RICHARD E. ZEEBE and DIETER WOLF-GLADROW

CO_2 IN SEAWATER: EQUILIBRIUM, KINETICS, ISOTOPES

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CO$_2$ IN SEAWATER: EQUILIBRIUM, KINETICS, ISOTOPES

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Preface

Carbon dioxide is the most important greenhouse gas after water vapor in the atmosphere of the earth. More than 98% of the carbon of the atmosphere-ocean system is stored in the oceans as dissolved inorganic carbon. The carbon reservoirs of ocean and atmosphere may be pictured as a dog (the ocean) and its tail (the atmosphere). An understanding of the dynamics of the global carbon cycle and of changes of atmospheric CO_2 concentrations in the past and future therefore demands a comprehension of the role of the ocean in the carbon cycle. Analyses of air trapped in the ice sheets of Greenland and Antarctica have revealed that atmospheric carbon dioxide concentrations varied between glacial and interglacial times, with low values during glacials. These natural variations are most probably driven by oceanic processes. With the beginning of the industrial revolution, the anthropogenic influence on the global carbon cycle became increasingly important. The burning of coal, gas, and oil and the change in land use including deforestation resulted in an increase of atmospheric carbon dioxide that is comparable to the increase from the last glacial to preindustrial times. Wagging the tail provokes a response of the dog. Invasion of 'anthropogenic' carbon dioxide into the ocean has already led to an appreciable increase of the acidity of the surface ocean since the year 1800.

Comprehension of past and prediction of future changes of the marine carbon cycle requires an understanding of several questions of which two are of major importance. (1) Which processes are responsible for the variations of atmospheric carbon dioxide concentrations on glacial-interglacial time scales and (2) How does the ocean (including the biota) respond to anthropogenic perturbations and natural variations? Working on these questions indispensably demands an interdisciplinary approach in which scientists from different backgrounds join their abilities and efforts to benefit from each other.

The authors of this book have been working for several years in an interdisciplinary group which encompasses biologists, physicists, mathematicians, and geologists. In our everyday work we have experienced that the key for understanding critical processes of the marine carbon cycle is a sound knowledge of the seawater carbonate chemistry, including equilibrium and nonequilibrium properties as well as stable isotope fractionation. Unfortunately, it appears to be quite difficult for non-chemists to obtain a good knowledge of these subjects from, e.g., original contributions to chemical journals. Text books on chemical oceanography usually include an introduction to the equilibrium properties of the carbonate system. However, hitherto there is no coherent description of equilibrium *and* nonequilibrium properties *and* of stable isotope fractionation among the elements of the carbonate system in form of a comprehensible text. It is our intention to provide an overview and a synthesis of these subjects which should be useful for graduate students and researchers in various fields such as biogeochemistry, chemical oceanography, paleoceanography, marine biology, marine chemistry, marine geology, and others. In addition to the presentation of well known topics in the book, outcome of original research is included which has not been published previously (see, for instance, Sections 1.6, 2.3.5, 3.5.3, and Appendix B and C).

One of our main goals is to provide a quantitative description of the topics discussed in connection with the carbonate system. In this regard, the treatment given in the current book differs from many other presentations which are often of qualitative nature. We feel that our approach is a very useful one because it provides the reader with strong tools that can be used in her/his own studies and research. Naturally, this requires a little mathematics. We have tried to keep the mathematical level as low as possible in order to make the text accessible to a wide range of scientists from different disciplines. However, an adequate description of reaction kinetics, for example, inevitably requires the application of ordinary differential equations. Partial derivatives are used in the derivation of the Revelle factor. Diffusion is governed by a partial differential equation which simplifies, however, to an ordinary differential equation by restriction to stationary problems in one spatial dimension. The Schrödinger equation, which is a partial differential equation, is only briefly mentioned in the appendix. Whenever a mathematical or physical derivation is given in the text, a smaller font size is used to indicate that these sections or paragraphs may be skipped by the reader when studying the subject for the first time. Details and elaborate calculations are given in the appendix.

For the most part, we have attempted to explain the concepts of chemistry, biology, and physics used in the text. However, since the aspects discussed touch on many different branches of various disciplines, it was impossible to recapitulate all basics in detail. In these cases it might be useful for the reader to consult additional text books.

The outline of the book is as follows. The text begins with an introduction to the equilibrium properties of the carbonate system (Chapter 1, Equilibrium) in which basic concepts such as equilibrium constants, alkalinity, pH scales, and buffering are discussed. In addition, the application of these concepts is emphasized, including a discussion of the Revelle factor and future scenarios of atmospheric CO_2 concentrations. Chapter 2 (Kinetics) deals with the nonequilibrium properties of the seawater carbonate chemistry. Whereas principles of chemical kinetics are recapitulated, reaction rates and relaxation times of the carbonate system are considered in detail. Chapter 3 (Stable Isotope Fractionation) provides a general introduction to stable isotope fractionation and describes the partitioning of carbon, oxygen, and boron isotopes between the species of the carbonate system. The appendix contains formulas for the equilibrium constants of the carbonate system, mathematical expressions to calculate carbonate system parameters, answers to exercises and more. Numerical routines for the calculation of carbonate system parameters are available on our web-page: 'http://www.awi-bremerhaven.de/Carbon/co2book.html'.

Last but not least, a few comments on the exercises are added. Problems with one asterisk ($*$) should be very easy to solve (in a few minutes); those with two asterisks require more thinking or somewhat lengthy ('... after some algebra ...') calculations. Exercises with three asterisks are difficult. They are addressed to the reader who is interested in solving advanced problems and puzzles. Answers to exercises are given in Appendix D.

Acknowledgments. We are indebted to many people who helped us to write this book. Some of them spent a lot of time on discussing aspects of the carbonate chemistry with us, others provided comments on the manuscript or proof-read the manuscript. Many scientists have encouraged our work by the stimulating outcome of their own research. Unfortunately, it is impossible to name them all here. Being aware that any list must be incomplete, we still thank the following people for their support (in alphabetical order): D. C. E. Bakker, J. Bijma, A. G. Dickson, A. Engel, K. Fahl, N. G. Hemming, M. Hoppema, H. Jansen, M. M. Rutgers van der Loeff, F. Louanchi, J. D. Ortiz, U. Riebesell, A. Sanyal, H. J. Spero, M. H. C. Stoll, Ch. Völker, D. W. R. Wallace, and A. Wischmeyer. We thank H. J. W. de Baar for his suggestions to improve the manuscript. R. E. Z. is particularly grateful to Mira Djokić for her patience.

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Contents

Chapter 1

Equilibrium

Next to nitrogen, oxygen and argon, carbon dioxide is the most abundant gas in the earth's atmosphere. Next to water vapor it is the most important greenhouse gas. In contrast to nitrogen and oxygen most carbon dioxide of the combined atmosphere - ocean system is dissolved in water (98%), because carbon dioxide is not simply dissolved in water as other gases, but it reacts with water and forms bicarbonate and carbonate ions.

Although the carbonate system in seawater comprises only a few components, essentially CO_2, HCO_3^-, CO_3^{2-}, H^+, OH^-, and may be described by equations derived from the law of mass action, its behavior in response to perturbations is in some cases not easily predictable by intuitive reasoning. A doubling of the CO_2 concentration in the atmosphere will not cause a doubling of the total dissolved inorganic carbon, DIC, at equilibrium, but results in an increase of only $\sim 10\%$. This unexpectedly low increase is due to the dissociation of carbon dioxide and the simultaneous change of pH, see Section 1.5 on Revelle factor. Another example is biological precipitation of calcium carbonate, which will remove inorganic carbon from the oceanic surface layer, but does not result in further uptake of atmospheric carbon dioxide. On the contrary, because of a change of alkalinity, carbon dioxide will outgas as a consequence of production of calcium carbonate!

The main goal of this chapter is to present the equilibrium aspects of the carbonate system. The basic equations derived from the law of mass action allow us to calculate the ratios between the different forms of dissolved inorganic carbon (Section 1.1). Chemical concepts such as alkalinity, pH, and fugacity will be discussed in some detail (Sections 1.2 - 1.4) in order to make the text understandable also for non-chemists. The Revelle factor, which is important for the determination of oceanic CO_2 uptake, is introduced in Section 1.5. The final section (Section 1.6) of this chapter contains several interesting problems that can be addressed with knowledge of the equilibrium properties of the carbonate system. In particular, the first two problems, $CaCO_3$ formation and Revelle factor, are of relevance to the global carbon cycle. Values of the equilibrium constants and their dependence on temperature, salinity, and pressure can be found in Appendix A. In Appendix B it is shown how to calculate all components of the carbonate system from any two given quantities, for instance, from $[CO_2]$ and pH. The appendices are meant for reference only.

Various aspects of equilibrium properties of the carbonate system have been discussed, for example, in reviews by Skirrow (1965, 1975), in DOE (1994), or in textbooks such as Drever (1982), Morel and Hering (1993), Millero (1996), Stumm and Morgan (1996), to name only a few.

1.1 The carbonate system

In the ocean, carbon dioxide exists in three different inorganic forms: as free carbon dioxide, $CO_2(aq)$ = aqueous carbon dioxide, as bicarbonate, HCO_3^-,[1] and as carbonate ion, CO_3^{2-}(see Figure 1.1.1). A fourth form is H_2CO_3 (true carbonic acid); the concentration of H_2CO_3 is, however, much smaller than that of $CO_2(aq)$ ($\lesssim$ 0.3%). The sum of the two electrically neutral forms, true carbonic acid, H_2CO_3, and aqueous carbon dioxide, $CO_2(aq)$, which are chemically not separable, is usually denoted by CO_2 or $H_2CO_3^*$. We will use the former notation in this book:

$$[\mathrm{CO_2}] = [\mathrm{CO_2(aq)}] + [\mathrm{H_2CO_3}] \ , \tag{1.1.1}$$

where brackets represent total stoichiometric concentrations. Note that in the literature also the symbol CO_{2T} is used. In thermodynamic equilibrium with gaseous carbon dioxide ($CO_2(g)$):

$$\mathrm{CO_2(g)} \ \overset{K_0}{\rightleftharpoons} \ \mathrm{CO_2} \ , \tag{1.1.2}$$

the concentration of CO_2 is given by Henry's law (see Section 1.5) with K_0 being the solubility coefficient of CO_2 in seawater. The carbonate species are related by the following equilibria:

$$\mathrm{CO_2(aq)} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_2CO_3} \rightleftharpoons \mathrm{HCO_3^-} + \mathrm{H^+} \rightleftharpoons \mathrm{CO_3^{2-}} + 2\mathrm{H^+} \ . \tag{1.1.3}$$

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[1] The prefix 'bi' in bicarbonate has the following origin: the carbonate ion, CO_3^{2-}, may bind a second single positive ion in addition to H^+.

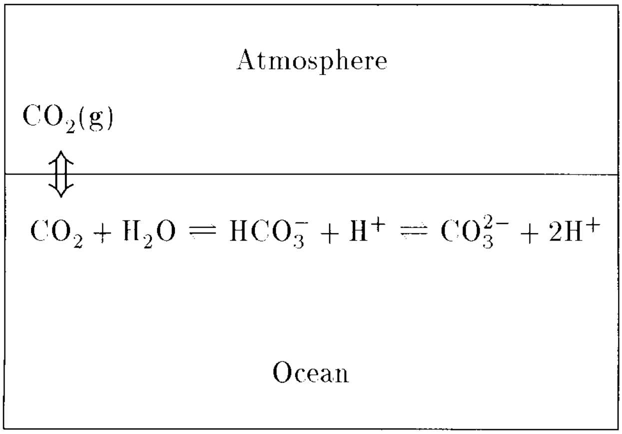

Figure 1.1.1: Schematic illustration of the carbonate system in the ocean. CO_2 is exchanged between atmosphere and ocean via equilibration of $CO_2(g)$ and dissolved CO_2. Dissolved CO_2 is part of the carbonate system in seawater that includes bicarbonate, HCO_3^-, and carbonate ion, CO_3^{2-}.

It is noted that equilibria are considered and not reaction pathways. Thus the hydroxylation $CO_2 + OH^- = HCO_3^-$, does not show up in Eq. (1.1.3). Using CO_2 instead of carbonic acid and aqueous carbon dioxide (Eq. (1.1.1)), the equilibria (Eq. (1.1.3)) simplify:

$$CO_2 + H_2O \overset{K_1}{\rightleftharpoons} HCO_3^- + H^+ \overset{K_2}{\rightleftharpoons} CO_3^{2-} + 2H^+ \qquad (1.1.4)$$

where K_1 and K_2 are equilibrium constants, often referred to as the first and second dissociation constants of carbonic acid, respectively. For the description of the carbonate system in seawater, stoichiometric equilibrium constants are used which are related to concentrations:

$$K_1^* = \frac{[HCO_3^-][H^+]}{[CO_2]} \qquad (1.1.5)$$

$$K_2^* = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \; . \qquad (1.1.6)$$

Stoichiometric equilibrium constants depend on temperature T, pressure P, and salinity S and are conventionally denoted by a star (refer to discussion in Section 1.1.3, 1.1.6, and Appendix A).

The sum of the dissolved forms CO_2, HCO_3^-, and CO_3^{2-}, is called total dissolved inorganic carbon, which we will denote by DIC or ΣCO_2:

$$\mathrm{DIC} \equiv \Sigma CO_2 = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \; . \qquad (1.1.7)$$

Note that in the literature also the symbols TCO_2 and C_T are used. A further essential quantity for the description of the carbonate system is the alkalinity, which is closely related to the charge balance in seawater. One might say that while DIC keeps track of the carbon, the alkalinity keeps track of the charges. The carbonate alkalinity, CA, is defined as[2]:

$$\mathrm{CA} = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] \,, \tag{1.1.8}$$

where the carbonate ion, $\mathrm{CO_3^{2-}}$, is counted twice because it has a double negative charge. Note that the current treatment of alkalinity is a simplification and that the carbonate alkalinity is part of the total alkalinity, TA, which also includes boron compounds and more (see below):

$$\begin{aligned} \mathrm{TA} = {} & [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] - [\mathrm{H^+}] \\ & + \text{minor components} \,. \end{aligned}$$

The concept of total alkalinity is extensively examined in Section 1.2.

The quantities introduced above are used for the quantitative description of the carbonate system in seawater. The two equilibrium conditions, Eqs. (1.1.5) and (1.1.6), the mass balance for total inorganic carbon, Eq. (1.1.7), and the charge balance, Eq. (1.1.8), constitute four equations with six unknown variables $[\mathrm{CO_2}]$, $[\mathrm{HCO_3^-}]$, $[\mathrm{CO_3^{2-}}]$, $[\mathrm{H^+}]$, DIC, and CA. As a result, when $2 = 6 - 4$ variables are known, the system is determined and all other components can be calculated. Theoretically, this goal could be achieved by measuring any two of the six quantities. In principle, however, only $[\mathrm{CO_2}]$, $[\mathrm{H^+}]$, DIC, and TA can be measured directly. This is the reason, for example, why for a quantitative description the dissolved boron species and other minor species have to be taken into account as they contribute to the total alkalinity. The procedure how to determine all components of the carbonate system from any two given quantities, including boron compounds, is demonstrated in Appendix B.

As an example, consider the case in which DIC and $[\mathrm{H^+}]$ (i.e. pH) have been obtained by direct measurement. The concentrations of $\mathrm{CO_2}$, $\mathrm{HCO_3^-}$, and $\mathrm{CO_3^{2-}}$ and CA can then be expressed as functions of DIC and $[\mathrm{H^+}]$:

$$[\mathrm{CO_2}] = \mathrm{DIC} \Big/ \left(1 + \frac{K_1^*}{[\mathrm{H^+}]} + \frac{K_1^* K_2^*}{[\mathrm{H^+}]^2}\right) \tag{1.1.9}$$

$$[\mathrm{HCO_3^-}] = \mathrm{DIC} \Big/ \left(1 + \frac{[\mathrm{H^+}]}{K_1^*} + \frac{K_2^*}{[\mathrm{H^+}]}\right) \tag{1.1.10}$$

$$[\mathrm{CO_3^{2-}}] = \mathrm{DIC} \Big/ \left(1 + \frac{[\mathrm{H^+}]}{K_2^*} + \frac{[\mathrm{H^+}]^2}{K_1^* K_2^*}\right) \tag{1.1.11}$$

$$\mathrm{CA} = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] \,. \tag{1.1.12}$$

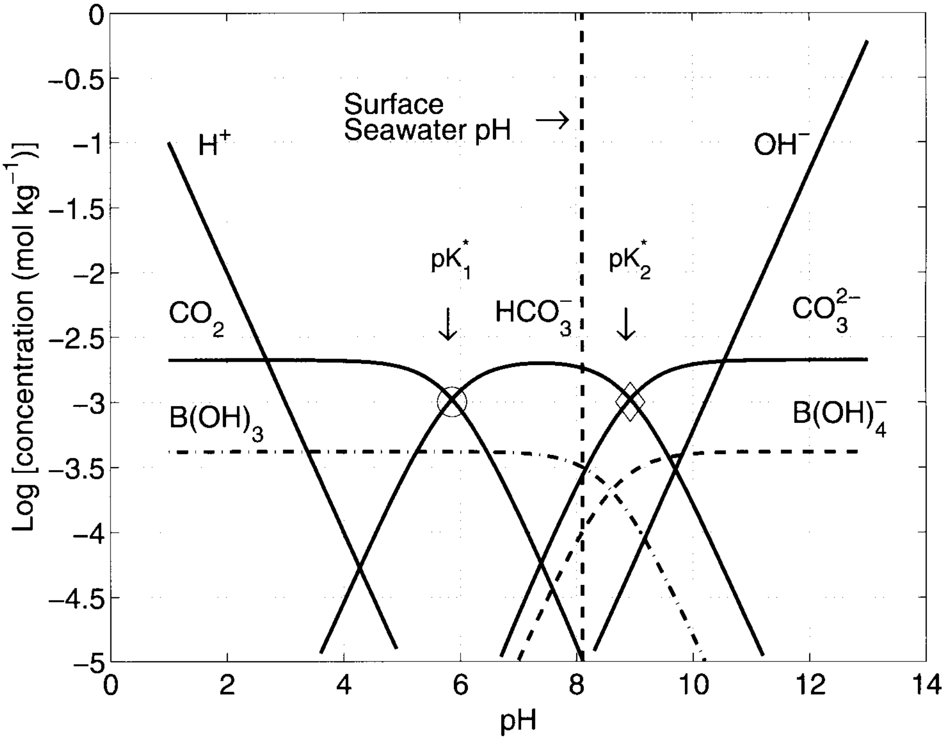

Figure 1.1.2: Carbonate system: Bjerrum plot (named after N. Bjerrum who invented the graphical representation of equilibrium relationships in 1914); DIC = 2.1 mmol kg^{-1}, $S = 35$, $T_c = 25°C$. The circle and the diamond indicate $pK_1^* = 5.86$ and $pK_2^* = 8.92$ of carbonic acid. The values of pK_B^* and pK_W^* used are 8.60 and 13.22, respectively (DOE, 1994). Note that in seawater, the relative proportions of CO_2, HCO_3^-, and CO_3^{2-} control the pH and not vice versa as this plot might suggest (see text).

Let us assume that a surface seawater sample in equilibrium with today's atmosphere at $pCO_2 = 365$ μatm has a pH of 8.1 and DIC = 2.1 mmol kg^{-1} at a salinity[3] $S = 35$ and $T_c = 25°C$. Using Eqs. (1.1.9)-(1.1.11), we calculate $[CO_2] = 10.4$ μmol kg^{-1}, $[HCO_3^-] = 1818$ μmol kg^{-1}, and $[CO_3^{2-}] = 272$ μmol kg^{-1}; the constants used for the calculations are summarized in DOE (1994), see Appendix A. In other words, the percentage of the dis-

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[2] The alkalinity is expressed in units of mol kg^{-1}. Note that the unit eq kg^{-1} is also widely used in the literature.

