	5.834	7.534	9.099	10.57	11.99	**13.34**	14.66
35	**0.573**	4.426	6.792	8.831	10.72	12.50	14.22	**15.89**	17.50
40	**0.617**	5.070	7.870	10.28	12.53	14.69	16.79	**18.79**	20.75

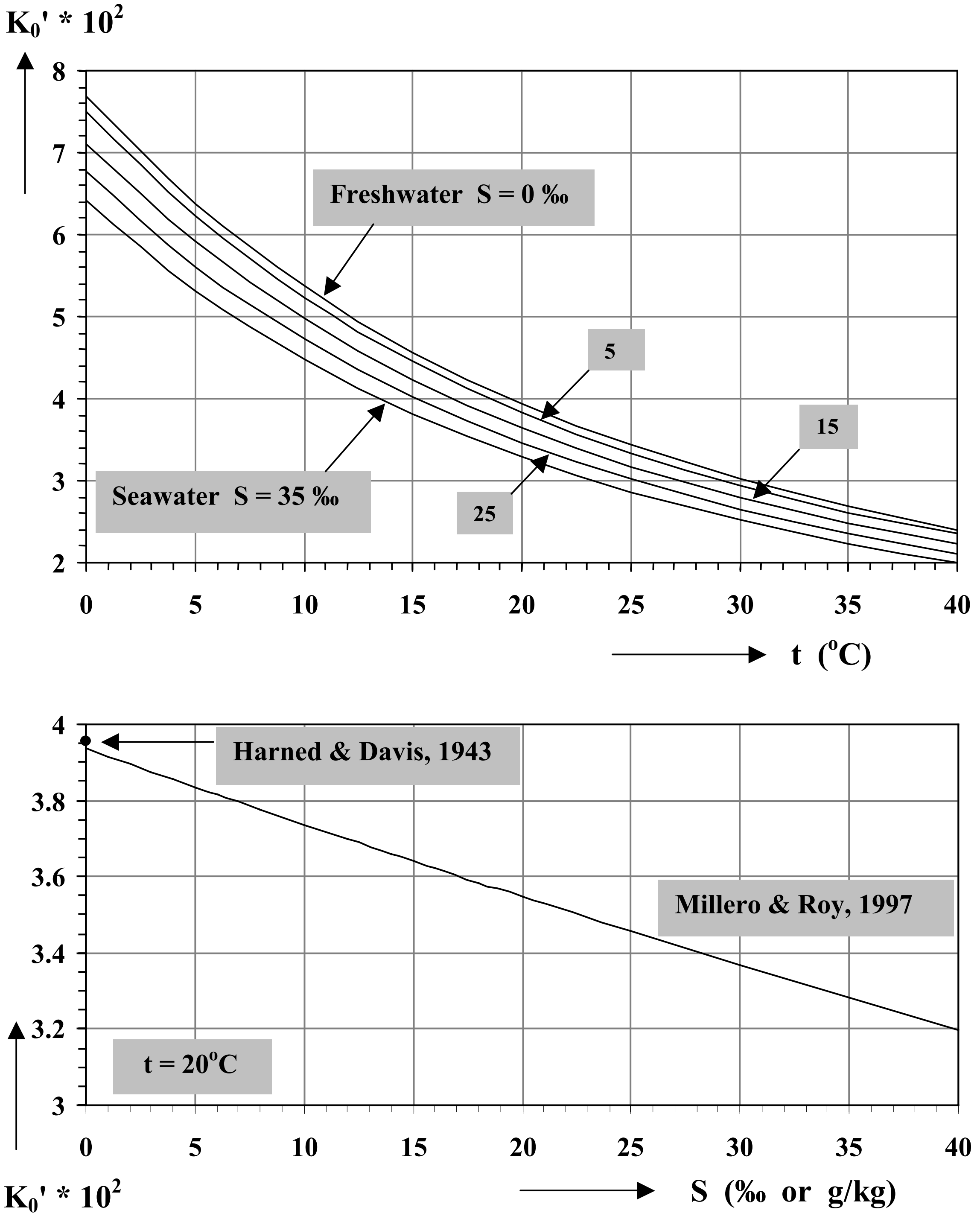


Fig.9.1 The solubility constants (= solubilities in M/L.atm) for CO_2 in freshwater, seawater and brackish water as a function of temperature at salinities of 0, 5, 15, 25, and 35‰ (= g of salt per kg of water) (upper graph) and as a function of salinity at 20 °C (lower graph). All values are according to Millero and Roy (1997), at higher salinities similar to Weiss (1974) (Eq.9.26); the values for freshwater are similar to those of Harned and Davis (1943) (Eq.9.22).

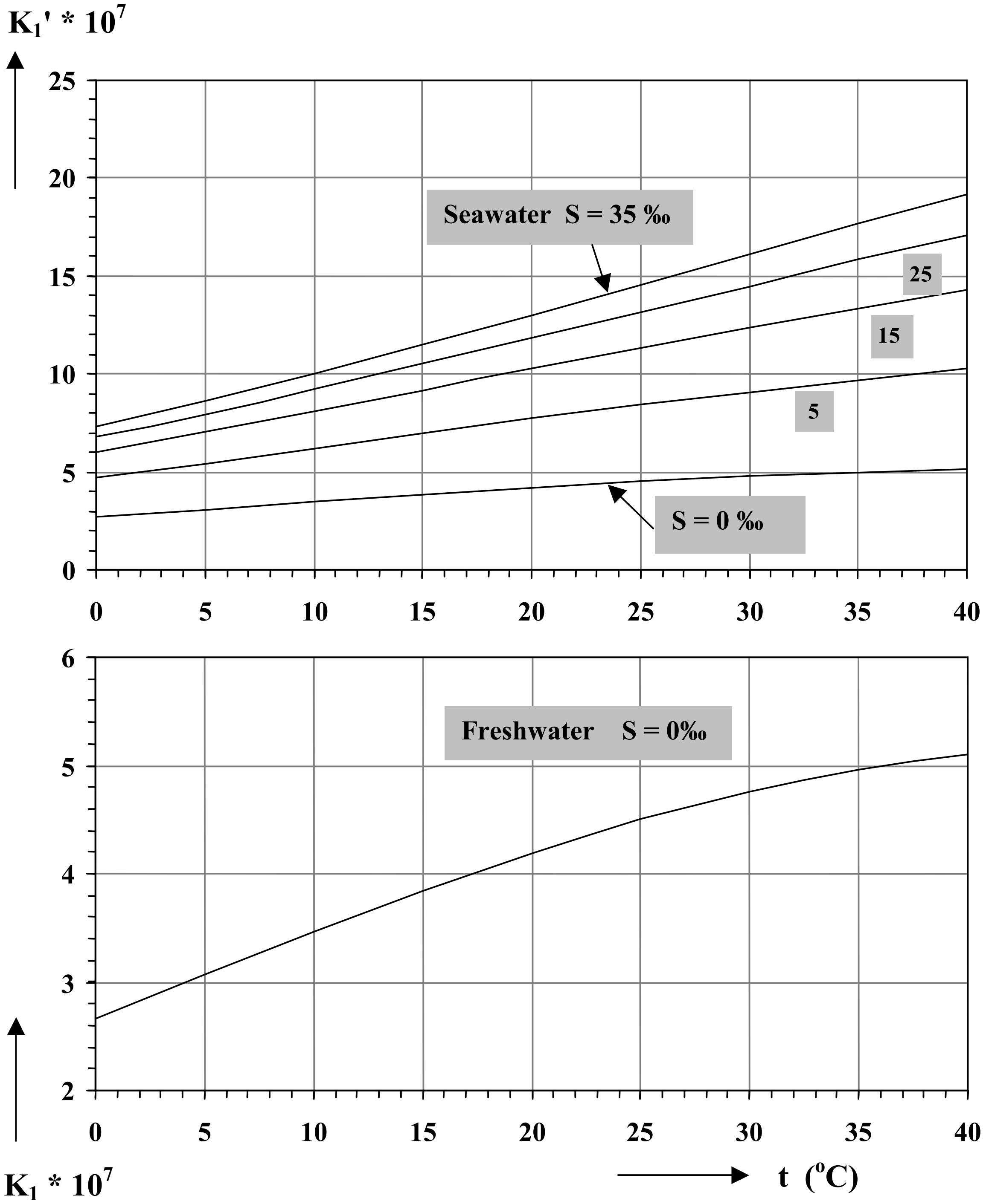


Fig.9.2 The acidity constants for the first dissociation of carbonic acid in freshwater and seawater as a function of the water temperature at salinities of 0, 5, 15, 25, and 35‰. The values are according to Millero and Roy (1997). The freshwater values are equal to those of Harned and Davis (1943) (Eq.9.23), the marine values are in good agreement with those reported by Mehrbach et al. (1973) as discussed by Dickson and Millero (1987) (Eq.9.27).

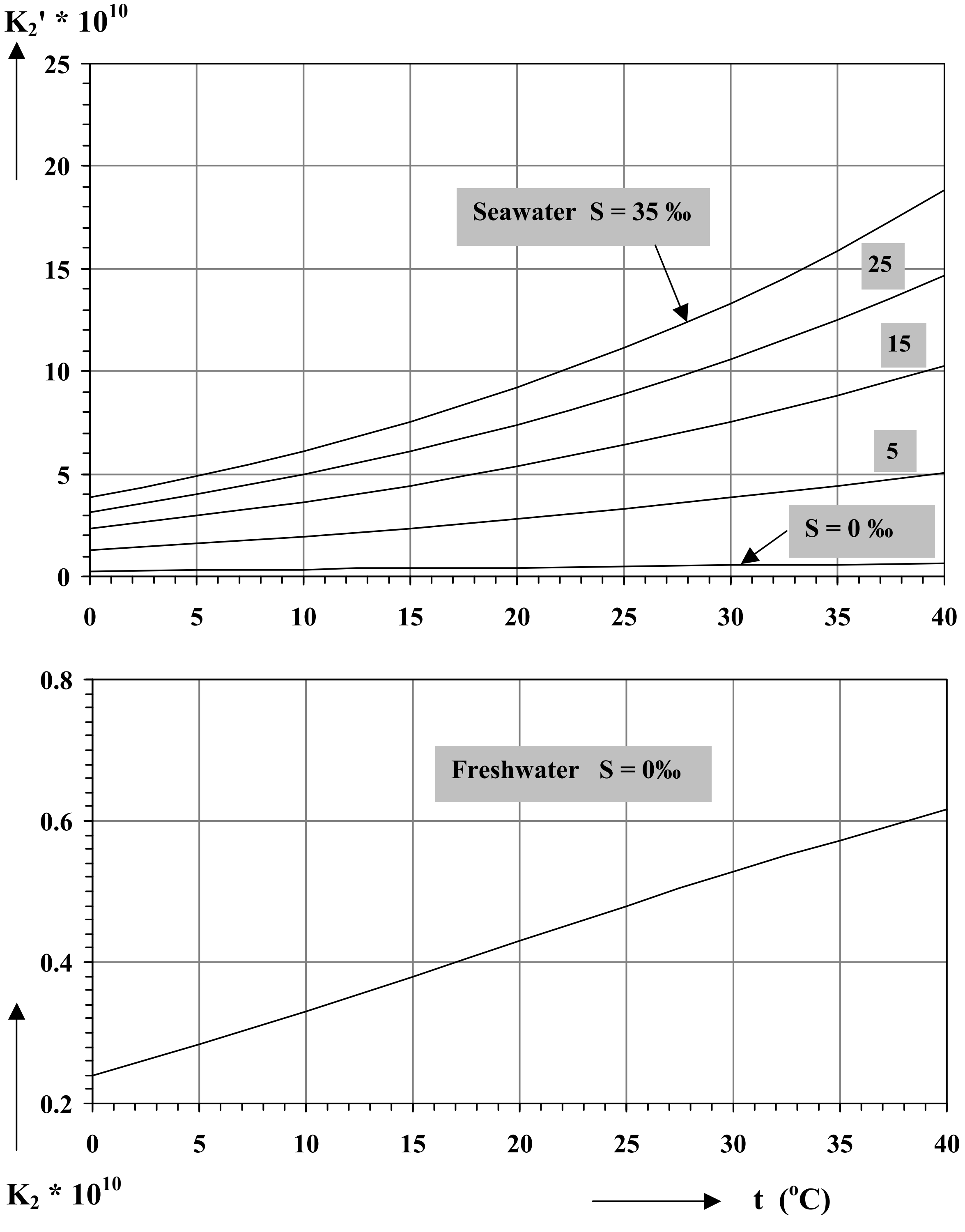


Fig.9.3 The acidity constants for the second dissociation of carbonic acid in freshwater and seawater as a function of the water temperature at salinities of 0, 5, 15, 25, and 35‰. The values are according to Millero and Roy (1997). The freshwater values are equal to those of Harned and Scholes (1941) (Eq.9.24), the marine values are in good agreement with those reported by Mehrbach et al. (1973) as reported by Dickson and Millero (1987) (Eq.9.28).