[3] Note that no unit is assigned to the practical salinity S (for definition see e.g. Müller, 1999). Roughly, $S = 35$ corresponds to ~ 35 g salt per kg seawater. If not stated otherwise, quantities will be given for $S = 35$ and $T_c = 25°C$ in order to allow comparison with values in the chemical literature. The calculation of quantities at other temperatures and salinities will be left as an exercise to the reader.

solved species is $[CO_2] : [HCO_3^-] : [CO_3^{2-}] \simeq 0.5\% : 86.5\% : 13\%$. Thus, at typical seawater conditions, bicarbonate is the dominant species, followed by carbonate ion, whereas dissolved carbon dioxide is present only in small concentrations. This is illustrated in Figure 1.1.2 by the crossover between the concentration curves and the dashed vertical line at pH = 8.1. Also indicated in Figure 1.1.2 are the pH values at which the concentration of CO_2 equals the concentration of HCO_3^- and at which the concentration of HCO_3^- equals the concentration of CO_3^{2-}. These pH values correspond to pK_1^* and pK_2^*, the pK values of the first and second dissociation constants of carbonic acid, respectively (cf. box on pK values).

***pK*-values.** Mathematically, the pK value of an equilibrium constant, K, is simply the negative common logarithm of K:

$$pK := -\log_{10}(K) \ .$$

This is in analogy to the pH value which is the negative common logarithm of $[H^+]$. Chemically, the pK value has an interesting interpretation. Consider, for example, the first acidity constant of carbonic acid:

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

Let us assume that in a given solution the concentration of CO_2 is equal to the concentration of HCO_3^-. It follows that $[H^+]$ is equal to K_1^*:

$$[H^+] = K_1^* \qquad \text{at } [CO_2] = [HCO_3^-]$$

and thus (taking the negative common logarithm) that the pH of the solution is equal to pK_1^*, i.e.:

$$pH = pK_1^* \qquad \text{at } [CO_2] = [HCO_3^-] \ .$$

This feature is graphically indicated by the circle in Figure 1.1.2 where the curves of CO_2 and HCO_3^- intersect. Consequently, $[CO_2]$ is larger than $[HCO_3^-]$ for pH values below pK_1^* (and vice versa). A similar reasoning holds for pK_2^*: $[HCO_3^-]$ is equal to $[CO_3^{2-}]$ at $pH = pK_2^*$.

Because the Bjerrum plot (Figure 1.1.2) shows the concentrations of the carbonate species as a function of pH, one might be tempted to believe that the pH is controlling the concentrations and relative proportions of the carbonate species in the ocean. However, the reverse is true: the carbonate system is the natural buffer for the seawater pH. For instance, if strong acid is added to seawater, HCO_3^- and CO_3^{2-} ions are transformed to CO_2 and the pH will remain between 8 and 6. Only after almost 3 mmol H^+ per

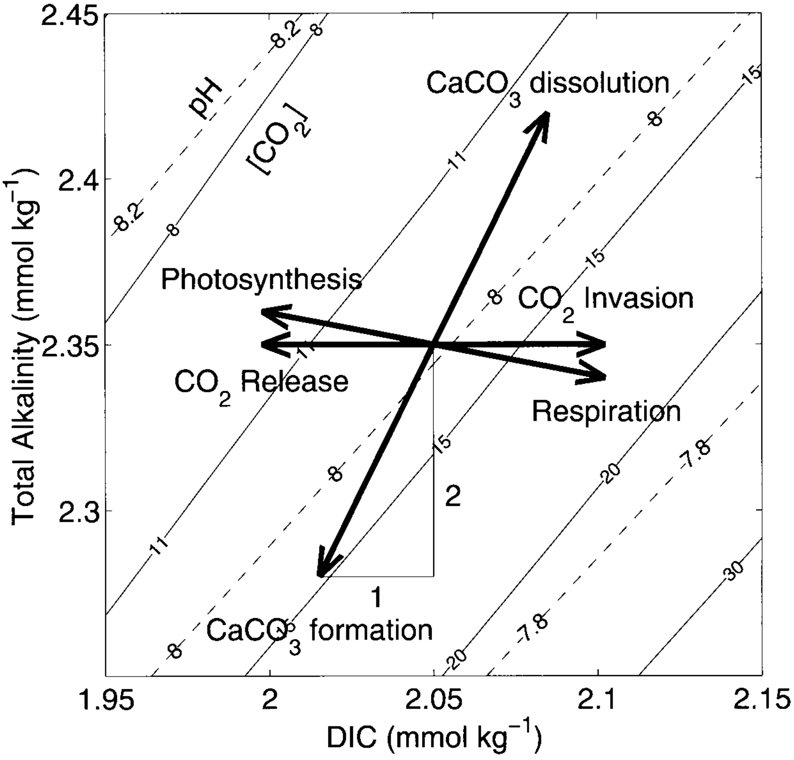

Figure 1.1.3: Effect of various processes on DIC and TA (arrows). Solid and dashed lines indicate levels of constant dissolved CO_2 (in μmol kg^{-1}) and pH, respectively, as a function of DIC and TA. $CaCO_3$ formation, for example, reduces DIC by one and TA by two units, therefore driving the system to higher CO_2 levels and lower pH. Invasion of atmospheric CO_2 into the ocean increases DIC, while release of CO_2 to the atmosphere has the opposite effect. TA stays constant in these two cases.

kg seawater have been added, the pH will drop appreciably (see, however, Sillén (1961, 1967); Holland (1984) for further reading).

Many processes affecting the carbonate system in the ocean are best described by considering the change of DIC and TA that is associated with them (Figure 1.1.3). For example, the invasion of anthropogenic CO_2 leads to an increase of DIC but does not change TA because the charge balance is not affected (see Section 1.5). The formation of $CaCO_3$ decreases both DIC and TA. For each mole of $CaCO_3$ precipitated, one mole of carbon and one mole of double positively charged Ca^{2+} ions are taken up which leads to a decrease of DIC and TA in a ratio of 1:2 (Section 1.6.1). As a result, the system shifts to higher CO_2 levels and lower pH (Figure 1.1.3). Photosynthesis reduces DIC and slightly increases TA because in addition to inorganic carbon, nutrients are taken up (Section 1.2.7). As a result of these various processes, the carbonate species and *p*H adjust according to the equilibrium conditions given by the set of equations (1.1.5)-(1.1.8) that has to be obeyed simultaneously. In summary, it is very useful to keep in mind that the *p*H and the concentrations of the carbonate species in the ocean are governed by the distribution of DIC and TA in many cases. This fact and the various processes depicted in Figure 1.1.3 will be elaborated in subsequent chapters.

Water equilibrium

The carbonate system includes water, H_2O, and its dissociation products H^+ and OH^-:

$$H_2O \overset{K_W}{\rightleftharpoons} H^+ + OH^-$$

where K_W is the dissociation constant, or ion product, of water. The stoichiometric equilibrium constant is defined as:

$$K_w^* = [H^+][OH^-] \, . \qquad (1.1.13)$$

It is important to note that the symbol 'H^+' represents hydrate complexes associated with H_3O^+ and $H_9O_4^+$ rather than the concentration of free hydrogen ions. Free hydrogen ions do not exist in any significant amount in aqueous solutions. It is, however, convenient to refer to $[H^+]$ as the hydrogen ion concentration. This subject and the different *p*H scales which are used to determine the hydrogen ion concentration in aqueous solutions are discussed in more detail in Section 1.3.

Boric acid-borate equilibrium

For quantitative calculations of the carbonate system, boric acid, $B(OH)_3$, and borate, $B(OH)_4^-$, and some other minor species have to be taken into account as well. This is because those minor species contribute to the total alkalinity (TA) from which, in combination with DIC, carbon system parameters are frequently determined. The boric acid - borate equilibrium can be written as:

$$B(OH)_3 + H_2O \overset{K_B}{\rightleftharpoons} B(OH)_4^- + H^+$$

where K_B is the dissociation constant of boric acid. The stoichiometric equilibrium constant is defined as:

$$K_B^* = \frac{[B(OH)_4^-][H^+]}{[B(OH)_3]} \, . \qquad (1.1.14)$$

The total boron concentration B_T is given by

$$B_T = [B(OH)_4^-] + [B(OH)_3] \, . \qquad (1.1.15)$$

1.1.1 Effect of temperature, salinity, and pressure

As mentioned before, temperature, salinity, and pressure influence the values of the dissociation constants. It can be derived from thermodynamics that the equilibrium constant is related to the standard free energy of the reaction. Varying the temperature or the pressure of the system results in a change of this energy and thus of the thermodynamic equilibrium constant. Using the laws of thermodynamics, expressions for the temperature and pressure effects on equilibrium constants can be derived. The details of the calculations for temperature and pressure will not be discussed here - we refer the reader to e.g. Millero (1979) and Millero (1982).

From what has been said so far, it is comprehensible that the equilibrium constants (K^*'s) depend on temperature and pressure. The effect of salinity, however, is not *a priori* comprehensible since the K^*'s should not depend on e.g. the composition of the solution. The reason for the salinity dependence of the dissociation constants which are used for the description of the carbonate system (so-called 'stoichiometric constants'), is that they are not the 'true thermodynamic constants'. Thermodynamic constants are expressed in terms of ion activities whereas stoichiometric constants are expressed in terms of concentrations - this subject is discussed in more detail in Section 1.1.3.

Figure 1.1.4 shows the dependence of pK_1^* and pK_2^* on temperature, salinity, and pressure. As is obvious, shifts in the pK^* values lead to shifts in the relative proportions of CO_2, HCO_3^-, and CO_3^{2-} at a given pH. With respect to the reference values of the pK^*'s at $T_c = 25°C$, $S = 35$, and $P = 1$ atm, a decrease of temperature or salinity ($T_c = 0°C$ or $S = 0$) results in an increase of the pK^* values (cf. Table 1.1.1). Consequently, when comparing e.g. seawater at $S = 35$ and fresh water at $S = 0$ at the same pH and temperature, the relative proportion of CO_3^{2-} ions, with respect to $[CO_2]$ and $[HCO_3^-]$, will be appreciably higher in seawater than in fresh water.

Another important example of the dependence of the carbonate system parameters on e.g. T and P are the different chemical properties of water masses within the surface and the deep ocean. Let us consider a water parcel which is cooled from 25°C to 0°C, and is then sinking from the surface ocean ($S = 35$, and $P = 1$ atm) into the deep ocean ($S = 35$, and $P = 300$ atm, i.e., depth ~ 3 km). The conserved quantities, when only temperature and pressure are changed, are DIC and TA. Note that this example considers a hypothetical 'abiotic' case because biological processes such as primary

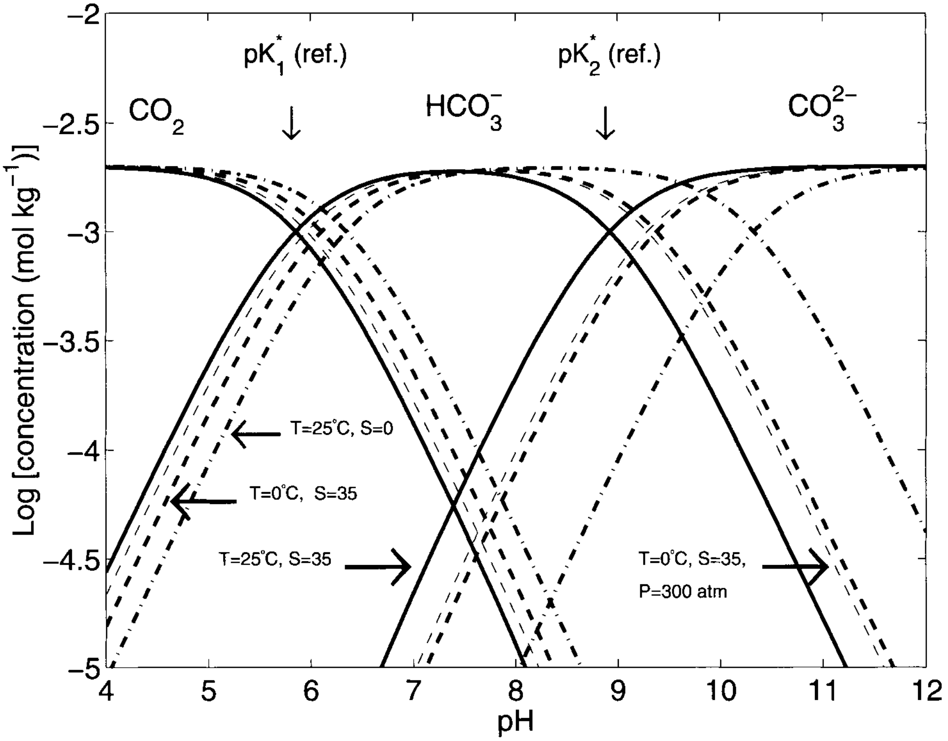

Figure 1.1.4: Illustration of the effect of temperature, pressure, and salinity on pK_1^* and pK_2^*. The reference case is T_c = 25°C, S = 35, and P = 1 atm (solid line). See Table 1.1.1 for values. Note that DIC = 2 mmol kg^{-1} in all cases.

production and calcification which do change DIC and TA in the real ocean are not considered. As is obvious from Figure 1.1.4, the drop in temperature from 25° to 0°C causes a large increase in the pK^* values which is only slightly modified by the pressure change. At constant DIC = 2 mmol kg^{-1}, and TA = 2.44 mmol kg^{-1}, the carbonate ion concentration of the sinking water parcel would drop from 316 to 286 μmol kg^{-1}. In reality much larger differences in [CO$_3^{2-}$] between surface and deep ocean are observed, i.e. ~ 300 μmol kg^{-1} in the surface vs. ~100 μmol kg^{-1} in the deep ocean. These differences are mainly due to biological processes which produce vertical gradients in DIC and TA.

In summary, decreasing T, S, or P results in an increase of pK_1^* and pK_2^* of carbonic acid. The same is true for the pK^*'s of the dissociation constants of water, pK_W^*, and boric acid, pK_B^*, cf. Table 1.1.1.

Table 1.1.1: Influence of salinity, temperature, and pressure on pK_1^*, pK_2^*, pK_W^*, and pK_B^*.

T_c(°C)	S	P (atm)	pK_1^*	pK_2^*	pK_W^*	pK_B^*
25	35	1	5.86[a]	8.92[a]	13.22[a]	8.60[a]
25	0	1	6.35[b]	10.33[b]	14.00[c]	9.24[d]
0	35	1	6.11[a]	9.38[a]	14.31[a]	8.91[a]
0	35	300	5.96[e]	9.29[e]	14.16[e]	8.75[e]

[a] DOE (1994) - for a discussion of seawater pK^*'s used in this book, see Section 1.1.6.

[b] Usdowski (1982).

[c] Stumm and Morgan (1996).

[d] Hershey et al. (1986).

[e] Pressure correction from Millero (1995).

Exercise 1.1 (*)

What is the dominant carbonate species at typical seawater pH of 8.2 (~ surface ocean) and 7.8 (~ deep ocean)? See Appendix D for answers.

Exercise 1.2 (**)

Using Eqs. (1.1.9)-(1.1.11) and the values of pK_1^* and pK_2^* at $T_c = 25$°C and $S = 35$ given in Table 1.1.1, calculate the concentrations of CO_2, HCO_3^-, and CO_3^{2-} at pH 8.2 and DIC = 2 mmol kg^{-1}.

1.1.2 Ionic strength and activity coefficient

The major difference between fresh water and seawater is the total concentration and the relative proportion of ions dissolved in the solution. In concentrated solutions, the ions interact with each other and thus do not exhibit their full potential to react chemically with other chemical compounds. Before getting into the details of this subject, let us briefly summarize the content of the current section with the following example.

Imagine a volume of water on its journey from the spring of a river to the ocean. As the solution changes from fresh water to seawater, i.e. the number of ions in solution increases, the ion activity decreases due to (a) long-range electrostatic interactions and (b) ion pairing and complex formation. Because the activity of different chemical species with different charges are affected in a different way, the ratio of their activities changes. Considering the example of pK_2^* (see Figure 1.1.4), the activity of CO_3^{2-} is decreasing more strongly than, e.g. the activity of HCO_3^-. Consequently, the pK_2^* of carbonic acid in seawater is smaller (K_2^* is greater) than its corresponding value in fresh water. This explains why seawater has a higher CO_3^{2-} concentration (relative to the concentrations of CO_2 and HCO_3^-) than fresh water at the same pH.

Ionic strength

The quantity used to characterize aqueous solutions that contain different concentrations of ions is the ionic strength. The ionic strength of the medium, I, is defined as:

$$I = \frac{1}{2} \Sigma\, c_i\, z_i^2 \ , \tag{1.1.16}$$

where c_i is the concentration and z_i the charge of ion i in solution. The sum runs over all ions present in the medium which gives e.g. for a pure NaCl solution:

$$I = \frac{1}{2} \left([\mathrm{Cl}^-] \times 1 + [\mathrm{Na}^+] \times 1\right) .$$

Although NaCl is the major salt component of seawater, the properties of seawater and pure NaCl solutions are quite different. Seawater is a complex solution of electrolyte mixtures of unlike charge types where many more ions such as Mg^{2+} and SO_4^{2-} have to be considered (for chemical composition of seawater, see Table A.12.3, Appendix A). The ionic strength of seawater is approximately 0.7:

$$I = \frac{1}{2} \left([\mathrm{Cl}^-] \times 1 + [\mathrm{Na}^+] \times 1 + [\mathrm{Mg}^{2+}] \times 4 + [\mathrm{SO}_4^{2-}] \times 4 + ...\right) \approx 0.7 \ , \tag{1.1.17}$$

which corresponds to a seawater salinity of $S \sim 35$. The ionic strength of seawater may be calculated from salinity by (DOE, 1994):

$$I = \frac{19.924\ S}{1000 - 1.005\ S} \ .$$

As is obvious from Figure 1.1.5, the ionic strength is a fairly linear function of S within the range $30 < S < 40$ and might be approximated by $I \simeq 0.02\ S$.

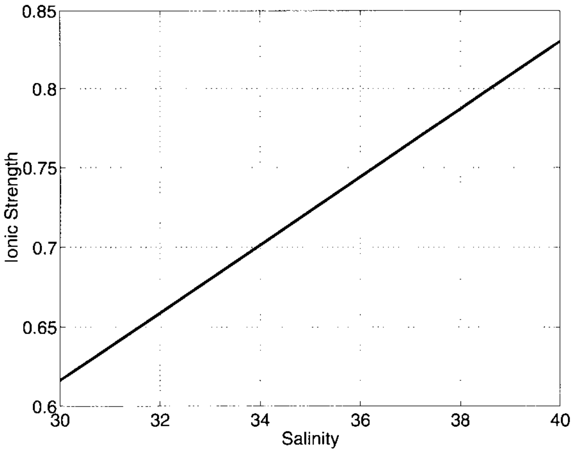

Figure 1.1.5: Relationship between salinity and ionic strength in seawater.

Activity coefficient

Central to the description of the chemical behavior of an ion dissolved in fresh water and in seawater is its activity. This concept might be illustrated as follows (note that the illustration is not a rigorous analogy). Consider two automobiles, one of them driving through New York City during rush hour, the other one driving through Death Valley at night. While the car in New York City is hindered by the interaction with all other vehicles in the streets (corresponding to the interaction with a large number of ions present in solution), the car in Death Valley is free to move (the solution is highly diluted). One might say that the 'activity' of the car in the New York City traffic is low while the 'activity' of the car in Death Valley is high. The chemical quantity which expresses such a behavior of ions in solution is indeed called activity.

The activity of a chemical species A, denoted by $\{\mathrm{A}\}$, is related to the concentration of this species, $[\mathrm{A}]$, by the activity coefficient γ_A:

$$\{\mathrm{A}\} = \gamma_\mathrm{A}[\mathrm{A}] \ .$$

Ideally, the activity coefficient is 1.0, referring to the infinite dilution activity for which the concentrations of all solutes approach zero. It is to note that this definition refers to a reference state in pure water and that *p*H scales in seawater, for example, are based on seawater as the reference state (cf. Section 1.3 and Wedborg et al. (1999)). In dilute solutions of simple electrolytes, deviations from ideal behavior are caused by long-range electrostatic interactions. For those interactions approximations can be derived to describe the dependence of activity coefficients on the ionic strength (see below). In seawater the situation is more complicated because of (a) the higher ionic strength of seawater and (b) because various different ions with different charges are present. This leads to ion pairing and complex formation in electrolyte mixtures of unlike charge types such as seawater. For example, negatively charged carbonate ions (CO_3^{2-}) are associated with positively charged Mg^{2+} or Na^+ ions, forming ion pairs such as $NaCO_3^-$ or $MgCO_3^0$. The most important ion pair equilibria in seawater are (Skirrow, 1975):

$$\begin{aligned}
Ca^{2+} + CO_3^{2-} &\rightleftharpoons CaCO_3^0 \\
Mg^{2+} + CO_3^{2-} &\rightleftharpoons MgCO_3^0 \\
Na^{+} + CO_3^{2-} &\rightleftharpoons NaCO_3^- \\
Ca^{2+} + HCO_3^{-} &\rightleftharpoons CaHCO_3^+ \\
Mg^{2+} + HCO_3^{-} &\rightleftharpoons MgHCO_3^+ \\
Na^{+} + HCO_3^{-} &\rightleftharpoons NaHCO_3^0 \,.
\end{aligned}$$

Thus, in addition to the diminution of the activity of the CO_3^{2-} ion due to electrostatic interaction with all the other ions in solution, the carbonate ion in seawater is not 'free' - it forms pairs with oppositely charged ions. With respect to our illustration of the traffic analogy this might correspond to a vehicle in New York City traffic hauling a trailer.