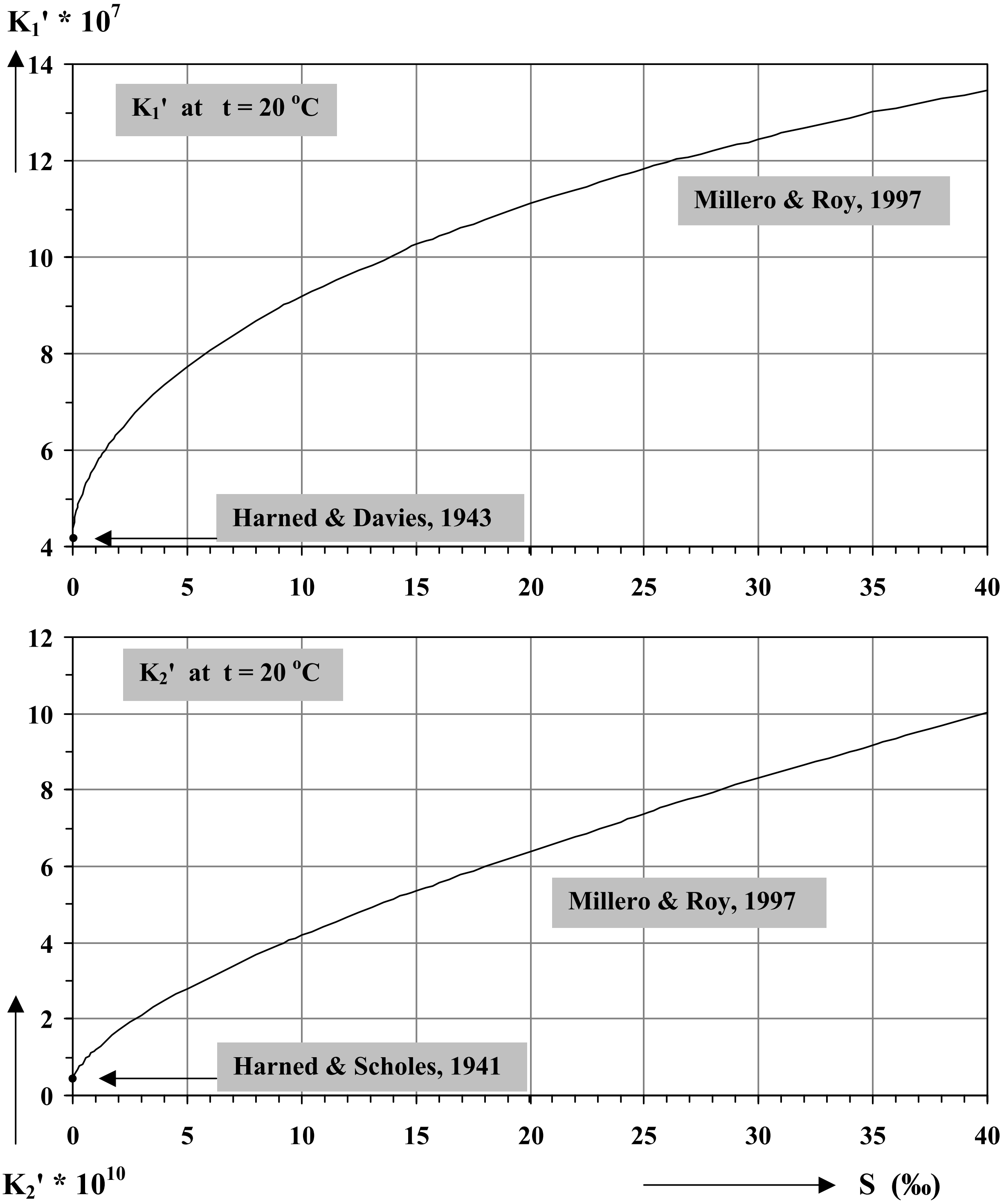


Fig.9.4 Values for the first and second dissociation constants of dissolved carbonic acid as a function of the salinity (Millero and Roy, 1997). The values are valid for a water temperature of 20 °C.

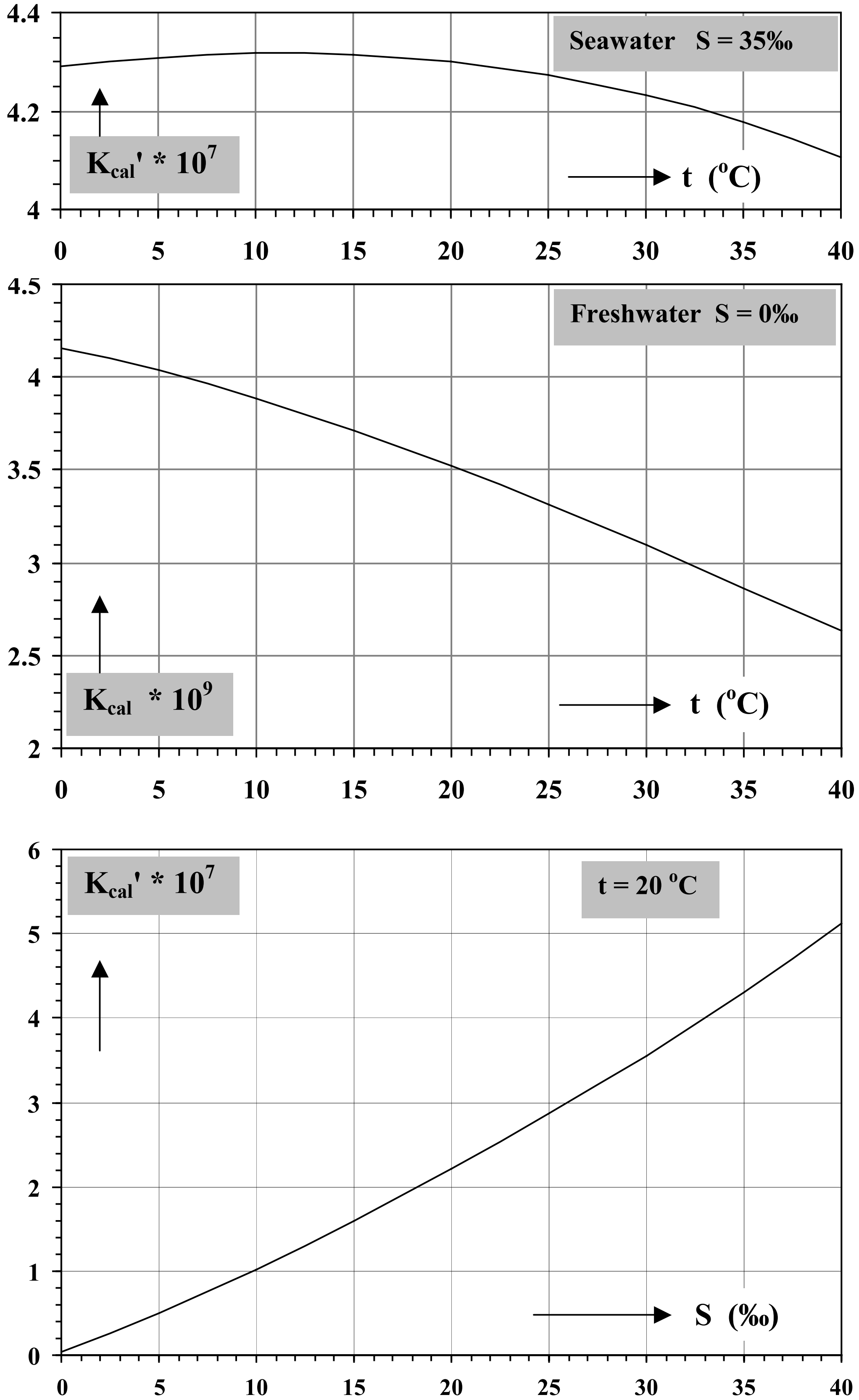


Fig.9.5 The solubility product (Eq.9.17) of calcite ($CaCO_3$) depending on the water temperature and salinity during precipitation (values according to Eq.9.43 (Mucci, 1983)).