The concentrations of HCO_3^- and CO_3^{2-} used in the definitions of the stoichiometric constants (Eqs. 1.1.5 and 1.1.6) refer to total concentrations, i.e. free ions plus ion pairs; they are sometimes denoted by $[HCO_{3T}^-]$ and $[CO_{3T}^{2-}]$, respectively (Skirrow, 1975).

Considering the effects of ion pairing on activities, it is useful to talk about 'free' and 'total' activity coefficients. In case of a dilute solution, there are no differences between free and total activity coefficients because all ions are thought to be 'free' (i.e. no ion pairing or complex formation). In seawater, however, the total activity coefficient can be dramatically lower than the free activity coefficient due to e.g. formation of ion pairs.

The free activity coefficient of an ion, or single-ion activity, of simple electrolytes, γ_f, might be calculated using the Debye-Hückel limiting law (see, e.g. Stumm and Morgan, 1996):

$$\log(\gamma_f) = -Az^2\sqrt{I} \qquad I < 10^{-2.3} \qquad (1.1.18)$$

or the Davies equation:

$$\log(\gamma_f) = -Az^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right) \qquad I < 0.5 \qquad (1.1.19)$$

with $A = 1.82 \times 10^6(\epsilon T)^{-3/2}$, where $\epsilon \approx 79$ is the dielectric constant of water, and T is the temperature in Kelvin. At 25°C, A is about 0.5 for water. The charge of the ion is denoted as z and I is the ionic strength of the medium. Using the approximations given in Eqs. (1.1.18) and (1.1.19), activity coefficients for simple dilute solutions can then be calculated (Table 1.1.2). The question to be addressed is: can those approximations also be used to calculate total activity coefficients of ions in seawater?

Table 1.1.2: Free activity coefficient γ_f of some ions in dilute solutions at $T_c = 25°C$.

Ion	γ_f [a]	γ_f [b]	γ_f [b]	γ_f [b]
Ionic strength:	$I = 10^{-3}$	10^{-2}	0.1	0.5
$Cl^-, Na^+, HCO_3^-, H^+,$ $OH^-, B(OH)_4^-$	0.96	0.90	0.77	0.69
$Mg^{2+}, SO_4^{2-}, Ca^{2+}, CO_3^{2-}$	0.86	0.66	0.36	0.23
PO_4^{3-}	0.72	0.40	0.10	0.04

[a] Calculated using the Debye-Hückel limiting law, Eq. (1.1.18).
[b] Calculated using the Davies equation, Eq. (1.1.19).

The ionic strength of seawater is approximately 0.7 which is only slightly higher than the ionic strength limit up to which the Davies equation should hold. Thus, one might be tempted to use the Davies equation to calculate activities of ions in seawater. However, as already said, for seawater the Debye-Hückel limiting law or the Davies equation no longer apply since they only hold for dilute solutions and simple electrolytes (as opposed to concentrated solutions and electrolyte mixtures of unlike charge type). In seawater, ion pairing and complex formation occur which makes it necessary to consider total activity coefficients. The models that are widely used to describe total activity coefficients of ionic solutes in natural waters including seawater are the 'ion pairing model' (e.g. Bjerrum, 1926; Garrels and Thompson, 1962; Sillén, 1961; Millero and Schreiber, 1982) and the 'Pitzer chemical equilibrium model' (e.g. Pitzer, 1973; Millero and Pierrot 1998). The description of these rather elaborated models is beyond the scope of this book. A model for natural waters based on the Pitzer model has recently been published by Millero and Pierrot (1998), yielding good results for activity coefficients in seawater when compared to measured values (Table 1.1.3; compare also Millero, 2001).

Table 1.1.3: Total activity coefficient γ_t of some ions in seawater at $T_c = 25°C$ and $S = 35$.

Ion	γ_t (measured)[a]	γ_t (calculated)[b]	γ_f (Davies eq.)[c]
Cl^-	0.666	0.666[d]	0.69
Na^+	0.668	0.664	0.69
H^+	0.590	0.581	0.69
OH^-	0.255	0.263	0.69
HCO_3^-	0.570	0.574	0.69
$B(OH)_4^-$	0.390	0.384	0.69
Mg^{2+}	0.240	0.219	0.23
SO_4^{2-}	0.104	0.102	0.23
Ca^{2+}	0.203	0.214	0.23
CO_3^{2-}	0.039	0.040	0.23
$H_2PO_4^-$	0.453	0.514	0.69
HPO_4^{2-}	0.043	0.054	0.23
PO_4^{3-}	0.00002	0.00002	0.04

[a] For references, see Millero and Pierrot (1998).

[b] Millero and Pierrot (1998).

[c] Free activity coefficient, Davies equation, Eq. (1.1.19).

[d] Assigned value.

Exercise 1.3 (*)

What is the fundamental difference between NaCl solutions and seawater at the same ionic strength?

Exercise 1.4 (**)

Calculate the ionic strength of seawater using Eq. (1.1.17) and Table A.12.3 (see Appendix A). How many percent of the total ionic strength is due to the sum of Na^+, Cl^-, Mg^{2+}, and SO_4^{2-} ions?

1.1.3 Thermodynamic, hybrid, and stoichiometric equilibrium constants

Several concepts are in use in order to describe proton transfer reactions in aqueous media. Here we shall only briefly summarize the different equilibrium constants, also called acidity or dissociation constants, associated with these concepts (for review see Dickson, 1984). The second dissociation constant of carbonic acid, K_2, may serve as an example.

(1) The standard acidity, or thermodynamic equilibrium constant K_2 for the proton-transfer reaction:

$$\mathrm{HCO_3^-} \rightleftharpoons \mathrm{CO_3^{2-}} + \mathrm{H^+}$$

is expressed entirely in terms of activities:

$$K_2 = \frac{\{\mathrm{H^+}\}\{\mathrm{CO_3^{2-}}\}}{\{\mathrm{HCO_3^-}\}} \; . \tag{1.1.20}$$

From a theoretical point of view, activity is the appropriate quantity in equilibrium thermodynamics.[4] A severe disadvantage in using activity is, however, the fact that activities are not as easy (if at all) measurable as concentrations, and the conversion from concentrations to activities at typical seawater salinities requires rather laborious and uncertain calculations of activity coefficients. Fortunately, equilibrium relations can also be formulated in terms of concentrations.

(2) A useful concept employed in oceanography is based on so-called hybrid (mixed) constant where concentrations and activities occur at the same time:

$$K_2' = \frac{a_\mathrm{H}[\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} \; . \tag{1.1.21}$$

where a_H is operationally defined under the infinite dilution convention (for a detailed discussion of this approach, cf. Dickson, 1984; Skirrow, 1975).

(3) The constant entirely expressed in terms of concentrations is the classical mass action product for the acid dissociation reaction, also called stoichiometric constant as introduced in Section 1.1:

$$K_2^* = \frac{[\mathrm{H^+}][\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} \tag{1.1.22}$$

where $[\mathrm{H^+}]$ is operationally defined under the constant ionic medium convention. Stoichiometric constants are conventionally denoted by K^*. Please note that some authors omit the star for the sake of simplicity (cf. DOE (1994) and Millero (1995)).

An apparent constant was defined with apparent activities of the proton based on measurements using NBS buffers. These constants are no longer

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[4] Note that concentration (not activity) is the appropriate quantity in chemical kinetics (see Chapter 2) because the reaction rate depends on the number of colliding molecules per volume and thus on concentrations (Lasaga, 1981).

used in chemical oceanography since all the constants are determined using the total proton scale or seawater scale (compare Section 1.3). The following quotes by Skirrow (1975) that refer to apparent constants apply to stoichiometric and hybrid constants as well. The occurrence of ion pair formation "is the principal reason for the dependence of apparent constants not only on the ionic strength of a solution, but also on the ionic composition" (Skirrow, 1975, p. 76).

1.1.4 Effect of ionic strength on pK^* values

Having introduced the concept of the ionic strength, activity, and the different acidity constants, we can now quantify the effect of ionic strength (and therefore salinity) on the pK^* values as described earlier.

Combining Eqs. (1.1.20) and (1.1.22), K_2^* can be expressed as (note that $\{CO_3^{2-}\} = \gamma_{CO_3^{2-}}[CO_3^{2-}]$):

$$K_2^* = K_2 \, \frac{\gamma_{HCO_3^-}}{\gamma_{H^+} \, \gamma_{CO_3^{2-}}} \, . \tag{1.1.23}$$

As is obvious from Eq. (1.1.23), relative changes in the *total* activity coefficients with higher ionic strength lead to changes in the dissociation constant K_2^*. Using values for γ_t given in Table 1.1.3 and the fresh water value of 10.33 for K_2 at 25°C, the value of pK_2^* in seawater at $S = 35$ can be estimated (evaluate the negative common logarithm of Eq. (1.1.23)):

$$\begin{aligned} pK^*_{2,\text{seawater}} &= 10.33 - \log\left(\frac{0.570}{0.590 \times 0.039}\right) \\ &= 8.94 \end{aligned}$$

which is close to the experimentally determined value of 8.92 (DOE, 1994; Table 1.1.1).

In summary, considering a solution that changes from fresh water to seawater, the number of ions in solution increases, the relative proportion of ions changes, and the ion activity decreases. Since the activities of different ions are affected differently, the ratio of their activity coefficients changes (cf. Eq. (1.1.23)). Considering the example of pK_2^* as discussed above, the activity coefficient of CO_3^{2-} is decreasing more strongly (from 1 at infinite dilution to 0.039 in seawater) than, e.g. the activity coefficient of HCO_3^- (from 1 to 0.570). Consequently, pK_2^* in seawater is smaller (K_2^* is greater) than in fresh water. As a result, seawater has a higher CO_3^{2-} concentration (relative to the concentrations of CO_2 and HCO_3^-) than fresh water at the same pH (cf. Figure 1.1.4).

1.1.5 Effect of chemical composition on pK^* values

In general, the stoichiometric equilibrium constants of an electrolyte (including seawater) depend on the composition of the solution. Fortunately, the composition of seawater is fairly constant. Thus, the pK^*'s are functions of P, T, and S (or I) only. In certain regions of the oceans (for example, the Baltic Sea), in pore waters or in many laboratory experiments the salt composition differs from standard mean ocean values. Ben-Yaakov and Goldhaber (1973) estimated the variation in pK_1^* and pK_2^* with changing salt composition. Their approach made use of a seawater model and calculation procedure similar to that described by Garrels and Thompson (1962) and Berner (1971). Ben-Yaakov and Goldhaber (1973) provide sensitivity parameters:

$$s_{K^*} = \frac{\Delta K^*/K^*}{\Delta c_i/c_i}$$

where ΔK^* is the change in K^* due to relative change in concentration, $\Delta c_i/c_i$, of component i. As expected from its known tendency to form ion pairs in seawater, magnesium has the largest sensitivity parameters: $s_{K_1^*,\mathrm{Mg}^{2+}} = 0.155$, $s_{K_2^*,\mathrm{Mg}^{2+}} = 0.442$ (at 19‰ chlorinity, which corresponds to a salinity of 34.3, and $T_c = 25°\mathrm{C}$). A doubling of the Mg^{2+} concentration, for example, will reduce pK_1^* from 5.86 to 5.80 and pK_2^* from 8.93 to 8.77. The consequences of changes in the salt composition on the equilibrium partial pressure will be investigated in Exercise 1.5. Nowadays it is recommended to calculate pK^*'s directly from a state-of-the-art seawater model such as the one developed by Millero and Roy (1997).

Exercise 1.5 (**)

Consider seawater at $T_c = 25°$, $S = 34.3$, $P = 1$ bar with DIC = 2 mmol kg^{-1} and TA = 2.35 mmol kg^{-1}. Calculate the equilibrium partial pressure of CO_2 (hint: use formulas given in the Appendix). Estimate the change in pCO_2 when the natural concentration of Mg^{2+} ions is doubled.

1.1.6 The choice of equilibrium constants

At this stage we have to discuss an area of the carbonate chemistry which, we feel, is somewhat unsatisfactory at its present state. The equilibrium constants for the dissociation of carbonic acid, boric acid, water and so forth, have been measured by different authors in different media, i.e. natural seawater and artificial seawater, and on different pH scales (cf. Section 1.3 and

Appendix A). Using dissociation constants for the calculation of carbonate system parameters given by different authors, one obtains different results. Particularly huge differences may arise when the conversion between pH scales is not taken into account. Although there have been attempts to agree on a single consistent set of constants and a single pH scale (cf. e.g. Dickson (1984), UNESCO (1987)), this approach has hitherto not become standard.

An example of the potential problems associated with the calculations of the concentrations of the carbonate species is listed in Table 1.1.4. Let us assume that the pH and the DIC of a sample have been measured but that the pH scale on which the measurements were made, has not been reported. In other words, it is not clear whether the seawater scale, the total scale, or the free pH scale has been used - for definitions, see Section 1.3. With $p\text{H} = 8.08$ and DIC = 2 mmol kg^{-1}, the carbonate system parameters can be calculated for all three scales (Table 1.1.4). Whereas the differences between the seawater and the total scale are rather small (~ 10 μatm in terms of $p\text{CO}_2$), the differences between these two scales and the free scale are huge (> 100 μatm in terms of $p\text{CO}_2$). It is emphasized that the calculated differences result from the fact that the scale on which the pH was measured has not been defined. If the pH scale used in the measurements was known and the pH for the calculations would then be converted to the correct pH scale (corresponding to the scale of the dissociation constants), one would obtain exactly the same results in each case. This scenario requires, however, that a single set of constants is used, see below. In practice, one could use any pH scale for the calculations - the crucial point is that the pH scale and the dissociation constants used, have to agree.

Table 1.1.4: Calculated carbonate system parameters when the scale on which pH was measured is not known ($p\text{H} = 8.08$, DIC = 2 mmol kg^{-1}, $S = 35$, $T_c = 25°\text{C}$).[a]

pH scale	pH	$p\text{CO}_2$ μatm	CO_2(aq.) μmol kg^{-1}	HCO_3^- μmol kg^{-1}	CO_3^{2-} μmol kg^{-1}
Seawater	8.08	354	10.0	1735	255
Total	8.08	363	10.3	1739	250
Free	8.08	478	13.6	1786	201

[a] The constants of Roy et al. (1993a) as converted to different pH scales (see Section 1.3) have been used in all calculations.

Even when the calculations are carried out on the same pH scale, differences in the values may occur because dissociation constants are used which have been determined by different authors. The differences are, however, usually smaller than in the case mentioned above. Table 1.1.5 shows values for the concentrations of the carbonate species calculated from DIC and TA using constants (all converted to the seawater scale) referred to as 'Roy', 'Hansson', and 'Mehrbach' (for definition, see footnote to Table 1.1.5). The calculated values for $p\mathrm{CO}_2$ differ by up to ~ 30 μatm in this particular example.

Very recently, it has been demonstrated that using Mehrbach constants for the dissociation of carbonic acid yields the best results when determining $p\mathrm{CO}_2$ from DIC and TA (Wanninkhof et al., 1999; Johnson et al., 1999; Lee et al., 2000; Lueker et al., 2000). One could therefore agree to use Mehrbach constants in this particular case, which we actually recommend. However, which set of constants should we use when, e.g. determining $p\mathrm{CO}_2$ from pH and DIC or $[\mathrm{CO}_3^{2-}]$ from $p\mathrm{CO}_2$ and TA? The fact that Mehrbach constants do a good job in the important case mentioned above does not imply that they do so in every case. As Wanninkhof et al. (1999) put it: " ... the good agreement between $p\mathrm{CO}_2$(SST) and $p\mathrm{CO}_2$(TA, DIC) using the constants of Mehrbach does not necessarily imply that these constants yield the best agreement with other carbon system parameters". Here is the problem: when calculating various parameters of the carbonate system using different input variables (as is done in this book, for example) one cannot use different sets of constants since this would lead to inconsistent results.

Table 1.1.5: Calculated carbonate system parameters using dissociation constants given by different authors (DIC = 2 mmol kg^{-1}, TA = 2.35 mmol kg^{-1}, $S = 35$, $T_c = 25$°C).

Author	$p\mathrm{H}_{\mathrm{SWS}}$	$p\mathrm{CO}_2$ μatm	CO_2(aq.) μmol kg^{-1}	HCO_3^- μmol kg^{-1}	CO_3^{2-} μmol kg^{-1}
Roy[a]	8.08	354	10.0	1735	255
Hansson[b]	8.10	343	9.7	1739	251
Mehrbach[c]	8.11	327	9.3	1742	249

[a] Roy et al. (1993a) converted to seawater scale (Millero, 1995).

[b] Mehrbach et al. (1973) as refit by Dickson and Millero (1987).

[c] Hansson (1973b) as refit by Dickson and Millero (1987).

Another issue that should be kept in mind when choosing a particular set of dissociation constants is to make sure that all constants have been determined in the same medium, i.e. natural or artificial seawater. The constants referred to as 'Mehrbach' have been determined in natural seawater, whereas 'Roy' and 'Hansson' have been determined in artificial seawater. It is likely that this is the reason for the fact that Mehrbach constants do a good job when measurements in the ocean, i.e. in natural seawater are considered. Precise calculations of the carbonate system parameters include (besides the dissociation of carbonic acid) the dissociation of water, boric acid, hydrogen sulfate, hydrogen fluoride, phosphoric acid, silicic acid and more. In order to achieve internal consistency of the calculations, all the constants used should be determined in a single medium, i.e. in natural seawater *or* in artificial seawater.

Regarding the calculations presented throughout this book, we have decided to use the set of constants summarized in DOE (1994), including the dissociation constants of carbonic acid referred to as 'Roy', see Appendix for values. These constants, which have been determined in artificial seawater, are all expressed in terms of the total hydrogen ion concentration (i.e., total *p*H scale, see Section 1.3) and in units of moles per kilogram of solution. For the reasons given above, it appears that this set is the most appropriate one for our current purposes. We note, however, that e.g. Mehrbach constants may be more appropriate under particular circumstances.

It is extremely desirable that the problems described here will be solved in the future. We believe that major steps towards this goal are (a) the agreement on a single *p*H scale by the community and (b) the high-precision determination of all relevant dissociation constants in natural seawater.

1.1.7 $CaCO_3$ solubility and the saturation state of seawater

Formation and dissolution of calcium carbonate ($CaCO_3$) in the ocean are important players in the global carbon cycle and are intimately related to the control of atmospheric CO_2 on various time scales. For instance, anthropogenic CO_2, which is currently accumulating in the atmosphere, is thought to be mostly absorbed by the oceans and ultimately neutralized by the reaction with $CaCO_3$ in marine sediments (the so-called fossil fuel neutralization, e.g. Broecker and Takahashi, 1977; Sundquist, 1986; Archer et al., 1998). A determining factor in the context of formation and dissolution of calcium carbonate is the $CaCO_3$ saturation state of seawater, which is a function of the carbonate ion concentration. In other words, the equilibrium between the solid state and the solution is controlled by the corrosiveness of seawater. The $CaCO_3$ saturation state of seawater is therefore an important aspect of the seawater carbonate chemistry.

In this section, $CaCO_3$ solubility in seawater, the seawater saturation state, and the distribution of $CaCO_3$ in marine sediments are discussed. The effect of $CaCO_3$ production on the carbonate system is examined in Section 1.6.1 while potential effects of increasing atmospheric CO_2 on calcification in the future are mentioned in Section 1.6.5. For further reading, see e.g. Berger et al. (1976), Broecker and Peng (1982), Mucci (1983), Morse and Mackenzie (1990), Holligan and Robertson (1993), Millero (1996).