The acidity constant values published by Millero and Roy (1997) are derived from the above considerations on non-ideal solutions taking into account a series of different compounds. Sets of data for various temperatures and salinities are further presented in Table 9.1.

Values of the solubility product of calcite ($CaCO_3$) (Eq.9.17) used in this volume are taken from Mucci (1983):

$$\begin{aligned} pK_{cal} = -{}^{10}\log K_{cal} &= 171.9065 + 0.077993\ T - 2839.319 / T - 71.595 \log T + \\ &+ (0.77712 - 0.0028426\ T - 178.34 / T)S^{1/2} + \\ &+ 0.07711\ S - 0.0041249\ S^{3/2} \end{aligned} \quad \textbf{(9.32)}$$

Values are shown in Fig.9.5 as functions of the water temperature for fresh- and seawater and as a function of salinity at 20 °C.

9.4 CARBONIC ACID CONCENTRATIONS

As we have mentioned the difference between the acidity constants for the fresh and seawater are considerable. This greatly effects the distribution of the carbonic acid fractions in natural waters. Examples of this will be shown in the following sections.

The distribution of the dissolved carbonic acid species in pure water can be specified as a fraction of the total dissolved inorganic carbon. From Eqs.9.6, 9.9 and 9.10, respectively, Eqs.9.18, 9.19 and 9.20 we obtain:

$$[H_2CO_3] = K_0 P_{CO2} \quad \textbf{(9.33)}$$

$$[H_2CO_3] = \frac{[H^+]}{K_1}[HCO_3^-] \quad \textbf{(9.34)}$$

$$[CO_3^{2-}] = \frac{K_2}{[H^+]}[HCO_3^-] \quad \textbf{(9.35)}$$

so that

$$C_T = \left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]} \right)[HCO_3^-] \quad \textbf{(9.36)}$$

The fractional concentrations can now be given in terms of the total carbon content:

$$[HCO_3^-] = \frac{[H^+]K_1}{[H^+]^2 + [H^+]K_1 + K_1K_2} * C_T \qquad \textbf{(9.37)}$$

$$[H_2CO_3] = [CO_2aq] = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_1 + K_1K_2} * C_T \qquad \textbf{(9.38)}$$

$$[CO_3^{2-}] = \frac{K_1K_2}{[H^+]^2 + [H^+]K_1 + K_1K_2} * C_T \qquad \textbf{(9.39)}$$

and likewise for the apparent acidity constants K' in non-ideal solutions such as seawater.

The relative contributions of $[H_2CO_3]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ to the total carbon content is shown in Fig.9.6 as a function of pH for two different temperatures for freshwater (at ionic strength = 0) and average seawater (S = 35.0‰ or Cl = $19.37^o/_{oo}$).

As was anticipated, the acidity constants of carbonic acid change so rapidly with temperature and with the ionic strength of the solution that it results in a strong dependence of the distribution on both temperature and salinity.

9.5 EXAMPLES FOR OPEN AND CLOSED SYSTEMS

In this section a few examples will be given of how to deal with the above equations. We will refer to *closed systems* in which the dissolved carbonic acid fractions do not exchange, nor with the gaseous system (atmospheric or soil CO_2), neither the solid phase ($CaCO_3$). In an open system the solution exchanges with either the gaseous phase (=open to the gas phase), or the solid (open to $CaCO_3$). We will be dealing with **(i)** a comparison with fresh and seawater, both in equilibrium with atmospheric CO_2, **(ii)** a groundwater sample of which $[H_2CO_3]$ corresponds to a P_{CO2} value far exceeding the atmospheric concentration and which is brought into contact with the atmosphere at a constant temperature, **(iii)** water exposed to the atmosphere in the presence of calcium carbonate rock, and (**iv)** mixing freshwater and seawater (in an estuary) under closed conditions.

9.5.1 COMPARISON OF FRESHWATER AND SEAWATER EXPOSED TO THE ATMOSPHERE

Here we are dealing with an open system to the atmosphere (exchange with atmospheric CO_2) at a constant temperature. The latter is considered to be of infinite dimensions, so that P_{CO2} is constant. The system is closed to $CaCO_3$, so that the carbonate alkalinity (=the concentration of positive metal ions) is constant. The given conditions are shown in Fig.9.7.