The vast majority of marine calcium carbonate is produced by organisms which secrete calcitic or aragonitic shells and skeletons. The major calcite producers in the open ocean are coccolithophorids and foraminifera, while the most abundant pelagic aragonite organisms are pteropods. (For a review on $CaCO_3$ production including coral reefs and other environments, see Milliman, 1993; Milliman and Droxler, 1996.) Calcite and aragonite minerals both consist of $CaCO_3$, but differ in their mineralogy. The crystal structure of calcite is rhombohedral whereas the structure of aragonite is orthorhombic (for review cf. e.g. Hurlbut (1971) or Reeder (1983)). The different structures of the two minerals lead to different physical and chemical properties (Table 3.2.4, Chapter 3) of which the solubility is of major importance here.

The stoichiometric solubility product is defined as:

$$K^*_{sp} = [Ca^{2+}]_{sat} \times [CO_3^{2-}]_{sat} \,, \tag{1.1.24}$$

where e.g. $[CO_3^{2-}]_{sat}$ refers to the equilibrium total (free + complexed) carbonate ion concentration in a seawater solution saturated with $CaCO_3$. Aragonite is more soluble than calcite at a given temperature, salinity and pressure: $K^*_{sp} = 10^{-6.19}$ and $10^{-6.37}$ $mol^2\ kg^{-2}$ for aragonite and calcite, respectively ($T = 25°C$, $S = 35$, $P = 1$ atm). Formulas for the calculation of K^*_{sp} for aragonite and calcite as determined by Mucci (1983) are given in Appendix A.10. At equilibrium, the product of the Ca^{2+} and CO_3^{2-} concentration in solution is given by the left-hand side of Eq. (1.1.24). If $[Ca^{2+}] \times [CO_3^{2-}]$ is larger than this, the solution is supersaturated with respect to $CaCO_3$ - otherwise, the solution is undersaturated. The $CaCO_3$ saturation state of seawater, Ω, is expressed as:

$$\Omega = \frac{[Ca^{2+}]_{sw} \times [CO_3^{2-}]_{sw}}{K^*_{sp}} \,, \tag{1.1.25}$$

where $[Ca^{2+}]_{sw}$ and $[CO_3^{2-}]_{sw}$ are the concentrations of Ca^{2+} and CO_3^{2-} in seawater, respectively, and K^*_{sp} is the solubility product at the *in situ* conditions of temperature, salinity, and pressure. $\Omega > 1$ corresponds to supersaturation, whereas $\Omega < 1$ corresponds to undersaturation.

In the open ocean, $[Ca^{2+}]$ variations are rather small and closely related to variations in salinity. The $CaCO_3$ saturation state is therefore mainly determined by the carbonate ion concentration. Table 1.1.6 summarizes values for the carbonate ion concentration at saturation, $[CO_3^{2-}]_{sat}$, for calcite and aragonite as a function of temperature and pressure (Mucci, 1983).

Table 1.1.6: Saturation carbonate ion concentration at $S = 35$ and $[Ca^{2+}] = 10.28$ mmol kg^{-1} (cf. Broecker and Peng, 1982).[a]

Temperature (°C)	Pressure (atm)	$[CO_3^{2-}]_{sat}$ (μmol kg^{-1}) Calcite	Aragonite
25	1	41.6	63
2	1	41.9	67
2	250	69.4	107
2	500	111.7	167

[a] Values for K^*_{sp} after Mucci (1983). Pressure correction after Millero (1995). See Appendix A.10 for formulas.

Calcium carbonate is an unusual salt: the solubility increases at lower temperature! The effect of temperature on the solubility is, however, rather small (see Table 1.1.6). More important is the fact that the solubility increases with pressure. This is of great significance for the distribution of $CaCO_3$ in marine sediments. Assuming a constant temperature in the deep ocean, $[CO_3^{2-}]_{sat}$ increases with pressure and hence with depth in the ocean (Figure 1.1.6).

The crossover between *in situ* and saturation carbonate ion concentration is called the saturation horizon or saturation depth/level. Calcium carbonate falling from the surface to the deep ocean is mainly preserved in supersaturated waters above the saturation horizon, and starts to dissolve below the saturation horizon in undersaturated waters.[5] We might therefore think of the ocean floor as a landscape with snow-covered mountains (Sillén, 1967; Broecker and Peng, 1982). The upper parts of the ocean floor, such as ridge crests, are covered with $CaCO_3$ of a light color, whereas the

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[5] This description is highly simplified, see Broecker and Takahashi (1978), Broecker and Peng (1982) or Morse and Mackenzie (1990) for details.

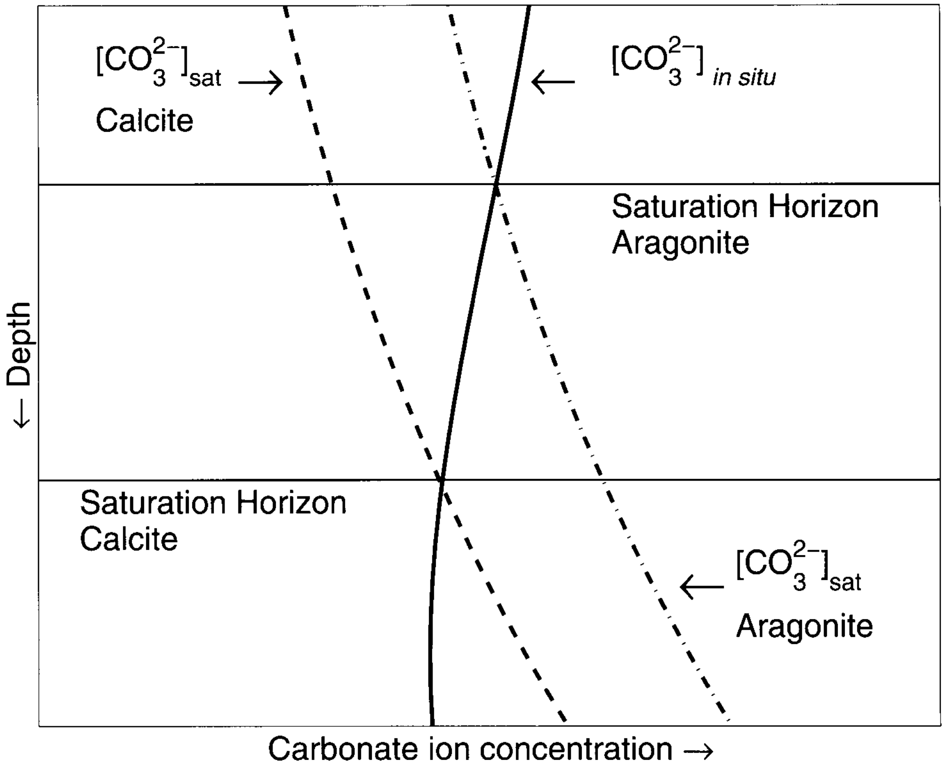

Figure 1.1.6: Illustration of the calcite and aragonite saturation horizon (SH) in the ocean (after Broecker and Peng, 1987). As pressure increases with depth, the solubility of calcite and aragonite increases as well ($[CO_3^{2-}]_{sat}$). The crossover between the *in situ* carbonate ion concentration (solid curve) and the saturation concentration for calcite (dashed curve) and aragonite (dot-dashed curve) determines the saturation horizon of the different mineral phases.

valleys are mostly free of $CaCO_3$ and covered with clay minerals of a darker color.

Figure 1.1.7 shows the calcite and aragonite saturation state of seawater in the North Pacific and North Atlantic Ocean. Surface seawater is roughly 6 and 4 times supersaturated with respect to calcite and aragonite, respectively. The supersaturation decreases with depth until it crosses the line $\Omega = 1$. The crossover occurs at shallower depth for aragonite than for calcite because aragonite is more soluble than calcite. In addition, the saturation state of the North Pacific Ocean is smaller than that of the North Atlantic Ocean. These regional differences are discussed below.

The depth of rapid increase in the rate of dissolution as observed

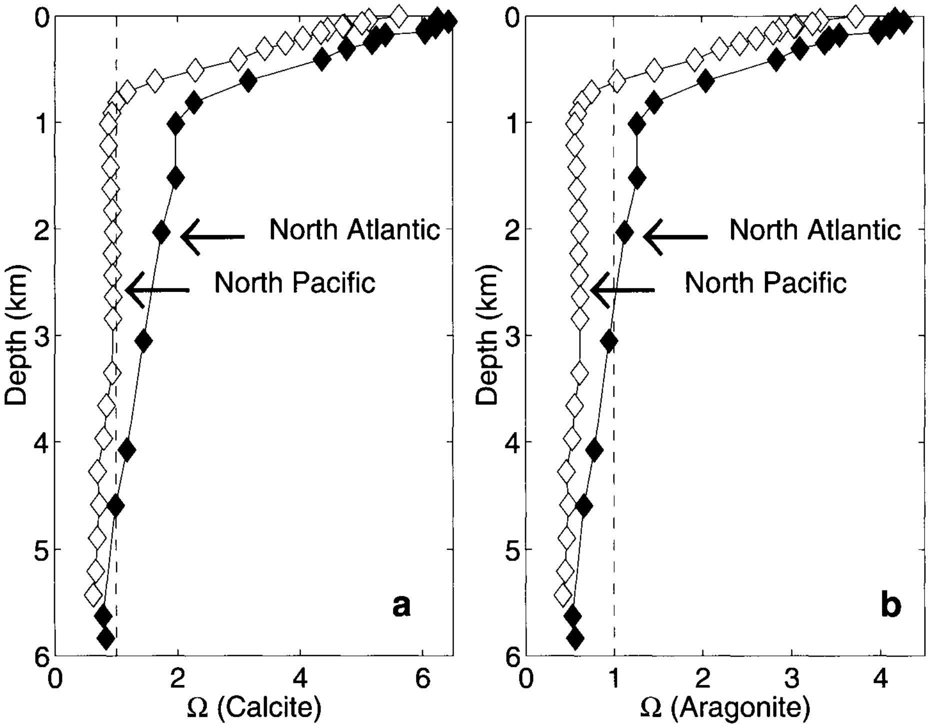

Figure 1.1.7: Saturation state of seawater, Ω, with respect to calcite (a) and aragonite (b) as a function of depth. Ω was calculated using Eq. (1.1.25) and DIC-TA profiles from the North Pacific and North Atlantic Ocean. The dashed vertical line separates areas of supersaturation ($\Omega > 1$) from undersaturation ($\Omega < 1$). Data are from WOCE Section P14N, Stn. 70 (F. Millero and Ch. Winn) and WOCE Section A05, Stn. 84, (F. Millero and S. Fiol), http://cdiac.esd.ornl.gov/oceans/CDIACmap.html.

in sediments is called the lysocline. The term lysocline stems from the Greek words for solution and inclination - in analogy to thermocline: see Berger (1968). The lysocline therefore separates poorly preserved and well-preserved $CaCO_3$ assemblages. Because of the higher solubility of aragonite in comparison to calcite, the aragonite lysocline is always found at lower depth than the calcite lysocline. The aragonite lysocline can be as shallow as 500 m in the Pacific Ocean and ~3 km in the Atlantic Ocean. The calcite lysocline is found at ~4 km in the Pacific and Indian Ocean and between 4 and 5 km in the Atlantic Ocean. The reason for the differences in the lysocline depth between Pacific and Atlantic Ocean is that deep water of the Pacific Ocean has a lower carbonate ion concentration (and a higher CO_2 content) than deep water of the Atlantic Ocean. In other words, the deep water of the Pacific Ocean is more corrosive (Figure 1.1.7). This is mainly a result of the interaction of ocean circulation and biological activity: Deep water of the Pacific Ocean is 'older' than that of the Atlantic Ocean and has therefore taken up more CO_2 from remineralization of organic matter which lowers its carbonate ion content. The age of a water mass here refers to the time elapsed since its last contact with the atmosphere.

The depth at which the sediments are virtually free of calcium carbonate is called the calcium carbonate compensation depth (CCD). Usually, a transition zone occurs between the lysocline and the CCD in which the calcium carbonate content of sediments gradually decreases with depth. The transition zone can be as large as several hundred meters which has to do with the supply rate of $CaCO_3$, i.e. the production in the surface ocean, and the kinetics of $CaCO_3$ dissolution in the deep ocean (Broecker and Peng, 1982; Morse and Mackenzie, 1990; Millero, 1996).

We will return to the production and dissolution of calcium carbonate in the sections to follow. Stable isotope fractionation of carbon, oxygen, and boron in marine calcium carbonate is examined in Chapter 3.

1.2 Alkalinity

> **"I found at least 20 different definitions of alkalinity!"**
> An ocean carbon cycle modeler from Hamburg.

> **"... alkalinity, one of the most central but perhaps not the best understood concept in aquatic chemistry."**
> Morel and Hering (1993, p.157)

Alkalinity is an important and very useful concept in the context of the carbonate system in seawater. It is also called total alkalinity or titration alkalinity and is denoted by TA. From the knowledge of TA and DIC together with T and S, all other quantities of the carbonate system, i.e. $[CO_2]$, $[HCO_3^-]$, $[CO_3^{2-}]$, and pH can be calculated. The definition of DIC as the sum of the concentrations of CO_2, HCO_3^-, and CO_3^{2-} is so simple that the meaning is understood in a second and one hesitates to call it a concept. In contrast, understanding the alkalinity concept takes much more time as we know from our own experience and from discussions with many colleagues: the meaning is not obvious from its expression in terms of concentrations of certain compounds. In what follows, the alkalinity concept will be introduced step by step. Approximations of increasing complexity will be presented that finally lead to the most exact definition given by Dickson (1981). Aqueous solutions of simple chemical compositions - compared to seawater - are discussed to clarify the alkalinity concept.

The alkalinity concept in natural waters is a non-trivial one and it therefore takes a little time to work through it. For the fast reader, who is not interested in all the details, a brief summary is given in the following subsection.

1.2.1 A shortcut to alkalinity

Dickson gives the following expression for alkalinity in seawater (DOE, 1994; compare also Dickson, 1981)

$$\boxed{\begin{aligned}\mathrm{TA} \;=\; & [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] \\ & +[\mathrm{HPO_4^{2-}}] + 2[\mathrm{PO_4^{3-}}] + [\mathrm{H_3SiO_4^-}] \qquad\qquad (1.2.26) \\ & +[\mathrm{NH_3}] + [\mathrm{HS^-}] - [\mathrm{H^+}]_F - [\mathrm{HSO_4^-}] - [\mathrm{HF}] - [\mathrm{H_3PO_4}]\end{aligned}}$$

where $[\mathrm{H^+}]_F$ is the free concentration of hydrogen ion (compare Section 1.3).

TA is derived from titration with a strong acid,[6] which explains the term ‘titration alkalinity’. The expression (1.2.26) contains several species whose contribution to TA is very small at typical surface seawater *p*H values around 8.2. They have to be included, however, to derive TA from inverse calculation using titration data over a large *p*H range as their contribution to TA becomes increasingly important at low *p*H.

Total alkalinity is a conservative quantity such as mass, salt, and dissolved inorganic carbon (see box on page 29 and Section 1.2.6). For example, if total alkalinity of a sample is expressed in units of mol kg^{-1}, then the total alkalinity will stay constant during changes of temperature and pressure. Moreover, when two water samples are mixed, then the resulting alkalinity is simply given by the weighted mean

$$M_m \cdot \mathrm{TA}_m = M_1 \cdot \mathrm{TA}_1 + M_2 \cdot \mathrm{TA}_2 \qquad (1.2.27)$$

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[6] In aqueous solutions, strong acids may be defined as follows. Consider an acid HA that can provide protons according to the equilibrium $\mathrm{HA} \rightleftharpoons \mathrm{A^-} + \mathrm{H^+}$ with acidity constant $K_A^* = [\mathrm{H^+}][\mathrm{A^-}]/[\mathrm{HA}]$. A strong acid is a strong proton donor, and its acidity constant is very large in water, i.e. the acid is virtually completely dissociated (examples: HCl, HBr). A strong base is a strong proton acceptor, and it is virtually fully protonated in water (an example is the $\mathrm{O^{2-}}$ ion, which does not exist as such in water because it is fully protonated: $\mathrm{O^{2-}} + \mathrm{H_2O} \longrightarrow 2\mathrm{OH^-}$; Atkins, 1990).

where M_1, M_2, and M_m and TA_1, TA_2, and TA_m are the masses and alkalinities of the two samples and the mixture, respectively.

At *p*H values above 8, the alkalinity of natural seawater is given to a very good approximation (for almost all practical purposes) by

$$\boxed{\mathrm{TA} \simeq [\mathrm{HCO}_3^-] + 2[\mathrm{CO}_3^{2-}] + [\mathrm{B(OH)}_4^-] + [\mathrm{OH}^-] - [\mathrm{H}^+] = \mathrm{PA}, \quad (1.2.28)}$$

i.e. by the sum of carbonate alkalinity ($[\mathrm{HCO}_3^-] + 2\,[\mathrm{CO}_3^{2-}]$), borate alkalinity ($[\mathrm{B(OH)}_4^-]$), and water alkalinity ($[\mathrm{OH}^-] - [\mathrm{H}^+]$).[7] This approximate expression will be denoted as practical alkalinity, PA. It is the sum of the charges of the major weak acids in seawater plus the charge of OH^- minus the charge of H^+. If not stated otherwise this approximation is used in calculations involving alkalinity.

Conservative quantities.

The term 'conservative ions' can be defined according to Drever (1982, p.52):

"Ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, and NO_3^- can be regarded as 'conservative' in the sense that their concentrations are unaffected by changes in *p*H, pressure, or temperature (within the ranges normally encountered near the earth's surface and assuming no precipitation or dissolution of solid phases, or biological transformations)."

When a larger *p*H range is considered, say down to a value of 4 which may be reached during titration, the species SO_4^{2-} has to be removed from Drever's list (see below). Other quantities such as total phosphate or total ammonia whose the concentrations are unaffected by changes in *p*H, pressure, and temperature will also be called 'conservative'. Later on, it will be shown that alkalinity is a conservative quantity that can be expressed in terms of non-conservative quantities (the traditional expression) or in terms of conservative quantities only (explicitly conservative expression).

In the following, the concept of alkalinity is introduced, starting with the carbonate alkalinity. Adding water and borate alkalinity, this will then lead us to a formal definition of total alkalinity. The first two sections of this chapter (Sections 1.2.2 to 1.2.3) consider alkalinity from a chemical point

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[7] The interpretation of the symbol $[\mathrm{H}^+]$ depends on the *p*H scale used (compare Section 1.3)

of view. This part is of central importance to the use of alkalinity in chemical oceanography, because it provides a definition of total alkalinity and a procedure to measure total alkalinity. In the context of CO_2 measurements in the ocean this is a crucial issue. However, we believe that more is required to understand the concept of total alkalinity. This is elaborated in subsequent sections in which the relationship between charge balance and alkalinity is derived and variations of total alkalinity in the ocean are discussed. One may say that the latter part of this chapter considers alkalinity from a physical or geochemical point of view.

1.2.2 Carbonate alkalinity

In order to illustrate the concept of alkalinity, the carbonate alkalinity is discussed first. We will study the carbonate chemistry of a seawater sample of simple chemistry during titration with strong acid. In contrast to natural seawater this 'simplified seawater' considered here does not contain any boron, phosphate, silicate, and ammonia[8]. In our example, it will be shown that the carbonate alkalinity measures the charge concentration of the anions of carbonic acid present in solution. Approaching the concept of alkalinity from this side, we might say that:

'Alkalinity keeps track of the charges of the ions of weak acids'

Consider one kilogram of 'simplified seawater' with pH of 8.2 and $\Sigma CO_2 = 2$ mmol kg^{-1}. We can use the equations derived in Section 1.1 to calculate the concentrations of the dissolved carbonate species. At $T = 25$°C, and $S = 35$ we have: $[CO_2] \simeq 8$ μmol kg^{-1}, $[HCO_3^-] \simeq 1.7$ mmol kg^{-1}, and $[CO_3^{2-}] \simeq 0.3$ mmol kg^{-1} (see left vertical axis in Figure 1.2.8).

Now let us add strong acid to the sample, i.e. we titrate the 'simplified seawater' by, say HCl. Hydrochloric acid is a strong acid and dissociates completely into H^+ and Cl^-. Upon addition of HCl to the sample, the protons will mainly combine with carbonate ion to form bicarbonate. As a result, $[CO_3^{2-}]$ decreases and $[HCO_3^-]$ initially increases (Figure 1.2.8). (The small change of volume during titration is neglected because it is not relevant to the current discussion.) After addition of roughly 0.5 mmol kg^{-1} HCl, $[HCO_3^-]$ is strictly decreasing while CO_2 is increasing because bicarbonate is converted to carbon dioxide. After addition of ~ 2.3 mmol kg^{-1} HCl,

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[8] The species HSO_4^-, HF, and HS^- are ignored, as well.

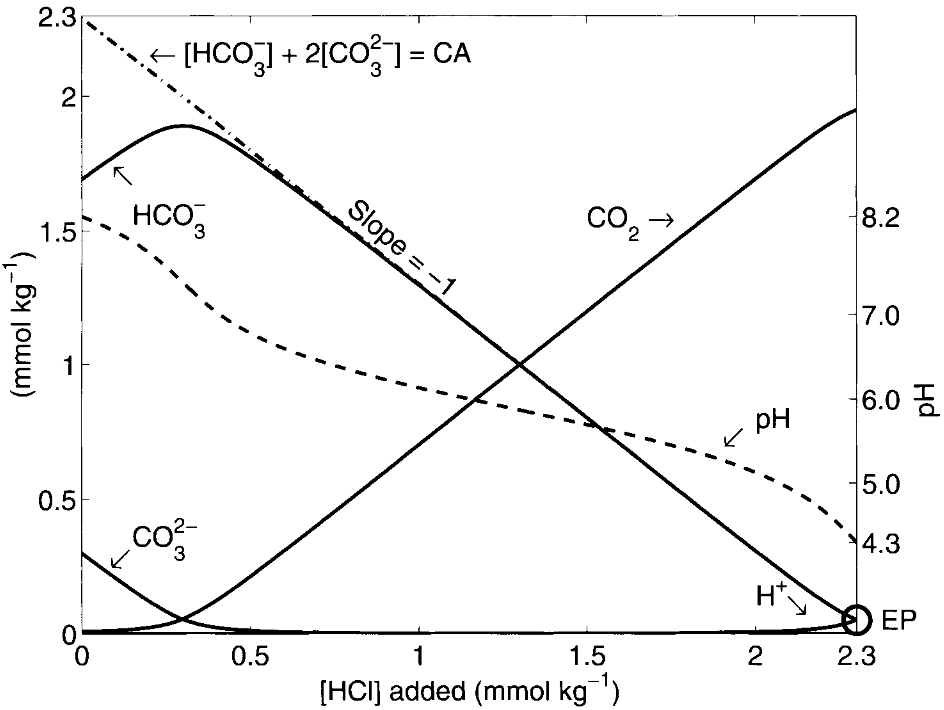

Figure 1.2.8: Titration of 'simplified seawater' with strong acid. Left vertical axis: concentrations of HCO_3^-, CO_3^{2-}, and CO_2. Right vertical axis: *p*H. Bicarbonate and carbonate ion have almost completely been converted to CO_2 when ~2.3 mmol kg^{-1} HCl have been added. This number is just equal to the initial carbonate alkalinity, CA = $[HCO_3^-] + 2[CO_3^{2-}]$, at the intercept with the left vertical axis. The second equivalence point is indicated by the circle (EP).

virtually all carbonate ion and bicarbonate have been converted to CO_2. In other words, the charge of the anions of carbonic acid have been neutralized by H^+.

If the quantity $[HCO_3^-]+2[CO_3^{2-}]$ is plotted as a function of acid added, a linear relationship is found over a wide range with a slope of −1 (Figure 1.2.8, dot-dashed line). This quantity is called the carbonate alkalinity:

$$CA \; = \; [HCO_3^-]+2[CO_3^{2-}] \, . \qquad (1.2.29)$$

For the 'simplified seawater' considered here, the number of moles of HCl that need to be added in order to neutralize the anions of the weak acid is approximately equal to the carbonate alkalinity. Graphically, this corresponds to the point where the graph of CA approaches the horizontal axis, that is, where the carbonate alkalinity goes to zero. More precisely, this point is approached at the so-called second equivalence point where

$$[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] , \tag{1.2.30}$$

(Dyrssen and Sillén, 1967) which is also referred to as a proton condition (see circle in Figure 1.2.8).[9] The proton condition is very important because it can be determined from titration data, see below. The number of moles of HCl added to reach this point is just equal to the initial carbonate alkalinity of our sample (~2.3 mmol kg^{-1}).

We see that the carbonate alkalinity in our example measures the charge concentration of the anions of the weak acid present in solution. If, for a given ΣCO_2, the sample initially had a higher pH and thus a higher carbonate ion content, more acid would have been required to neutralize the charge of the weak acid - and vice versa. The carbonate alkalinity here is the number of equivalents of strong acid required to neutralize 1 kg of seawater until the second equivalence point is reached.

As mentioned above, the proton condition is very useful because it can be determined from titration data. As a result, the definition of alkalinity is based on an analytical procedure that measures alkalinity in terms of acid added and is therefore an operational definition. Historically, this concept was widely used to determine alkalinity, for example, by the Gran method (cf. e.g. Gran, 1952; Dyrssen and Sillén, 1967). We will see that the modern definition of total alkalinity is explicitly based on a chemical model of the acid-base processes occurring in seawater (Section 1.2.3). The result is that total alkalinity can be defined unambiguously and a procedure is provided to measure it - the methods frequently used are the modified Gran method or curve-fitting procedures (for summary, see Barron et al., 1983; Dickson,

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[9] The second equivalence point is located at a pH value of about 4.3. At this pH the concentrations of CO_3^{2-} and OH^- are much smaller than those of HCO_3^- and H^+ (compare Fig. 1.1.2). Thus the second equivalence point condition can be stated as $[H^+] \simeq [HCO_3^-]$.

1992; DOE, 1994; Anderson et al., 1999).

Alkalinity as a master variable.
Given the alkalinity and ΣCO_2, carbonate system parameters can be determined. Assume that the total alkalinity and ΣCO_2 of a seawater sample have been determined to be 2.3 and 2.0 mmol kg^{-1}, respectively. To a first approximation we may take the total alkalinity equal to the carbonate alkalinity:

$$\mathrm{TA} \simeq [HCO_3^-] + 2[CO_3^{2-}] \, .$$

Furthermore, because $[CO_2]$ is small, we may set

$$\Sigma CO_2 \simeq [HCO_3^-] + [CO_3^{2-}] \, .$$

Thus, the carbonate ion concentration in seawater is roughly given by the difference between TA and ΣCO_2:

$$[CO_3^{2-}] \simeq \mathrm{TA} - \Sigma CO_2 \, ,$$

which yields $[CO_3^{2-}] = 300$ μmol kg^{-1} and thus $[HCO_3^-] = 1700$ μmol kg^{-1}. Including CO_2, and using $\mathrm{TA} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$ (see below), one obtains an equation of fifth order in $[H^+]$ which can be solved numerically (see Appendix B). The result is $[CO_3^{2-}] = 220$ μmol kg^{-1}, $[HCO_3^-] = 1768$ μmol kg^{-1}, and $[CO_2] = 12$ μmol kg^{-1} at $T = 25$°C and $S = 35$. The difference between the two calculations is mainly due to the fact that the contribution of boron to the total alkalinity has been ignored in the first case.

Including borate and water alkalinity

Considering the titration outlined in the previous section, it is clear that in natural seawater not only the carbonic acid system but every similar acid-base system present in solution will contribute to the alkalinity as determined by titration. Upon addition of strong acid, all proton acceptors will take up protons, regardless whether the anions of, for example, carbonic acid, boric acid, or phosphoric acid are considered. If we want to use alkalinity as a master variable of the carbonate system in natural seawater, we therefore have to be careful because the total alkalinity is not equal to the carbonate alkalinity. In order to calculate carbonate system parameters correctly, our definition of alkalinity has to include additional terms arising from the presence of acid-base systems other than carbonic acid.

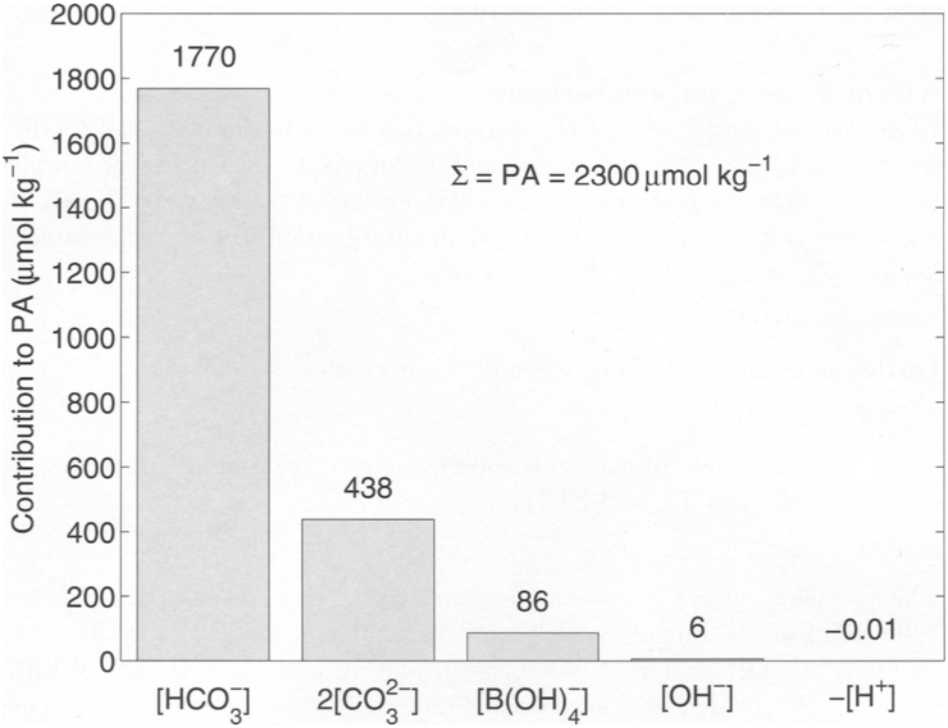

Figure 1.2.9: Contribution of the various species to PA (alkalinity for most practical purposes) at PA = 2300 μmol kg^{-1}, DIC = 2000 μmol kg^{-1}, $T_c = 25$°C, and $S = 35$. It is often sufficient to consider this subset of total alkalinity.

In many ocean waters, the most important acid-base systems that contribute to total alkalinity in addition to carbonic acid are boric acid and water itself. The borate alkalinity and water alkalinity are:

$$\begin{aligned} \text{borate alkalinity} &= [B(OH)_4^-] \\ \text{water alkalinity} &= [OH^-] - [H^+] \ . \end{aligned}$$

Adding these contributions to the carbonate alkalinity, we have:

$$\boxed{PA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] \ . \qquad (1.2.31)}$$

In many cases this is a good approximation to the total alkalinity at seawater *p*H and we denote it by PA (alkalinity for most practical purposes). This approximation will be used in the vast majority of calculations given in the current book. Typical contributions of the various compounds to PA are

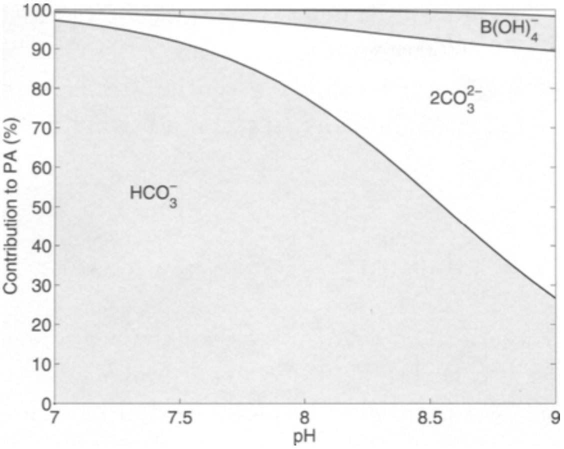

Figure 1.2.10: Relative contribution of various compounds to PA as a function of pH (DIC $= 2000$ μmol kg^{-1}, $T_c =$ 25°C, $S = 35$). Areas show the percentage of each compound HCO_3^- (lower shaded area and left vertical axis), $2CO_3^{2-}$ (large white area), $B(OH)_4^-$ (upper shaded area), and OH^- (upper small white area).

shown in Figure 1.2.9. In our example, the carbonate alkalinity contributes 96% to PA, demonstrating that the carbonate alkalinity is by far the most important part of PA. This statement also holds true for a wide range of pH (Figure 1.2.10).

Proton acceptors and donors

The necessity for the inclusion of further acid-base systems such as the dissociation of boric acid and water into the alkalinity shows that a more general concept of alkalinity is required. It turns out that considering a balance between proton acceptors and proton donors is a very useful approach which will finally be included in the definition of the total alkalinity (Section 1.2.3). For example, carbonate ion and bicarbonate are proton acceptors that act as bases. On the other hand, H^+ is a proton donor that acts as an acid (recall that the symbol H^+ actually represents species such as H_3O^+). We can thus state that the alkalinity defined by Eq. (1.2.31) is the excess of bases (proton acceptors) over acids (proton donors) in seawater, where the proton acceptors are $[HCO_3^-]$, $[CO_3^{2-}]$, $[B(OH)_4^-]$, and $[OH^-]$ and the proton donor is H^+ (cf. Rakestraw, 1949). The point at which PA equals zero defines the following proton condition:

$$\underbrace{[H^+]}_{\text{proton donor}} = \underbrace{[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-]}_{\text{proton acceptors}} . \tag{1.2.32}$$

This expression is analogous to the proton condition defined in Eq. (1.2.30) for the 'simplified seawater'.

Having introduced the basic concept of alkalinity, proton acceptors and donors, and the proton condition, we now move on to the definition of total alkalinity. The task of defining total alkalinity essentially is how to correctly expand Eqs. (1.2.31) and (1.2.32) in order to include further acid-base systems (Dickson, 1981).

1.2.3 Dickson's definition of alkalinity

The currently most precise definition of titration or total alkalinity was given by Dickson (DOE, 1994; compare also Dickson, 1981): "The total alkalinity of a natural water is thus defined 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."[10] For the compounds found in seawater, the expression for total alkalinity following from Dickson's definition reads:

$$\boxed{\begin{aligned} \mathrm{TA} \;=\; & [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] \\ & +[\mathrm{HPO_4^{2-}}] + 2[\mathrm{PO_4^{3-}}] + [\mathrm{H_3SiO_4^-}] \\ & +[\mathrm{NH_3}] + [\mathrm{HS^-}] - [\mathrm{H^+}]_\mathrm{F} - [\mathrm{HSO_4^-}] - [\mathrm{HF}] - [\mathrm{H_3PO_4}] \end{aligned} \qquad (1.2.33)}$$

where $[\mathrm{H^+}]_\mathrm{F}$ is the free concentration of hydrogen ion (compare Section 1.3). The possible contribution of unknown protolytes to the total alkalinity is discussed in Bradshaw and Brewer (1988a).

The appropriate proton condition that defines the equivalence point is given by:

$$\begin{aligned} & [\mathrm{H^+}]_\mathrm{F} + [\mathrm{HSO_4^-}] + [\mathrm{HF}] + [\mathrm{H_3PO_4}] \\ = \; & [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] \\ & +[\mathrm{HPO_4^{2-}}] + 2[\mathrm{PO_4^{3-}}] + [\mathrm{H_3SiO_4^-}] \\ & +[\mathrm{HS^-}] + [\mathrm{NH_3}] \; , \end{aligned} \qquad (1.2.34)$$

where the proton donors appear on the left-hand side and the proton acceptors appear on the right-hand side.

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[10] It is noted that the thermodynamic constant K is used in this case, and not the stoichiometric constant K^* which is usually employed for seawater. The reason for this is that K is independent of salinity. Thus, the constraint on the dissociation constants of the weak acids is unambiguous.

The total alkalinity of a sample according to Eq. (1.2.33) is determined as follows. The sample is titrated with strong acid, usually HCl, and the pH is recorded as a function of acid added. Then TA is calculated by non-linear curve fitting of the theoretical titration curve based on Eq. (1.2.33) to the actual data using all the titration points. This procedure is also called inverse calculation (e.g. Dickson, 1981; Johansson and Wedborg, 1982; Anderson et al., 1999). It is important that this determination of TA uses an explicit model of the acid-base reactions occurring in seawater. This modern definition of alkalinity is conceptually different from the operational definition introduced in Section 1.2.2. That is, the right-hand side of Eq. (1.2.33) explicitly states which acid-base reactions contribute to TA, whereas an operational definition simply provides a numerical value for TA based on the analytical procedure.

Dickson's definition proposes that bases formed from weak acids with $p\mathrm{K} \geq 4.5$ (e.g. HCO_3^-) are to be considered proton acceptors, while acids with $p\mathrm{K} < 4.5$ (e.g. H_3PO_4) are to be considered proton donors. This definition unambiguously separates proton acceptors from proton donors. Figure 1.2.11 illustrates this separation by the vertical dashed line at $p\mathrm{H} = 4.5$ for the acid-base systems included in Eq. (1.2.33). With this definition at hand, the inclusion of other acid-base systems into the definition of TA is straightforward. Note that the choice of the value 4.5 which defines proton acceptors and donors is arbitrary, though thoughtfully chosen (Dickson, 1981).

Contribution of uncharged species

It may appear surprising that Eq. (1.2.33) contains also uncharged species such as NH_3, HF, and H_3PO_4. It is noted that Eq. (1.2.33) therefore cannot be derived from a charge balance because this would involve charged species only. The relationship between charge balance and alkalinity is examined in detail in Section 1.2.4. We shall here briefly explain why uncharged species occur in the definition of TA, using phosphoric acid as an example.

The proton condition (1.2.34) is a mass balance for hydrogen ion which defines the so-called zero level of protons. (Of course, this does not mean there are zero protons in solution!) With respect to a particular acid-base system, the proton condition defines which species are to be considered proton donors and acceptors. Figure 1.2.12 illustrates the situation for phosphoric acid. In this case, $H_2PO_4^-$ defines the zero level of protons

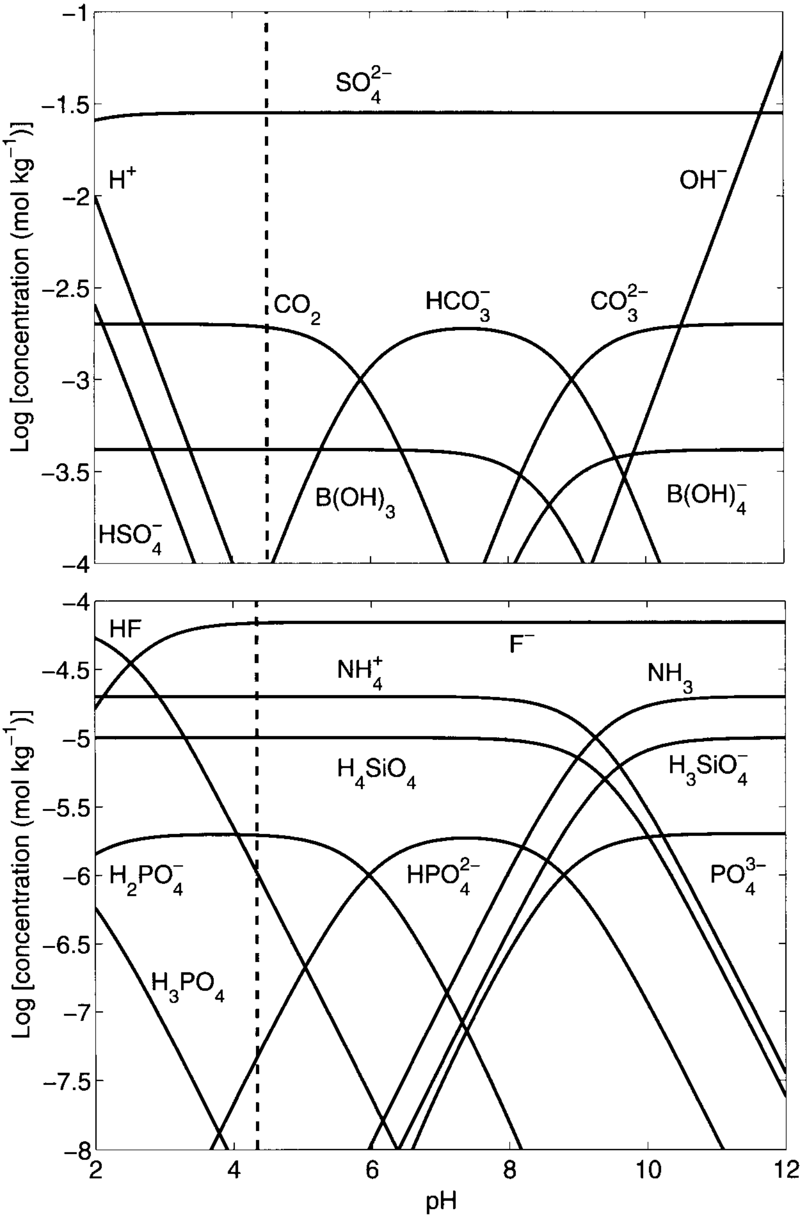

Figure 1.2.11: Extended Bjerrum plot showing the acid-base systems relevant to TA in seawater. The vertical dashed line at pH = 4.5 indicates which species are to be considered proton donors and acceptors (cf. Figure 1.2.12).