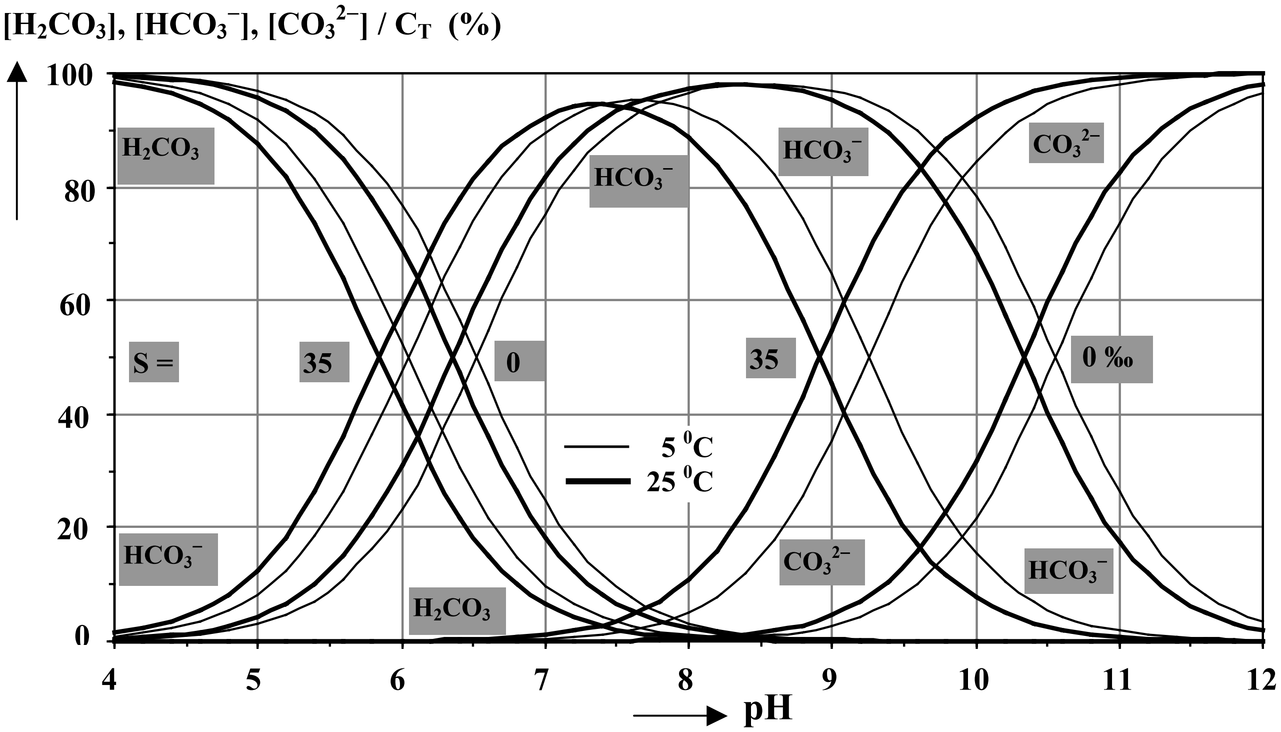


Fig.9.6 Distribution of the carbonic acid fractions as percentages of the total carbon content, C_T. The values are calculated using Eqs.9.37, 9.38, 9.39 for temperatures of 5 and 25 ^{0}C and for salinities of 0 and 35 ‰ as a function of the pH. Seawater has pH values around 8.2. However, the carbon distributions are shown for an (unrealistic) wider range of pH values, to illustrate the dependence of the carbon distribution on salinity.

Here we will use the symbols:

$a = [H_2CO_3] + [CO_2aq]$ $b = [HCO_3^-]$ $c = [CO_3^{2-}]$

The values of the first and second (apparent) acidity constants are calculated from Eqs.9.22 to 9.28. Furthermore, we apply the Eqs.9.37 to 9.39 for calculating the various dissolved fractions.

Starting with the known value of the atmospheric partial pressure of CO_2, the dissolved CO_2 concentration is obtained, and from that the pH dependent other concentrations.

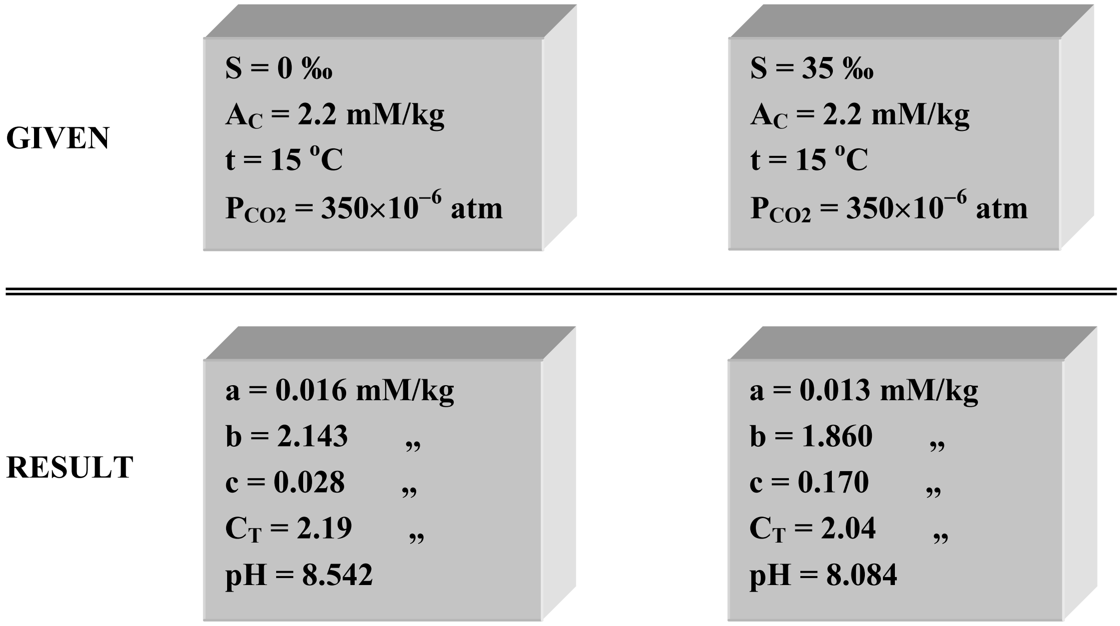
9.5.1.1 FOR FRESHWATER

$$a = [H_2CO_3] = K_0P_{CO2} = 0.04571(M/L.atm)\times350\times10^{-6}(atm) = 1.600\times10^{-5}\ M/L$$

$$b = [HCO_3^-] = (K_1/[H^+])a = (3.846\times10^{-7}/[H^+])a = 6.154\times10^{-12}/[H^+]$$

$$c = [CO_3^{2-}] = (K_1K_2/[H^+]^2)a = (3.846\times10^{-7}\times3.800\times10^{-11}/[H^+]^2)a = 2.338\times10^{-22}/[H^+]^2$$

The carbonate alkalinity is known:



GIVEN

$S = 0$ ‰
$A_C = 2.2$ mM/kg
$t = 15\ ^oC$
$P_{CO2} = 350\times10^{-6}$ atm

$S = 35$ ‰
$A_C = 2.2$ mM/kg
$t = 15\ ^oC$
$P_{CO2} = 350\times10^{-6}$ atm

RESULT

$a = 0.016$ mM/kg
$b = 2.143$ „
$c = 0.028$ „
$C_T = 2.19$ „
$pH = 8.542$

$a = 0.013$ mM/kg
$b = 1.860$ „
$c = 0.170$ „
$C_T = 2.04$ „
$pH = 8.084$

Fig.9.7 Schematic representation of the conditions of fresh (0‰) and seawater (35‰), both in equilibrium at a constant temperature with the atmosphere with constant CO_2 concentration (partial pressure). The upper part shows the given conditions, the lower part the resulting data.

$$A_C = b + 2c = 6.154\times10^{-12}/[H^+] + 4.677\times10^{-22}/[H^+]^2 = 2.2\times10^{-3} \text{ M/L}$$

From this quadratic equation $[H^+]$ and the pH can be obtained, resulting in:

$$[H^+] = 2.871\times10^{-9} \text{ M/L} \quad \text{and pH} = 8.542$$

The total carbon content of the water then is obtained by inserting $[H^+]$ in the above equations:

$$C_T = a + b + c = 0.016 + 2.14 + 0.028 = 2.19 \text{ mM/L}$$

9.5.1.2 FOR SEAWATER

$$a = 0.03811(\text{M/kg.atm})\times350\times10^{-6}(\text{atm}) = 1.334\times10^{-5} \text{ M/kg}$$

$$b = (11.480\times10^{-7}/[H^+])\times1.334\times10^{-5} = 15.314\times10^{-12}/[H^+]$$

$$c = (11.480\times10^{-7}\times7.516\times10^{-10}/[H^+]^2)\times1.334\times10^{-5} = 1.151\times10^{-20}/[H^+]^2$$