because it is the dominant species at pH = 4.5.[11] As a result, H_3PO_4 is

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[11] A significant confusion arises in the literature in some papers where the zero level

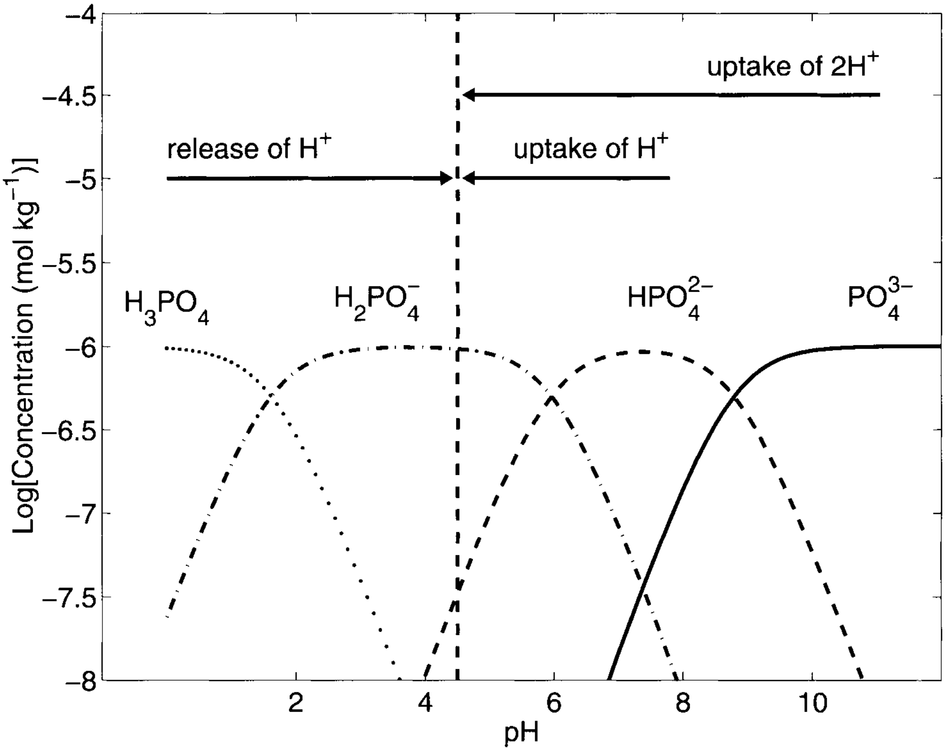

Figure 1.2.12: Application of the definition of TA to the phosphoric acid system. The species $H_2PO_4^-$ defines the zero level of protons. As a result, PO_4^{3-} is a proton acceptor with two protons less than $H_2PO_4^-$. H_3PO_4 is a proton donor with one proton more than $H_2PO_4^-$.

a proton donor that provides a proton when converted to $H_2PO_4^-$. This is the reason why also uncharged species appear in the definition of total alkalinity.

With respect to carbonic acid, HCO_3^- and CO_3^{2-} are to be considered proton acceptors because both species take up protons to form H_2CO_3. The dominant chemical species at $pH = 4.5$ which defines the zero level of protons is carbonic acid (H_2CO_3 and $CO_2 + H_2O$) and we can state that HCO_3^-, for instance, contains less protons than the defined zero level, H_2CO_3 (Figure 1.2.13). Generally, the right-hand side of Eq. (1.2.34) consists of those species which contain less protons than the defined zero level, while

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for phosphoric acid has been chosen to be H_3PO_4. This is not 'wrong' just confusing as it implies that adding H_3PO_4 will not change the total alkalinity - though you can acidify the solution enough to reduce the carbonate alkalinity to zero (Dickson, personal communication).

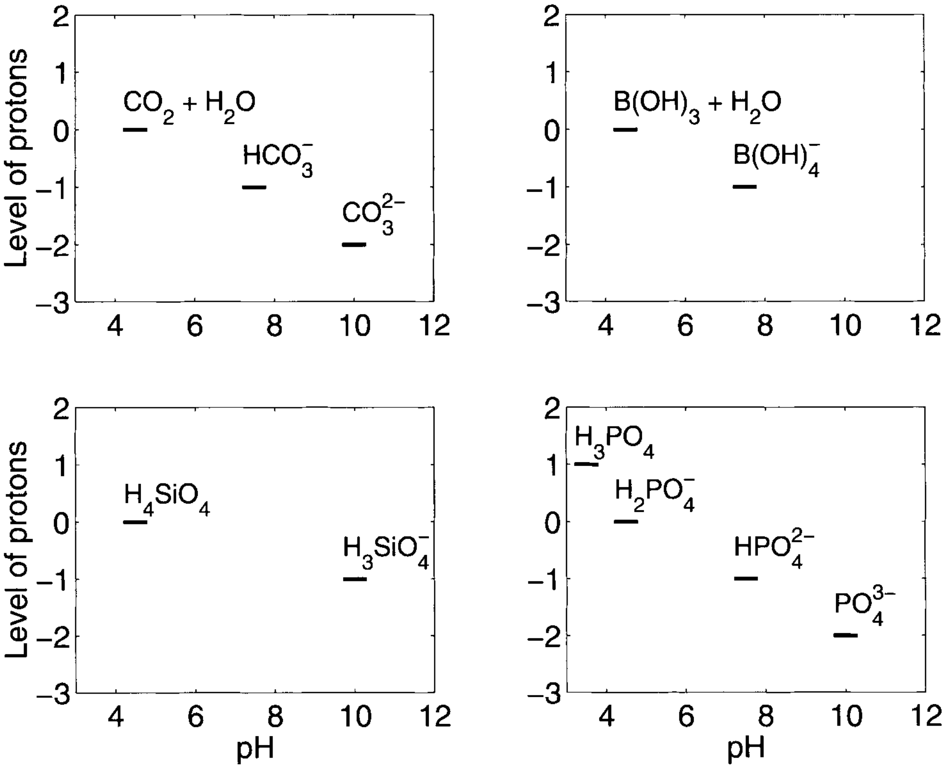

Figure 1.2.13: Chemical species of several acid-base systems and their proton levels; the dominant species over a given pH range is indicated. The zero level of protons of a particular acid-base system is defined by the dominant species at $p\mathrm{H} = 4.5$. For carbonic, boric, silicic, and phosphoric acid, these species are H_2CO_3, $B(OH)_3$, H_4SiO_4, and $H_2PO_4^-$. H_2O (not shown) is the dominant species over the whole pH range from below 4 to above 10 for the system encompassing H_2O, H^+, and OH^-, and thus defines the zero level of protons for the dissociation of water.

the left-hand side of Eq. (1.2.34) consists of those species with more protons than the defined zero level (Dickson, 1981).

Summary. The concept of alkalinity was introduced, starting with the carbonate alkalinity (CA). Summarizing this preliminary discussion of alkalinity, we may say that 'alkalinity keeps track of the charges of the ions of weak acids and can be determined by titration'. Further acid-base reactions occurring in natural seawater were included, i.e. the borate and water alkalinity were added to yield PA (alkalinity for most practical purposes). Finally, a formal definition of total alkalinity (TA) was given by Eq. (1.2.33) which is based on a balance of proton acceptors and donors. In addition, the procedure to measure TA was outlined (for details, see Dickson, 1981;

Johansson and Wedborg, 1982; Anderson et al., 1999). Equations to calculate carbonate system parameters using measured TA as a master variable are given in Appendix B. The subjects discussed so far are of central importance for CO_2 measurements in the ocean. This concludes our treatment of alkalinity from a chemical point of view.

The remainder of this chapter will add nothing new to the definition of total alkalinity. The formal definition may often suffice for the application of the total alkalinity concept but usually a deeper understanding is required in order to answer questions such as: Does alkalinity change due to nitrogen assimilation by algae and - if yes - how does it change? The answer is yes, it does - although NO_3^- and NH_4^+ do not show up in the formal definition of TA, see below.

1.2.4 Total alkalinity and charge balance

While the preceding sections considered total alkalinity from a chemical point of view, we will now approach the concept of alkalinity from a physical or geochemical point of view. It will be shown that alkalinity is closely related to the charge balance in seawater which makes it an appealing concept because properties such as the conservation of total alkalinity can be derived.

Sillén (1961) argued that considering the origin of the ocean, we might say that the ocean is the result of a gigantic acid-base titration in which acids such as HCl, H_2SO_4, and CO_2 that have leaked out from the interior of the earth are titrated with bases derived from the weathering of primary rock.[12] As we have seen in the previous chapters, the buffer capacity and alkaline properties of seawater can be mainly attributed to the dissolved carbonate species. One may therefore state that the ocean owes its buffer properties to the presence of carbonic acid, which is correct in some respect.

Sillén (1967) pointed out, however, that the buffer capacity of the carbonates in solution is pitifully small compared with the amounts of acids and bases that have passed through the ocean system in the course of time. With respect to the definition of total alkalinity in terms of an acid-base balance, this view suggests a more fundamental reason for the alkaline property of seawater. We will see that the origin of alkalinity in the ocean has to do with the charge balance of the major conservative ions in seawater.

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[12] Sillén continues: "In this acid-base titration, volcanoes against weathering, it would seem that we are about 0.5 per cent from the equivalence point. This, by the way, is better than most students of chemistry do in their first titrations."

The sum of the charges of the major cations Na^+, K^+, Mg^{2+}, and Ca^{2+} are not exactly balanced by the major anions Cl^- and SO_4^{2-}. This small charge imbalance is responsible for the total alkalinity in the ocean and is mainly compensated for by the anions of carbonic acid. We may say that:

> *'Total alkalinity is equal to the charge difference between conservative cations and anions'*

Total alkalinity in simple systems

The close relation between total alkalinity and charge balance will firstly be demonstrated by considering simple aqueous solutions which are less complicated than natural seawater. Seawater is a very complicated system because it contains many different cations and anions and a number of weak acids and bases. McClendon et al. (1917) stated that:

> *'The sea is of too complex a composition to admit of any simple mathematical relations'*

(cf. Dickson, 1992). In order to get rid of some of the complications associated with natural seawater, simple systems that contain only Cl^-, Na^+, and one weak acid are discussed first.

System I: Na^+, Cl^-, and one weak acid

Let us consider a solution that contains only Na^+, Cl^-, and a monoprotic weak acid, represented by HA:

$$\mathrm{HA} \rightleftharpoons \mathrm{A}^- + \mathrm{H}^+; \qquad K_\mathrm{A}$$

with $pK_\mathrm{A} = 6$. The following initial conditions are prescribed: $p\mathrm{H}_i = 8.2$, $[\mathrm{Na}^+]_i = 0.6$ mol kg^{-1}, and the total concentration of A, $\mathrm{A_T} = [\mathrm{A}^-]_i + [\mathrm{HA}]_i = 2300\ \mu$mol kg^{-1}. The pH value is therefore similar to typical surface ocean conditions, the concentration of sodium is similar to the total charge of all cations in seawater at $S = 35$, and the total concentration of A is numerically similar to typical alkalinity values in surface seawater.

From the prescribed values, the initial concentrations of OH^- and A^- can be calculated:

$$\begin{aligned} [\mathrm{OH}^-]_i &= K_\mathrm{W}/[\mathrm{H}^+]_i = 9.6\ \mu\mathrm{mol\ kg}^{-1} \\ [\mathrm{A}^-]_i &= \mathrm{A_T}/(1+[\mathrm{H}^+]_i/K_\mathrm{A}), = 2286\ \mu\mathrm{mol\ kg}^{-1} \end{aligned}$$

It is important to note that the concentration of Cl^- was not prescribed. It is set, however, by requiring electroneutrality:

$$[Cl^-] = [Na^+] + [H^+] - [A^-] - [OH^-] \; = \; 0.5977 \text{ mol kg}^{-1} \; .$$

Thus, the concentration of Cl^- is slightly smaller than that of Na^+. The difference of the concentration of the cations and anions of strong bases and acids, that is, the charge imbalance of the conservative ions, is:

$$[Na^+] - [Cl^-] = \mathrm{TA} = [A^-] + [OH^-] - [H^+] \; . \tag{1.2.35}$$

The right-hand side of Eq. (1.2.35) is analogous to the definition of TA in terms of acid-base reactions in Eq. (1.2.33). However, we have now expressed the alkalinity entirely in terms of the conservative ions, the left-hand side of Eq. (1.2.35). It is this property that makes TA a conservative quantity. The expression on the left-hand side of Eq. (1.2.35) will be denoted as 'explicitly conservative alkalinity' or $\mathrm{TA}^{(ec)}$ because each term and not only the whole expression is conservative; the expression on the right-hand side of Eq. (1.2.35) will be represented by the symbol TA. We will see that considering the $\mathrm{TA}^{(ec)}$ is extremely useful when determining changes of TA due to biogeochemical process (Section 1.2.7).

The relationship between the charge balance of the conservative ions and TA for the simple system can be illustrated by considering the titration of the system with HCl (Figure 1.2.14). $\mathrm{TA}^{(ec)}$ is plotted in Figure 1.2.14a, while TA, i.e. proton acceptors and donors, is included in Figure 1.2.14b. Initially, there is a small deficit of $[Cl^-]$ compared to $[Na^+]$ of about 2.3 mmol kg^{-1} which is exactly equal to the initial total alkalinity (Figure 1.2.14a). At the endpoint of the titration, the initial deficit has been compensated by addition of HCl. At this point, the pH is 4.32, the concentrations of chloride and sodium ions are equal, and the total alkalinity is zero.

The point at which $[Cl^-] = [Na^+]$ corresponds to the zero level of protons, i.e. the equivalence point of the acid-base system:

$$[H^+] = [A^-] + [OH^-] \tag{1.2.36}$$

which is indicated by the circle in Figure 1.2.14b. At this point, A^- has almost completely been neutralized by H^+ and converted to HA. The total alkalinity of the simple system considered here, can be equally well defined by the excess of proton acceptors over proton donors (TA) or by the charge difference of the conservative ions ($\mathrm{TA}^{(ec)}$). A glance at Figure 1.2.14 shows that it may be much more simple to consider the conservative ions instead of dealing with all the details of the acid-base system.

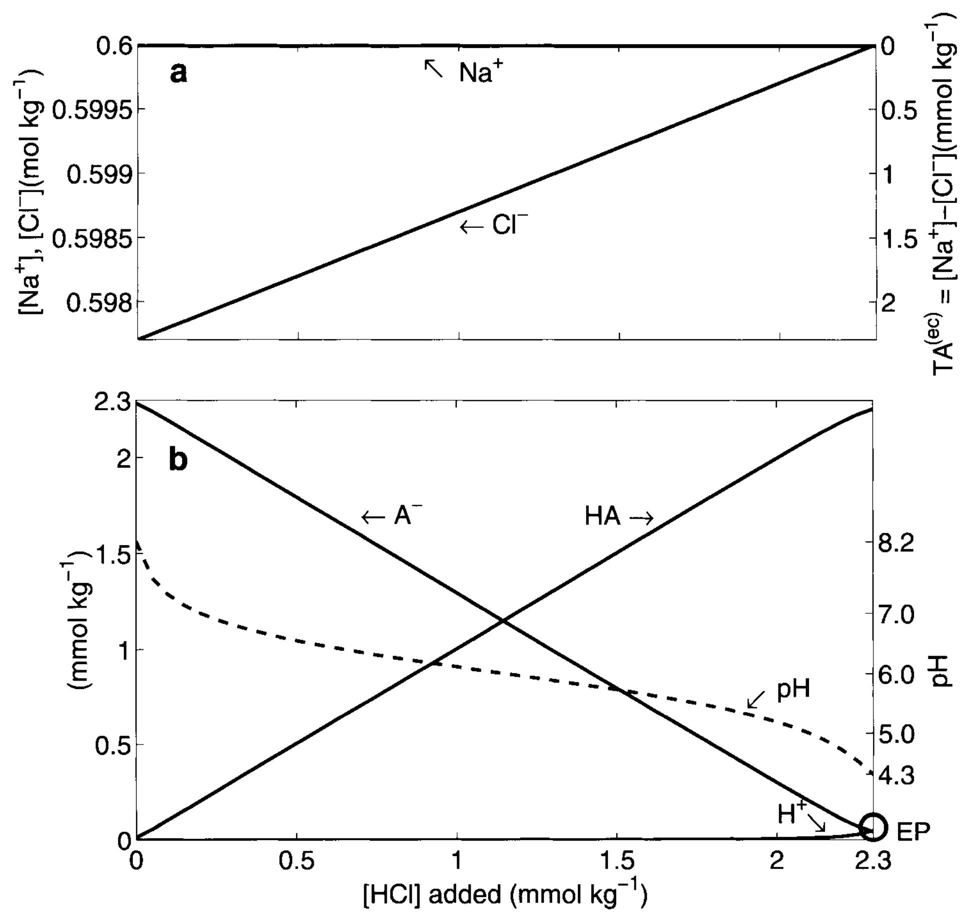

Figure 1.2.14: Titration of System I by hydrochloric acid. (a) Concentrations of the conservative ions. (b) Concentrations of the compounds of the acid-base system and pH. The difference $[Na^+] - [Cl^-]$ is exactly equal to the total alkalinity, $TA = [A^-] + [OH^-] - [H^+]$.

System II: Table salt and a weak acid dissolved in water

It was mentioned above that the total alkalinity of System I is similar to typical values observed in surface seawater. It was then shown that the alkalinity is due to the small but important charge imbalance of the conservative ions. In order to emphasize the significance of this small imbalance we will now consider a system in which the imbalance is missing. System II consists of an aqueous solution containing 2300 μmol kg^{-1} of the weak acid discussed in System I and of 0.6 mol kg^{-1} Na^+ and Cl^-. In other words, System II is made of pure water to which the weak acid and table salt (NaCl) have been added. System II is very similar to System I. However, the important difference is that the concentrations of Na^+ and Cl^- are identical in System II. In contrast to System I, the pH of System II is not an independent initial parameter but can be calculated from electroneutrality:

$$\begin{aligned} 0 &= \text{TA} = [\text{Na}^+] - [\text{Cl}^-] \\ &= [\text{A}^-] + [\text{OH}^-] - [\text{H}^+] \\ &= \frac{\text{A}_\text{T}}{1 + \dfrac{[\text{H}^+]}{K_\text{A}}} + \frac{K_W}{[\text{H}^+]} - [\text{H}^+]. \end{aligned}$$

The numerical solution of the resulting cubic equation for $[\text{H}^+]$ yields $p\text{H} \simeq 4.32$. Thus the addition of the weak acid to an otherwise neutral table salt solution at $p\text{H} = 7$ leads to a low pH value. This value is reached in System I only after addition of an appreciable amount of strong acid. Actually, the titration of System I to the pH of the proton condition transforms System I into System II. Therefore it is not surprising that the pH of System II is equal to the pH of System I after titration to the equivalence point where the total alkalinity equals zero (see Figure 1.2.14). In System II, most of the weak acid is in the uncharged form, i.e. $p\text{H} < p\text{K}$, and therefore the system is unable to buffer any addition of acids.

From the comparison of System I and II it is concluded that *the imbalance of the charge of the conservative ions is responsible for alkalinity.* As a result, the system is buffered. In seawater, TA varies with salinity, see Section 1.2.7. This variation is due to the total charge imbalance of the conservative ions which varies with salinity. (Note that the composition of sea salt is virtually constant). Seawater therefore owes its buffer capacity to the charge imbalance of the conservative ions. Freshwater systems usually contain only small amounts of conservative ions and are therefore only weakly buffered. Small changes in acid concentrations due to, for example, uptake of CO_2 by plants or input of acid rain thus result in large shifts of pH.

1.2.5 The charge balance in natural seawater

Natural seawater contains many more ions than the simple systems discussed above. Nevertheless, the same principle of electroneutrality applies to seawater, as well. The sum of the charges of all ions present in seawater must equal zero. This is mathematically expressed by:

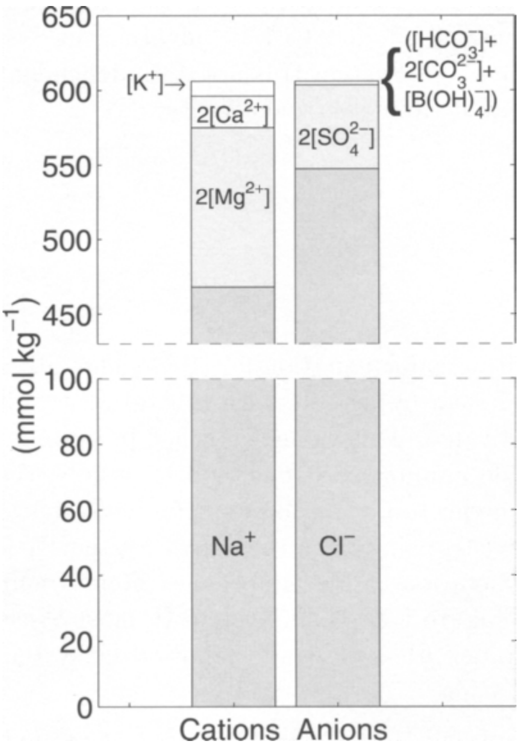

Figure 1.2.15: Charge balance of the major ions in seawater (cf. Broecker and Peng, 1998). The small excess charge of the conservative cations over anions is mainly balanced by $[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-]$.

$$\begin{aligned}&[Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + [K^+] + ... + [H^+]_F \\ &\qquad -[Cl^-] - 2[SO_4^{2-}] - [NO_3^-] \\ &-[HCO_3^-] - 2[CO_3^{2-}] - [B(OH)_4^-] - [OH^-] - ... \quad = \quad 0 \qquad (1.2.37)\end{aligned}$$

or

$$\sum_j z_j[c_j] = 0, \qquad (1.2.38)$$

where $[c_j]$ and z_j are the concentration and charge of compound j, respectively.

The charge balance of the major ions in seawater is illustrated in Figure 1.2.15, where all minor species have been neglected. First of all, it shows that the charge imbalance between the conservative cations and anions is very small compared to their total concentration ($\sim$ 2 vs. $\sim$ 600 mmol kg^{-1}). We also see that the small excess of positive charge

Table 1.2.7: Concentrations, $[c_i]$ (mmol kg^{-1}), and charge concentrations, $[q_i] = z_i \cdot [c_i]$ (mmol kg^{-1}), of conservative ions in seawater at $S = 35$ (after Bakker, 1998).

Cations	$[c_i]$	$[q_i]$	Anions	$[c_i]$	$[q_i]$
Na^+	467.8	467.8	Cl^-	545.5	545.5
Mg^{2+}	53.3	106.5	SO_4^{2-}	28.2	56.4
Ca^{2+}	10.3	20.6	Br^-	0.8	0.8
K^+	9.9	9.9	F^-	0.1	0.1
Sr^{2+}	0.1	0.2		.	.
Total	.	605.0	Total	.	602.8

($[Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + [K^+]$) over negative charge ($[Cl^-] + 2[SO_4^{2-}]$) is compensated by $[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-]$, where the latter sum represents the most important contribution to TA. Table 1.2.7 lists the concentrations and charge concentrations of the major conservative cations and anions in seawater at $S = 35$. The total charge concentration of the conservative cations yields 605.0 mmol kg^{-1}, while the total charge concentration of the conservative anions yields 602.8 mmol kg^{-1}. The small charge imbalance of 2.2 mmol kg^{-1} is equal to the total alkalinity in seawater (strictly, this is only correct when phosphate, ammonia and bisulfate ion are neglected, cf. Appendix C.1).

The fact that the alkalinity can be expressed in terms of the charge imbalance of the conservative ions allows us to derive a very useful equation. Equation (1.2.37) may be rewritten such that all conservative ions appear on the left-hand side and all non-conservative ions appear on the right-hand side:

$$\begin{aligned} &\sum \text{conservative cations} - \sum \text{conservative anions} \\ &= [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] \qquad (1.2.39) \\ &\pm \text{ minor compounds} \end{aligned}$$

This expression is very similar to the one given for PA in Eq. (1.2.31) (alkalinity for most practical purposes). Neglecting the term 'minor compounds', we can write:

$$\boxed{\begin{array}{l} [\mathrm{Na^+}] + 2[\mathrm{Mg^{2+}}] + 2[\mathrm{Ca^{2+}}] + [\mathrm{K^+}] + \ldots \\ -[\mathrm{Cl^-}] - 2[\mathrm{SO_4^{2-}}] - [\mathrm{NO_3^-}] - \ldots \\ = \mathrm{PA} = \\ [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] - [\mathrm{H^+}] \\ \text{or:} \\ \mathrm{TA^{(ec)}} = \mathrm{PA} \end{array} \qquad (1.2.40)}$$

The right-hand side of Eq. (1.2.40) simply expresses PA in terms of proton acceptors and donors as discussed in the first part of this chapter. However, the left-hand side of Eq. (1.2.40) expresses PA entirely in terms of the conservative ions (explicitly conservative alkalinity, $\mathrm{TA^{(ec)}}$). This is very useful as will be elaborated in the following.

1.2.6 Conservation of total alkalinity

The fact that total alkalinity can be expressed by the charge balance of the conservative ions in seawater allows us to make important inferences without using the formal definition of total alkalinity (Eq. 1.2.33).[13]

Firstly, if total alkalinity of a seawater sample is expressed in units of mol $\mathrm{kg^{-1}}$, then the total alkalinity will remain exactly conserved during changes of temperature and pressure. This follows directly from $\mathrm{TA^{(ec)}}$ because the concentration of the conservative ions in 1 kg seawater is unaffected by changes of temperature and pressure. This is not obvious from the alkalinity expression in terms of weak acids (right-hand side of Eq. (1.2.40)) because the individual concentrations of the chemical species in this expression do change as a function of temperature and pressure. The reason for this is that the chemical equilibria (pK's) depend on temperature and pressure.

Secondly, the charge of the conservative ions does not change when, for instance, $\mathrm{CO_2}$ is exchanged between water and air or when $\mathrm{CO_2}$ is taken up or respired by algae. During uptake and release of $\mathrm{CO_2}$, the individual concentrations on the right-hand side of Eq. (1.2.40) may change dramatically because of variations in $\Sigma\mathrm{CO_2}$ and pH. However, $\mathrm{TA^{(ec)}}$ is constant

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[13] Note that the relationship between charge balance and alkalinity in Eq. (1.2.40) was strictly derived here only for PA and not TA. The derivation for TA can be found in Appendix C.1.

because the conservative ions are not affected and therefore alkalinity is constant. On the other hand, if a strong base such as NaOH is added to the sample, the alkalinity increases because $[\mathrm{Na}^+]$ and therefore also $\mathrm{TA}^{(\mathrm{ec})}$ increases. If strong acid such as HCl is added to the sample, the alkalinity decreases because $[\mathrm{Cl}^-]$ (with a negative sign in the $\mathrm{TA}^{(\mathrm{ec})}$ expression) increases. Note that TA changes by one unit for every unit of strong base or acid added because these substances dissociate completely. Analogously, changes of TA due to biogeochemical processes in the ocean can be understood (Section 1.2.7).

Mixing and conservation of mass, salt, dissolved inorganic carbon, and total alkalinity.

When two bodies ($i = 1, 2$) of seawater with different properties are mixed, the amounts of mass (M_i), salt ($M_i \cdot S_i$), dissolved inorganic carbon ($M_i \cdot \mathrm{DIC}_i$), and total alkalinity ($M_i \cdot \mathrm{TA}_i$), respectively, add up to yield the exact property values of the mixture (index m):

$$M_m = M_1 + M_2 \tag{1.2.41}$$

$$M_m \cdot S_m = M_1 \cdot S_1 + M_2 \cdot S_2 \tag{1.2.42}$$

$$M_m \cdot \mathrm{DIC}_m = M_1 \cdot \mathrm{DIC}_1 + M_2 \cdot \mathrm{DIC}_2 \tag{1.2.43}$$

$$M_m \cdot \mathrm{TA}_m = M_1 \cdot \mathrm{TA}_1 + M_2 \cdot \mathrm{TA}_2 \tag{1.2.44}$$

whereby S_i, DIC_i, and TA_i are in gravimetric (per mass) units. In contrast, neither volume nor single components of DIC or TA such as $[\mathrm{CO}_2]$, $[\mathrm{HCO}_3^-]$, or $[\mathrm{CO}_3^{2-}]$ are conserved when two water bodies are mixed (see Exercises 1.9 and 1.10). The conservation property of DIC and TA is the reason for using these two quantities in oceanic models of the carbon cycle as prognostic variables.

Thirdly, total alkalinity is conserved during mixing. When two water masses are mixed with different properties (salinity S_i, temperature T_i, mass M_i, $i = 1, 2$), the charges of conservative ions are additive, i.e. the following relation is obeyed (cf. box on mixing):

$$M_m \cdot \sum_s [q_{m,s}] = M_1 \cdot \sum_s [q_{1,s}] + M_2 \cdot \sum_s [q_{2,s}], \tag{1.2.45}$$

where the summation index s runs over all conservative ions; the index m denotes quantities after mixing, and $M_m = M_1 + M_2$. As a consequence, total alkalinity is also additive and the the relation

$$M_m \cdot \mathrm{TA}_m = M_1 \cdot \mathrm{TA}_1 + M_2 \cdot \mathrm{TA}_2 \tag{1.2.46}$$

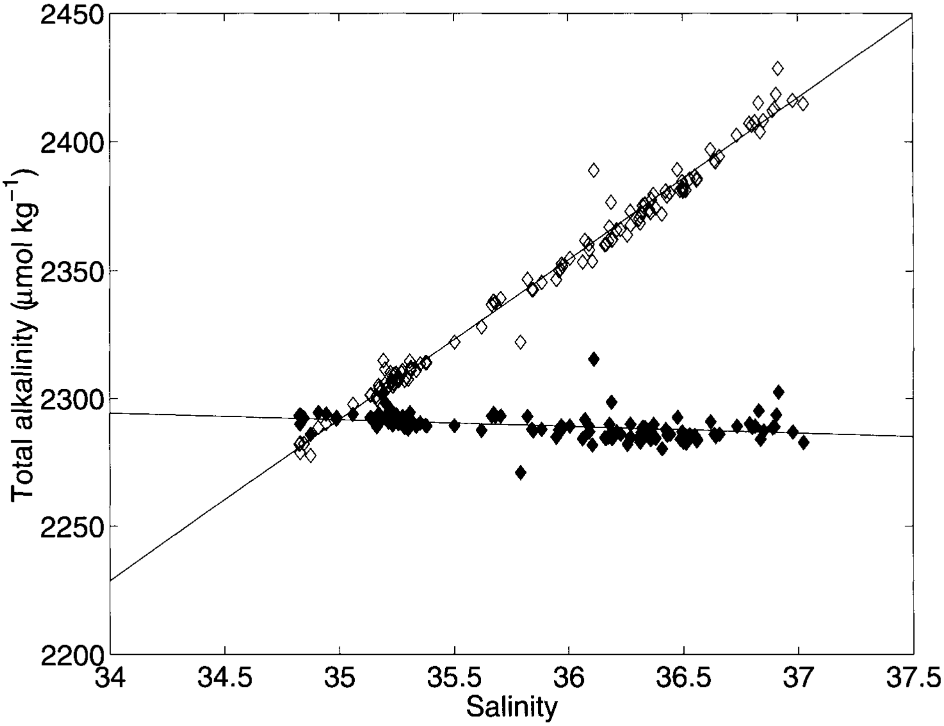

Figure 1.2.16: Total alkalinity (open diamonds) and total alkalinity normalized to $S = 35$ (closed diamonds) in surface waters of the Indian Ocean (WOCE Section I07N, F. Millero and K. Johnson, http://cdiac.esd.ornl.gov/oceans/CDIACmap.html). In this case, total alkalinity is linearly related to salinity.

holds. In other words, total alkalinity is a conserved quantity just like mass, salt, or dissolved inorganic carbon.

1.2.7 Total alkalinity in the ocean

There are several processes which lead to changes of total alkalinity.[14] First of all, the charge difference between conservative cations and anions varies with salinity. Therefore TA in the ocean is closely related to salinity (Figure 1.2.16). Salinity changes are due to precipitation, evaporation, fresh water input, and formation or melting of sea ice and cause corresponding changes in total alkalinity.

The second major change in total alkalinity in the ocean is due to biogenic precipitation of calcium carbonate ($CaCO_3$) by marine organisms such

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[14] A summary of this subject can also be found in Stoll (1994).

as coccolithophorids, foraminifera, pteropods, and corals, and dissolution of calcareous shells or skeletons. Precipitation leads to a decrease in Ca^{2+} concentration. Thus the charge difference between conservative cations and anions decreases and so does the total alkalinity. Precipitation of 1 mol $CaCO_3$ reduces DIC by 1 mol and TA by 2 mol. Please note that these changes are independent of the carbon source (HCO_3^-, CO_3^{2-}, or even CO_2) used by the organisms for calcification. As a result, the carbon source cannot be inferred from observations of changes in DIC and TA in seawater.

Minor changes of total alkalinity in the ocean are related to nitrogen assimilation by plants and release of dissolved inorganic nitrogen from organic compounds during remineralization. The change of alkalinity due to assimilation of nitrate, ammonia, or urea by plants has been investigated by Brewer and Goldman (1976) and Goldman and Brewer (1980). They found that alkalinity changes were consistent with a simple stoichiometric model in which NO_3^- uptake is balanced by OH^- production (that is, alkalinity increases) and NH_4^+ uptake is balanced by H^+ production (that is, alkalinity decreases); no change of alkalinity occurs when urea is assimilated.

The $TA^{(ec)}$ expression can be used to summarize changes of alkalinity due to certain biogeochemical processes. This approach is very convenient because each single component of $TA^{(ec)}$ (conservative ions) can be varied without affecting any other component in that expression. On the other hand, changes of a single component of the expression in terms of weak acids for alkalinity (proton acceptors and donors) affects all other components via changes in, for instance, ΣCO_2 and pH. Alkalinity changes due to several biogeochemical processes based on the $TA^{(ec)}$ expression, Eq. (1.2.40), are as follows:

1. Precipitation of one mole $CaCO_3$: alkalinity decreases by two moles (term: $2[Ca^{2+}]$).
2. Dissolution of one mole $CaCO_3$: alkalinity increases by two moles (term: $2[Ca^{2+}]$).
3. Uptake of DIC by algae under the assumption that electroneutrality of algae is ensured by parallel uptake of H^+ or release of OH^-: no change in alkalinity.
4. Uptake of one mole of nitrate (NO_3^-) by algae under the assumption that electroneutrality of algae is ensured by parallel uptake of H^+ or release of OH^-: alkalinity increases by one mole (term: $-[NO_3^-]$). This is consistent with laboratory experiments with algae grown on

different nitrogen sources (Brewer and Goldman (1976); Goldman and Brewer (1980)).

5. Remineralization of algal material has the reverse effects on alkalinity.

Determining changes of alkalinity due to algal uptake of ammonia, phosphate, etc. requires a definition of the left-hand side of TA corresponding to the full right-hand side of TA as given by Dickson (Eq. (1.2.33)). This can be found in Appendix C.1.

Summary. Total alkalinity is defined as the number of moles of hydrogen equivalent to the excess of proton acceptors over proton donors in 1 kg sample. For the most practical purposes total alkalinity in seawater can be defined as PA $= [\mathrm{HCO_3^-}]+2[\mathrm{CO_3^{2-}}]+[\mathrm{B(OH)_4^-}]+[\mathrm{OH^-}]-[\mathrm{H^+}]$. From the fact that TA is equal to the charge difference between conservative cations and anions, it follows that TA is a conservative quantity. Total alkalinity does not change when CO_2 is exchanged with the atmosphere or is taken up or released by plants. However, total alkalinity does change with salinity (precipitation, evaporation), precipitation and dissolution of calcium carbonate, and with the assimilation and release of dissolved inorganic nitrogen.

Further reading: Dickson (1992), Bradshaw and Brewer (1988b), Anderson et al. (1999).

Exercise 1.6 (**)

In laboratory experiments biologists often add nutrients at concentrations much higher than observed in the ocean. Does this lead to changes in alkalinity? If yes, how much does alkalinity change when you add nutrients to a natural seawater sample in order to match the concentrations of the f/2-medium? The f-medium contains 882 μmol kg^{-1} nitrate, 36 μmol kg^{-1} phosphate and 30 μmol kg^{-1} silicate (Guillard and Ryther, 1962). The f/2-medium contains half as much. The natural seawater sample shall already contain 15 μmol kg^{-1} nitrate, 1 μmol kg^{-1} phosphate, and 15 μmol kg^{-1} silicate. The nutrients are added in the form of $NaNO_3$, Na_2HPO_4 and Na_2SiO_3.

Exercise 1.7 (**)

Consider a culture of noncalcifying algae in a closed bottle at $T_c = 25°C$ and $S = 35$. The initial conditions are DIC = 2 mmol kg^{-1}, TA = 2.3 mmol kg^{-1} and $NO_3^- = 20$ μmol kg^{-1}. After some time the algae have taken up carbon and have assimilated all the nitrate. Calculate the change in $[CO_2]$ assuming a Redfield ratio C:N = 106:15. How much of this variation is due to a change in alkalinity?

Exercise 1.8 (**)

As carbon dioxide is taken up or lost from sea water the total alkalinity is conserved. What happens to the carbonate alkalinity?

Exercise 1.9 (**)
Consider two bodies of seawater with equal masses (1000 kg) and temperatures (25°C) but different salinities ($S_1 = 30$, $S_2 = 40$). Calculate the corresponding volumes of the water bodies before and after mixing at surface pressure. Is volume conserved? Hint: the density of seawater as a function of salinity, temperature, and pressure ($\rho(S, T, P)$) is given in Appendix A.13 (cf. Millero and Poisson, 1981; Gill, 1982). A MATLAB routine including $\rho(S, T, P)$ can be found on our web-page; 'http://www.awi-bremerhaven.de/Carbon/co2book.html'.

Exercise 1.10 (**)
Consider two bodies of seawater with equal masses (1 kg) and temperatures (25°C) but different salinities ($S_1 = 30$, $S_2 = 40$), dissolved inorganic carbon ($\mathrm{DIC}_1 = 1800$ μmol kg^{-1}, $\mathrm{DIC}_2 = 2000$ μmol kg^{-1}), and total alkalinity ($\mathrm{TA}_1 = 2100$ μmol kg^{-1}, $\mathrm{TA}_2 = 2300$ μmol kg^{-1}). Calculate the corresponding concentrations of CO_2, HCO_3^-, and CO_3^{2-} of the water bodies before and after mixing at surface pressure. Are the total amounts of CO_2, HCO_3^-, and CO_3^{2-} conserved?

1.3 *p*H scales

> **"The field of *p*H scales ... in sea water is one of the more confused areas of marine chemistry."**
> Dickson (1984) p. 2299.

> **"The choice of a suitable *p*H scale for the measurement of oceanic *p*H remains for many people a confused and mysterious topic ..."**
> Dickson (1993a) p. 109.

The goal of this section is to introduce the different *p*H scales used in chemical oceanography and briefly discuss the origin of these scales. This requires a little work but it will show that there is nothing mysterious about seawater *p*H scales. Based on a simple inter-conversion numerical differences between the scales will be estimated. By means of an example, we shall finally illustrate possible errors in the calculation of $p\mathrm{CO}_2$ if the differences between the *p*H scales are ignored.

In the following, we address two main questions: Why and when should we care about the different *p*H scales (definitions)?

Why? The equilibrium constants of proton-transfer reactions such as the first and second acidity constants of H_2CO_3 must be defined consistently with pH scales (see Dickson (1984; 1993a) for details). If this point is disregarded in calculations of the carbonate system, serious errors can occur (cf. Section 1.1.6).

When? The values of different pH scales in seawater differ by up to 0.12 units (see Eqs. (1.3.57), (1.3.58)) corresponding to a comparable difference in pK_1^* and pK_2^* (see Eq. (1.3.60)). Because these differences are much larger than the desired accuracy of pH measurements, we should care about the different pH scales whenever pH is a master variable. Please note that the differences between acidity constants from different publications may be mainly due to the use of different pH scales.