Again the carbonate alkalinity is known:

$$b + 2c = 15.31\times10^{-12}/[H^+] + 2.302\times10^{-20}/[H^+]^2 = 2.2\times10^{-3} \text{ M/kg}$$

Solving this quadratic equation results in:

$$[H^+] = 8.232\times10^{-9} \text{ M/kg} \quad \text{and} \quad \text{pH} = 8.084$$

The total carbon content is:

$$C_T = 0.013 + 1.86 + 0.170 = 2.04 \text{ mM/kg}$$

Comparison of these results, as shown in Fig.9.7, reveals that in the freshwater the carbonic species consists for 98% of dissolved bicarbonate, while the seawater with a lower pH still contains about 10% of dissolved carbonate ions.

9.5.2 SYSTEM OPEN FOR CO_2 ESCAPE AND $CaCO_3$ FORMATION

The second example describes the chemical changes in a certain given fresh (ground)water from which excess CO_2 escapes to the atmosphere and in which $CaCO_3$ precipitates at saturation. In part (1) we shall indicate how the various carbon concentrations are calculated. In part (2) the solution looses CO_2 to the air (open to the atmosphere) at constant temperature until chemical equilibrium between P_{CO2} and the dissolved CO_2 fraction. Part (3) considers the presence of Ca^{2+} ions and a possible precipitation of calcite (open to the solid phase).

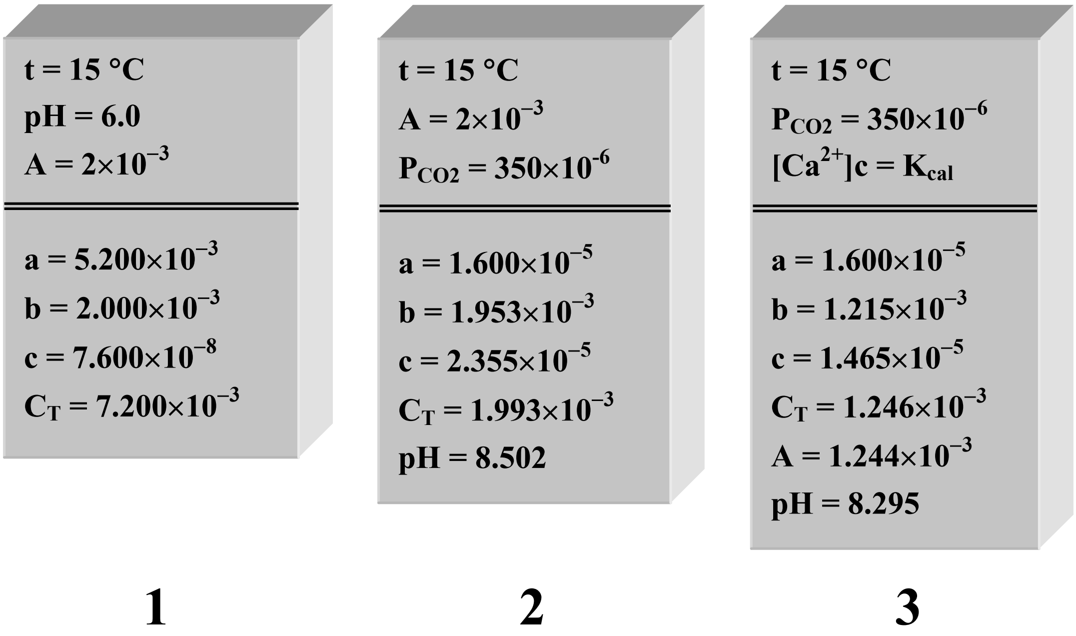


Fig.9.8 Schematic representation of the numerical results from exposing a water sample with given conditions (upper part of 1) to the atmosphere (upper part of 2) and allowing precipitation of calcite (upper part of 3). The lower part of the boxes show the calculated data. All concentrations are in M/kg.

9.5.2.1 STARTING CONDITIONS

We assume that the temperature, pH (resulting in $[H^+]=10^{-pH}$) and the titration alkalinity (A) are known by measurement. The H^+ concentration will be denoted by the symbol h instead of $[H^+]$.

We can use the equations:

$A = b + 2c + 10^{-14.34}/h - h$, where the latter 2 terms can be neglected

$b/a = K_1/h$

$c/b = K_2/h$

Multiplication of the latter two relations gives:

$c / a = K_1K_2 / h^2$ or $c = (K_1K_2 / h^2)\, a$

With

$A = b + 2c$

this results in:

$A = (K_1 / h)\, a + (2K_1K_2 / h^2)\, a$

so that:

$$a = \frac{h^2}{hK_1 + 2K_1K_2} A \qquad \textbf{(9.40)}$$

$$b = \frac{hK_1}{hK_1 + 2K_1K_2} A = \frac{h}{h + 2K_2} A \qquad \textbf{(9.41)}$$

$$c = \frac{K_1K_2}{hK_1 + 2K_1K_2} A = \frac{K_2}{h + 2K_2} A \qquad \textbf{(9.42)}$$

i.e. 3 equations with 3 unknowns. At a temperature of 15°C, a starting pH value of 6.0 and an alkalinity of 2 mM/L the resulting concentrations are given in Fig.9.8 phase 1.

9.5.2.2 ESCAPE OF CO_2

If the water looses CO_2 in contact with the atmosphere, and in the first instance neglecting the presence of Ca^{2+}, until equilibrium with the atmospheric P_{CO2} (denoted by p) has been reached, we have:

$\mathbf{a} = K_0p$

$\mathbf{b}^2/(\mathbf{ac}) = K_1/K_2$

$A \approx \mathbf{b} + 2\mathbf{c}$

again 3 equations with 3 unknowns (bald type). With the additional starting values for the atmospheric CO_2 concentration (p), the concentration can be calculated (Fig.9.8, phase 2).

9.5.2.3 PRECIPITATION OF $CaCO_3$

Here we have, apart from the known atmospheric P_{CO2}, the additional complication that calcite precipitates if the product of $[Ca^{2+}]$ and $[CO_3^{2-}]$ exceeds the solubility product given by Eq.9.32 (Fig.9.5), so that CA decreases.

The amount of calcite (or Ca^{2+}) removed from the water, $\Delta[Ca^{2+}]$, equals the amount of carbon removed from the water, ΔC_T. We then have the following equations:

$$a_2 = K_0 p = a_1 = a$$

$$b_2/c_2 = b_1/c_1 = (K_1/K_2)a \quad \text{or} \quad \mathbf{c_2} = (c_1/b_1)\mathbf{b_2}$$

$$A_2 - A_1 = [Ca^{2+}]_2 - [Ca^{2+}]_1 = C_{T2} - C_{T1} \quad \text{or} \quad \mathbf{\Delta[Ca^{2+}]} = \mathbf{\Delta C_T}$$

$$[Ca^{2+}]_2\, c_2 = 10^{-\,pKcal} \quad \text{or} \quad ([Ca^{2+}]_1 + \mathbf{\Delta C_T})\mathbf{c_2} = K_{cal}$$

$$\Delta C_T = (a + b_2 + c_2) - (a + b_1 + c_1) \quad \text{or} \quad \mathbf{\Delta C_T} = \mathbf{b_2} + \mathbf{c_2} - (b_1 + c_1)$$

For reasons of simplicity we assume that the alkalinity is balanced by the Ca^{2+} ions alone,

so that $[Ca^{2+}]_1 = 0.5A$

where the subscript (1) refers to the values obtained by step 2, and (2) to the final values after precipitation of $CaCO_3$. These 4 independent equations with 4 unknowns (bald type) can now be solved. The numerical result is shown in Fig.9.8.

Comparison of boxes 1 and 2 shows that:

1) the amount of CO_2 escaped to the atmosphere (= 143 mL STP) is of the order of the amount of dissolved CO_2 present at the start of the experiment

2) the amount of calcite formed is 25.4 mg/L

9.5.3 SYSTEM EXPOSED TO CO_2 IN THE PRESENCE OF $CaCO_3$

In the presence of carbonate rock water may be exposed to a certain CO_2 pressure. The question is how much $CaCO_3$ can be dissolved in equilibrium with the CO_2 atmosphere.

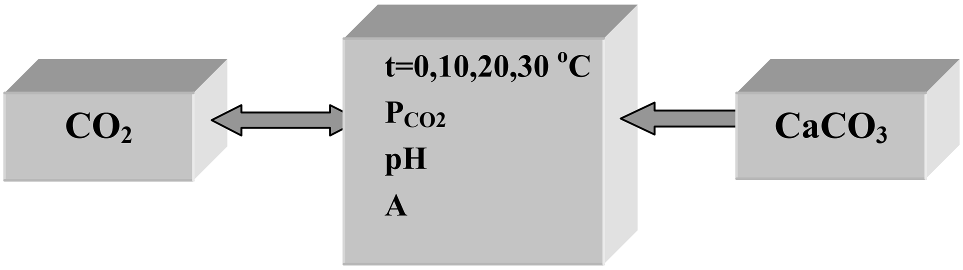


Fig.9.9 Schematic representation of an open system, consisting of a water mass in open contact with a CO_2 atmosphere and with solid $CaCO_3$.

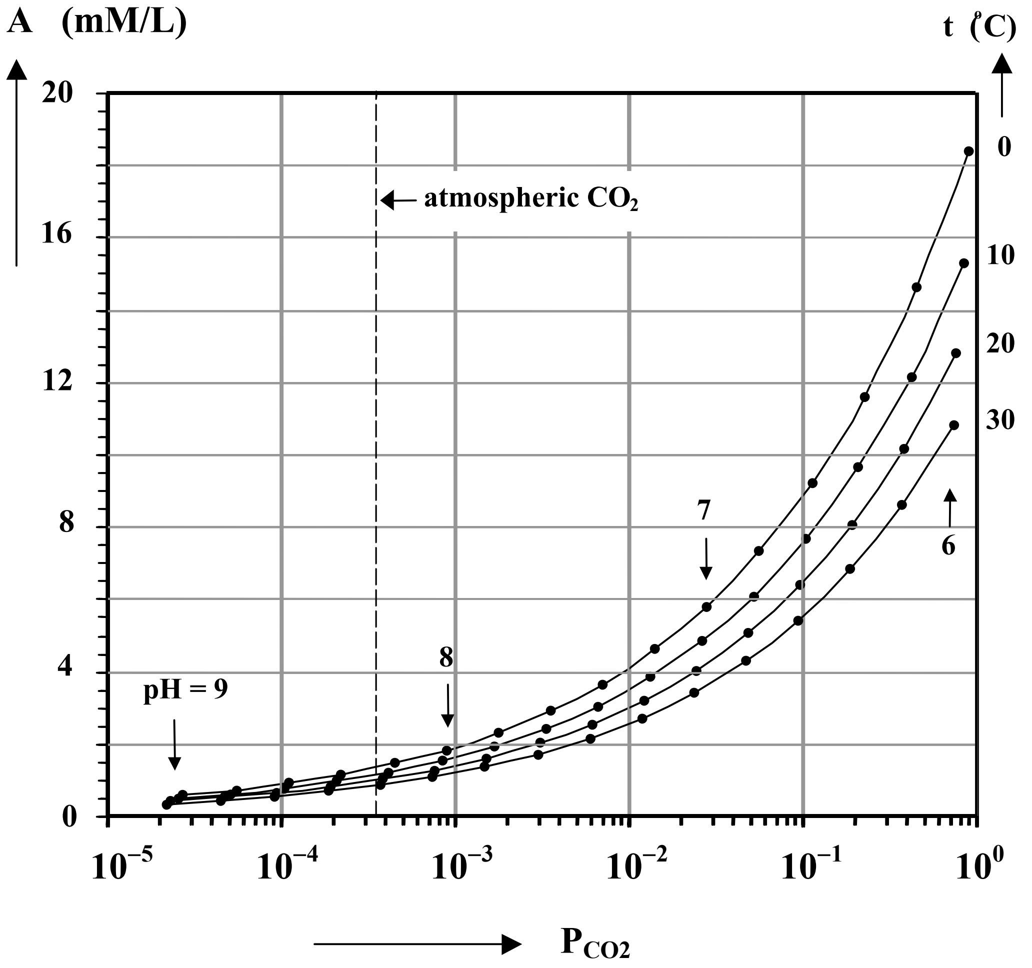


Fig.9.10 Schematic representation of an open system, consisting of a water mass in exchange with an infinite CO_2 reservoir and with carbonate rock. The alkalinities are calculated for 4 different temperatures. The corresponding pH values are indicated in the graph as well as the atmospheric CO_2 partial pressure (P_{CO2}).

Instead of choosing the CO_2 pressure, the calculation procedure is the easiest if we depart from the final pH the water will obtain. The alkalinity is defined by the electroneutrality requirement:

$$A = 2Ca^{2+} + [H^+] = [HCO_3^- + 2[CO_3^{2-}] + [OH^-] = \frac{2K_{cal}}{c} + h = b + 2c + \frac{K_w}{h} \qquad \textbf{(9.44)}$$

Inserting the Eqs.9.33, 9.34 and 9.35 results in the equation:

$$\left(\frac{K_0K_1}{h} + 2\frac{K_0K_1K_2}{h^2}\right)P_{CO_2}^2 + \left(\frac{K_w}{h} - h\right)P_{CO_2} + 2\frac{K_{cal}\,h^2}{K_0K_1K_2} = 0$$

The solution of this equation and the resulting A values for 4 different temperatures are shown in Fig.9.10. Also the corresponding pH values are indicated.

9.5.4 CLOSED SYSTEM, MIXING OF FRESHWATER AND SEAWATER

As an example of a closed system we will discuss the mixing of fresh river water and seawater, such as occurs in an estuary. Calculating $^{13}\delta$ of, for instance, the bicarbonate fraction of the brackish mixture from the $^{13}\delta$ values of bicarbonate in the end members (fresh and seawater) is not straightforward, because the mixing process of the mole fractions of bicarbonate is not conservative, i.e. the dissociation equilibria of carbonic acid shift by the changes pH, and the values of the acidity constants change by the changes in the salinity of the water. The system of the two components together is closed, however, so that, if the end members are denoted by f(resh) and m(arine), the final values for the conservative parameters, i.e. the salinity, the alkalinity and the total carbon content, are:

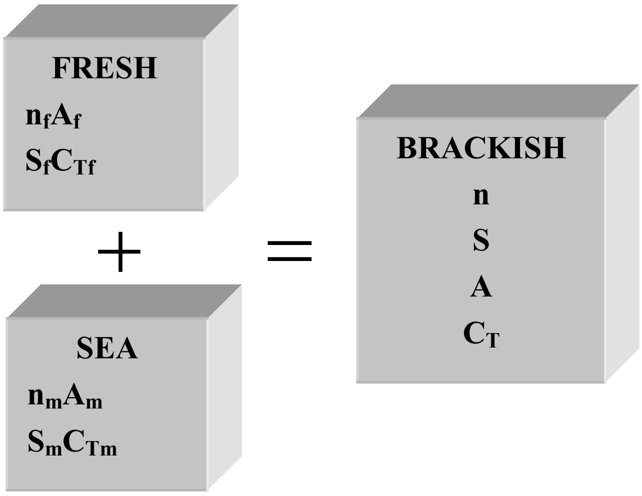


Fig.9.11 Schematic representation of the formation of brackish water as a mixture of fresh (river) and seawater. In the supposedly closed system the parameters shown in the figure are conservative.

$$nS = n_fS_f + n_mS_m \qquad \text{or} \qquad S = (n_f/n)S_f + (n_m/n)S_m \qquad \textbf{(9.45)}$$

where n + m = n, $S_f \approx 0‰$ and $S_m \approx 35‰$ (Fig.9.11).

Measurement of the salinity of the brackish water results in the (degree of) *brackishness* (X) of the water, here defined as the fraction of seawater (for seawater X =1, for freshwater X ≈ 0):

$$S = \frac{n_f}{n} S_f + \frac{n_m}{n} S_m = \left(1 - \frac{n_m}{n}\right) S_f + \frac{n_m}{n} S_m$$

or

$$X = \frac{n_m}{n} = \frac{S - S_f}{S_m - S_f} \approx \frac{S}{35} \qquad \textbf{(9.46)}$$

Furthermore:

$$nA = n_f A_f + n_m A_m \qquad \text{or} \qquad A = (1 - X)A_f + \mu A_m \qquad \textbf{(9.47)}$$

and

$$C_T = n_f C_{Tf} + n_m C_{Tm} \qquad \text{or} \qquad C_T = (1 - X)C_f + \mu C_m \qquad \textbf{(9.48)}$$

In order to calculate $^{13}\delta_a$ and $^{13}\delta_b$ and $^{13}\delta_c$ the carbonic acid fractions have to be obtained by solving the following 4 equations with 4 unknowns (in bald type):

$A = \mathbf{b} + 2\mathbf{c}$ $\qquad C_T = \mathbf{a} + \mathbf{b} + \mathbf{c}$

$K_1 = \mathbf{hb/a}$ $\qquad K_2 = \mathbf{hc/b}$

where again $h = [H^+]$, $a = [CO_2]$, $b = [HCO_3^-]$ and $c = [CO_3^{2-}]$. K_1 and K_2 refer to the brackish water values at the proper salinity.

A striking feature of estuaries is the non-linear behaviour of pH as a function of salinity. Examples were shown by Mook and Koene (1975). The position of the pH minimum strongly depends on the carbonate alkalinity ratio of the fresh and marine components (CA_f/CA_m).

The consequence of this non-linear behaviour of the pH, and thus also of the carbonic acid fractions, is that also $^{13}\delta$ of these fractions does not obey conservative mixing (Sect.7.3).

The only possible procedure for determining $^{13}\delta$ values of the dissolved carbonic components in water is by quantitatively converting the DIC into dissolved CO_2 by the addition of acid (such as H_3PO_4) to the water sample and extracting the CO_2 from the water. Consequently only $^{13}\delta_{DIC}$ can be obtained. If $^{13}\delta$ of the constituting fractions (a, b and c) are to be known, these should be calculated from the ^{13}C mass balance (cf. Sect.4.3.1):

$$C_T\,^{13}R_{DIC} = a\,^{13}R_a + b\,^{13}R_b + c\,^{13}R_c = a\,^{13}\alpha_{a/b}\,^{13}R_b + b\,^{13}R_b + c\,^{13}\alpha_{c/b}\,^{13}R_b \qquad \textbf{(9.49)}$$

or with $R/R_{std} = 1 + \delta$:

$$C_T\,^{13}\delta_{DIC} = a\,^{13}\delta_a + b\,^{13}\delta_b + c\,^{13}\delta_c = a(^{13}\delta_b - {}^{13}\varepsilon_{a/b}) + b\,^{13}\delta_b + c(^{13}\delta_c - {}^{13}\varepsilon_{c/b})$$

$$= C_T\ {}^{13}\delta_b - a\ {}^{13}\varepsilon_{a/b} - c\ {}^{13}\varepsilon_{c/b} \quad \textbf{(9.50)}$$

so that

$${}^{13}\delta_{DIC} = {}^{13}\delta_b - (a/C_T){}^{13}\varepsilon_{a/b} - (c/C_T){}^{13}\varepsilon_{c/b} \quad \textbf{(9.51)}$$

and similarly:

$${}^{13}\delta_{DIC} = {}^{13}\delta_a - (b/C_T){}^{13}\varepsilon_{b/a} - (c/C_T){}^{13}\varepsilon_{c/a} \quad \textbf{(9.52)}$$

$${}^{13}\delta_{DIC} = {}^{13}\delta_c - (a/C_T){}^{13}\varepsilon_{a/c} - (b/C_T){}^{13}\varepsilon_{b/c} \quad \textbf{(9.53)}$$

where the ${}^{13}\varepsilon$ values are given in Table 7.2.