Various definitions

In high school we learned that pH (lat.: *potentia hydrogenii* or also *pondus hydrogenii*) is the negative common logarithm of the concentration of hydrogen ions:

$$p\mathrm{H}_{\text{high school}} := -\log[\mathrm{H}^+]. \qquad (1.3.47)$$

This definition dates from Sørensen (1909). Things are a bit more complicated for several reasons:

- "It is safe to say that free protons" (hydrogen ions) "do not exist in any significant amount in aqueous solutions. Rather the proton is bonded to a water molecule thus forming an H_3O^+ ion; this in turn is hydrogen bonded to three other water molecules to form an $H_9O_4^+$ ion." (Dickson, 1984, p. 2299); compare also Marx et al. (1999) and Hynes (1999). Thus, the symbol 'H^+' represents hydrate complexes rather than the concentration of free hydrogen ions. As noted in Section 1.1, it is however convenient to refer to $[H^+]$ as the hydrogen ion concentration.
- In a refined theory one should use activity (an 'effective' concentration; denoted by a) instead of concentration

  $$p\mathrm{H}_a = -\log a_{\mathrm{H}^+} \ . \qquad (1.3.48)$$

  Unfortunately, it is not possible to measure pH according to Eq. (1.3.48). The reason for this is that individual ion activities cannot

> be determined experimentally since the concentration of a single ion cannot be varied independently because electroneutrality is required (e.g. Klotz and Rosenberg, 2000).

An operational definition of the NBS[15] pH scale was given by the International Union of Pure and Applied Chemistry (IUPAC). The NBS pH scale is defined by a series of standard buffer solutions with assigned pH values close to the best estimates of $-\log a_{\mathrm{H}^+}$, i.e. $p\mathrm{H}_{\mathrm{NBS}}$ is close to but not identical to $p\mathrm{H}_{\mathrm{a}}$

$$p\mathrm{H}_{\mathrm{NBS}} \approx p\mathrm{H}_{\mathrm{a}}. \tag{1.3.49}$$

The reference state for $p\mathrm{H}_{\mathrm{a}}$ and $p\mathrm{H}_{\mathrm{NBS}}$ is the infinite dilute solution, i.e. the activity coefficient of H^+, γ_{H^+}, approaches unity when $[\mathrm{H}^+]$ approaches zero in pure water.

NBS standard buffer solutions have very low ionic strength, ~ 0.1. In contrast, seawater has high ionic strength, ~ 0.7. The use of NBS buffers in pH measurements using electrodes in seawater is therefore not recommended because the large differences in ionic strength between the buffer and the seawater causes significant changes in the liquid junction potential[16] between calibration and sample measurement. To make it worse, these changes depend on the electrode system used. The error due to this change in liquid junction potential is larger than the desired accuracy of 0.01 - 0.001 pH units (Wedborg et al., 1999).

Hansson (1973a) greatly improved the situation by the adoption of seawater as the standard state and the introduction of a new pH scale based on artificial seawater. On this pH scale, called the 'total' scale, the activity coefficient $\gamma_{\mathrm{H}^+_{\mathrm{T}}}$ approaches unity when $[\mathrm{H}^+]_{\mathrm{T}}$ approaches zero in the pure synthetic seawater on which the scale is based[17] (for definition of $[\mathrm{H}^+]_{\mathrm{T}}$, see below). Hansson (1973a) introduced a new set of standard buffers based on artificial seawater and assigned pH values to these buffers according to

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[15] NBS: National Bureau of Standards, now NIST: National Institute of Standards and Technology.

[16] The liquid junction potential is the electric potential difference between the solution in the electrode and the measurement solution. Ideally it depends only on the composition of the electrode solution and measurement solution - in reality, however, it also depends on the practical design of the liquid junction (Wedborg et al., 1999).

[17] The chemical potential μ_i of species i is related to the concentration c_i and the activity a_i by $\mu_i - \mu_i^0 = RT \ln a_i = RT \ln (c_i \gamma_i)$ where μ_i^0 is the chemical potential of the reference state and γ_i is the activity coefficient. The relation $\gamma_i \to 1$ in seawater corresponds to a certain choice of the values of the μ_i^0.

his new pH scale. One of the great advantages of this approach is that the changes of liquid junction potential between the buffer and the sample are greatly reduced because of the very similar composition of the two solutions.

In addition to the total scale, the free scale and the seawater scale have been proposed for the use in seawater which will be discussed below. We denote the free scale by $p\mathrm{H_F}$, the total (or Hansson) scale by $p\mathrm{H_T}$, and the seawater scale by $p\mathrm{H_{SWS}}$. They are defined by:

$$p\mathrm{H_F} = -\log[\mathrm{H^+}]_\mathrm{F} \tag{1.3.50}$$

$$p\mathrm{H_T} = -\log\left([\mathrm{H^+}]_\mathrm{F} + [\mathrm{HSO_4^-}]\right) = -\log[\mathrm{H^+}]_\mathrm{T} \tag{1.3.51}$$

$$p\mathrm{H_{SWS}} = -\log\left([\mathrm{H^+}]_\mathrm{F} + [\mathrm{HSO_4^-}] + [\mathrm{HF}]\right) = -\log[\mathrm{H^+}]_\mathrm{SWS}. \tag{1.3.52}$$

where $[\mathrm{H^+}]_\mathrm{F}$ is the 'free' hydrogen ion concentration, including hydrated forms, see above.

The free scale

Certainly, the free scale is conceptually the clearest. However, it will become apparent very soon that this concept suffers from the fact that the stability constant of $\mathrm{HSO_4^-}$, K_S^*, has to be determined accurately in seawater which is not a simple task (Dickson, 1984; 1993b). In seawater, protonation of ions such as $\mathrm{SO_4^{2-}}$ occurs:

$$\mathrm{HSO_4^-} \rightleftharpoons \mathrm{H^+} + \mathrm{SO_4^{2-}}; \qquad K_\mathrm{S}^* .$$

Thus, in a seawater medium containing sulphate ions, the total hydrogen ion concentration is:

$$[\mathrm{H^+}]_\mathrm{T} = [\mathrm{H^+}]_\mathrm{F} + [\mathrm{HSO_4^-}] .$$

Analytically, only $[\mathrm{H^+}]_\mathrm{T}$ can be determined (Dickson, 1993b; Wedborg et al., 1999). As a result, $[\mathrm{H^+}]_\mathrm{F}$ has to be calculated according to

$$\begin{aligned} [\mathrm{H^+}]_\mathrm{F} &= [\mathrm{H^+}]_\mathrm{T} - [\mathrm{HSO_4^-}] \\ &= [\mathrm{H^+}]_\mathrm{T} \left(1 + [\mathrm{SO_4^{2-}}]/K_\mathrm{S}^*\right)^{-1} \end{aligned}$$

which involves K_S^*. The use of the free scale therefore requires an accurate value of K_S^* in seawater which is difficult to obtain.

The total scale

A medium containing sulphate ions was used by Hansson (1973a) who therefore defined the total scale as given in Eq. (1.3.51). This scale includes the effect of sulfate ion in its definition and therefore circumvents the problem of determining K_S^*. On this scale, the activity coefficient approaches unity when ($[H^+]_F + [HSO_4^-]$) approaches zero in the ionic medium.

The seawater scale

If the medium additionally contains fluoride ions, we also have to take the protonation of F^- into account:

$$HF \rightleftharpoons H^+ + F^-; \qquad K_F^* .$$

Such a medium was used, for instance, by Goyet and Poisson (1989). The total hydrogen ion concentration then is:

$$[H^+]_F + [HSO_4^-] + [HF]$$

which leads to the definition of the seawater scale, Eq. (1.3.52). The difference between the total and the seawater scale therefore simply arises from the fact whether the medium on which the scale is based contains fluoride ions or not. This difference is, however, small because the concentration of HSO_4^- in seawater is much larger than the concentration of HF.

The bottom line is as follows. Three *p*H scales have been proposed for the use in seawater. The use of the free scale requires an accurate determination of the stability constant of HSO_4^- in seawater which is not a simple matter. This problem is circumvented by the definition of the total and the seawater scale. The difference between the total and seawater scale is explained by differences in the laboratory protocols of the different researchers.

1.3.1 Conversion between *p*H scales

The various *p*H scales are inter-related by the following equation (after conversion to the same concentration unit, say mol kg^{-1}):

$$\begin{aligned} [H^+]_F &= \frac{[H^+]_T}{1 + S_T/K_S^*} = \frac{[H^+]_{SWS}}{1 + S_T/K_S^* + F_T/K_F^*} \\ &\text{or} \\ pH_F &= pH_T + \log(1 + S_T/K_S^*) \\ &= pH_{SWS} + \log(1 + S_T/K_S^* + F_T/K_F^*) \end{aligned} \qquad (1.3.53)$$

where K_S^* and K_F^* are the stability constants of hydrogen sulfate and hydrogen fluoride, respectively (see Appendix A). Furthermore,

$$S_T = [SO_4^{2-}] + [HSO_4^-] \simeq [SO_4^{2-}] \qquad (1.3.54)$$

is the total sulfate concentration and

$$F_T = [F^-] + [HF] \simeq [F^-] \qquad (1.3.55)$$

is the total fluoride concentration. Equation (1.3.53) shows that scale conversion is basically simple. It also shows that in order to convert accurately between the different scales, the stability constants K_S^* and K_F^* in seawater have to be known precisely. As said above, this appears to be difficult (Dickson, 1993a). Thus, uncertainties are introduced into calculations when values are compared between different scales. However, such uncertainties are small compared to those arising when scale conversion is simply ignored.

Let us estimate the numerical differences between the pH scales in seawater using the data available for K_S^* and K_F^*. The numerical differences are given by the terms $\log(1 + S_T/K_S^*)$ and $\log(1 + S_T/K_S^* + F_T/K_F^*)$. Values of S_T and F_T for seawater at $S = 35$ may be found in DOE (1994):

$$\begin{aligned} S_T &= 28.24\,\text{mmol (kg-soln)}^{-1} \\ F_T &= 70\,\mu\text{mol (kg-soln)}^{-1}\ . \end{aligned} \qquad (1.3.56)$$

At $S = 35$ and $T_c = 25°C$, $K_S^* \simeq 0.10$ mol kg^{-1} and $K_F^* \simeq 0.003$ mol kg^{-1}, and one obtains:

$$\boxed{\begin{aligned} \log(1 + S_T/K_S^*) &\simeq 0.11 & (1.3.57) \\ \log(1 + S_T/K_S^* + F_T/K_F^*) &\simeq 0.12 & (1.3.58) \end{aligned}}$$

In other words, under standard conditions, the pH value of a sample reported on the free scale is about 0.11 and 0.12 units higher than on the total and seawater scale, respectively. For example, if $p\text{H}_\text{F} = 8.22$, then $p\text{H}_\text{T} = 8.11$ and $p\text{H}_\text{SWS} = 8.10$. This gives us a feeling of the potential error occuring in calculations when scale conversion is ignored. Such differences are huge when compared to the accuracy and precision of pH measurements. Millero et al. (1993b) give an accuracy in measuring pH of ± 0.002 (for recent advances in measurement techniques see, for instance, Dickson (1993b), Bellerby et al. (1995), and Wedborg et al. (1999)). The currently used pH scales and the estimated differences between them are summarized in Table 1.3.8.

Table 1.3.8: The pH scales and the differences between them.

pH scale	applicable in	reference state	difference to free scale[a] $p\mathrm{H}_\mathrm{F} - p\mathrm{H}_i$
$p\mathrm{H}_\mathrm{NBS}$	freshwater	pure water	
$p\mathrm{H}_\mathrm{F}$	seawater	artificial seawater	
$p\mathrm{H}_\mathrm{T}$	seawater	artificial seawater	~0.11
$p\mathrm{H}_\mathrm{SWS}$	seawater	artificial seawater	~0.12

[a] At $S = 35$, $T_c = 25°\mathrm{C}$.

The most important lesson to be learned here is: check which pH scale is used! If this is ignored, large uncertainties can occur. Compared to these uncertainties, errors arising from the actual procedure of scale conversion, Eq. (1.3.53), which are due to uncertainties in the values of K_S^* and K_F^*, are small. Potential problems arising from the conversion between the different pH scales could be eliminated by agreement of the community on a single pH scale. One promising candidate for this is certainly the total scale.

1.3.2 Conversion of acidity constants

The conversion of acidity constants between different pH scales is described in Dickson and Millero (1987). A typical equilibrium relation reads:

$$[\mathrm{CO_3^{2-}}]/[\mathrm{HCO_3^-}] = K_{2\mathrm{T}}^*/[\mathrm{H^+}]_\mathrm{T} \tag{1.3.59}$$

where the index 'T' indicates that equilibrium constant and pH refer to the total scale. Now convert from total to free scale. Taking the negative logarithm results in:

$$\begin{aligned}
- \ \ & \log\ \left([\mathrm{CO_3^{2-}}]/[\mathrm{HCO_3^-}]\right) \\
= \ \ & pK_{2\mathrm{T}}^* - p\mathrm{H}_\mathrm{T} \\
= \ \ & \underbrace{pK_{2\mathrm{T}}^* + \log(1 + S_T/K_\mathrm{S}^*)}_{=:\, pK_{2\mathrm{F}}^*} - p\mathrm{H}_\mathrm{F} \\
= \ \ & pK_{2\mathrm{F}}^* - p\mathrm{H}_\mathrm{F}\ .
\end{aligned} \tag{1.3.60}$$

When we change the pH-scale, the left-hand side of Eq. (1.3.60) does not change because the concentrations of carbonate ion and bicarbonate are physical quantities that cannot depend on our choice of the pH scale. Thus the right-hand side of Eq. (1.3.60) does not change either. Consequently, if we switch from the total to the free pH scale, and the pH is higher on

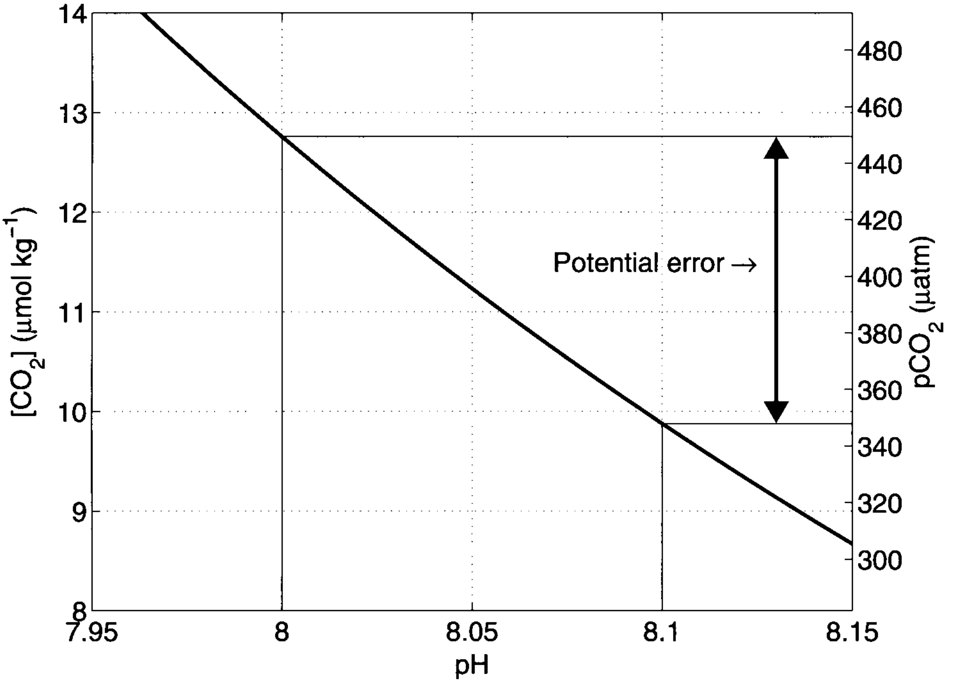

Figure 1.3.17: [CO_2] and pCO_2 as a function of pH (T_c = 25°C, S = 35, DIC = 2 mmol kg^{-1}). If conversion between pH scales is ignored, the error in pH may be as large as 0.1 units which causes a difference in the calculated pCO_2 of about 100 μatm.

this scale by say 0.1 units, then $pK^*_{2\text{F}}$ must be higher by 0.1 units as well. In order to illustrate the potential error that may occur if such differences are ignored, consider the CO_2 concentration as a function of pH at constant DIC (Figure 1.3.17). An increase of pH by 0.1 results in a decrease of [CO_2] by ca. 3 μmol kg^{-1} at $p\text{H} = 8.0$, $S = 35$, $T_c = 25$°C and DIC = 2 mmol kg^{-1}. The corresponding difference in the calculated pCO_2 would be about 100 μatm! This figure was already given in Section 1.1.6, where the choice of equilibrium constants was discussed.

In the handbook of Dickson and Goyet (DOE, 1994) it is stated that all acidity constants, with the exception of that for bisulfate ion, are expressed in terms of 'total' (Hansson) hydrogen ion concentration (DOE, 1994, Chapter 5, p. 12). This is very useful because confusion may arise when the pH scale used it is not explicitly stated.

In summary, the equilibrium constants are defined consistently with certain pH-scales. Currently, marine chemists use the scales $p\text{H}_\text{T}$ or $p\text{H}_\text{SWS}$

which differ by about 0.01; both scales differ from the free scale ($p\mathrm{H}_\mathrm{F}$) by approximately 0.1. The NBS scale is not recommended for measurements in seawater. Following DOE (1994) and Wedborg et al. (1999) the total pH scale will be used in the current book (unless stated otherwise).

Further reading: Dickson (1984, 1993a), Millero et al. (1993a), Wedborg et al. (1999).

1.4 Partial pressure and fugacity

The four carbonate system parameters that can be determined analytically are $\Sigma\mathrm{CO}_2$, TA, pH, and $p\mathrm{CO}_2$. The knowledge of any two of them allows us to calculate the carbonate chemistry of a seawater sample. The three variables $\Sigma\mathrm{CO}_2$, TA, and pH have been discussed in previous sections. This section deals with the partial pressure of CO_2. It is to point out that the CO_2 partial pressure assigned to a seawater sample refers to the partial pressure of CO_2 in the gas phase that is in equilibrium with that seawater. Once the $p\mathrm{CO}_2$, or more precisely the fugacity $f\mathrm{CO}_2$, has been determined, one may use Henry's law to calculate the concentration of dissolved CO_2 in solution and use it as a master variable (Appendix B). One may also calculate differences in $p\mathrm{CO}_2$ between the ocean and atmosphere and use the difference to estimate the net air-sea gas CO_2 flux (e.g. Takahashi et al., 1997).

Marine chemists report the amount of CO_2 in the surface ocean as fugacity which is related to the more widely known partial pressure. The quantity that is measured, however, is the mole fraction of CO_2. In the following we will explain the differences between these quantities.

1.4.1 Mole fraction and partial pressure

The mole fraction, x, of a gas A is the number of moles of A divided by the total number of moles of all components in the sample: $x_\mathrm{A} = n_\mathrm{A}/\Sigma_i n_i$. The mole fraction is expressed in units of mol mol^{-1}; $x\mathrm{CO}_2$, for example, is usually expressed in μmol mol^{-1}. For perfect gases, the mole fraction is equal to the volume mixing ratio (volume per volume), expressed in ppmv (parts per million by volume).

The partial pressure of a gas A is proportional to its mole fraction: $p_\mathrm{A} = x_\mathrm{A} \cdot p$, where p is the total pressure of the mixture. This serves as the definition of the partial pressure even when the gas is not behaving perfectly (Atkins, 1998). The unit of partial pressure is atmosphere (atm). For a mixture of gases we may write:

$$p_A + p_B + p_C + ... = (x_A + x_B + x_C + ...)\, p = p$$

which shows that the mole fraction of a gas is numerically only equal to its partial pressure when the total pressure is 1 atm. The various quantities used to describe CO_2 in the gas phase are summarized in Table 1.4.9.

Table 1.4.9: The different quantities used to describe CO_2 in the gas phase.

Quantity	Symbol used in literature	Unit	Value[a]	Remark
mole fraction	xCO_2	μmol mol^{-1}	360.0	in dry air
mixing ratio/ concentration[b]	xCO_2	ppmv	360.0	in dry air
partial pressure	pCO_2	μatm	349.0[c]	at 100% humidity
fugacity	fCO_2	μatm	347.9[d]	at 100% humidity

[a] Values refer to, or are calculated from $xCO_2 = 360$ μmol mol^{-1} measured in dry air.

[b] Also used for mole fraction, assuming that all gases in the mixture behave perfectly.

[c] At $T = 25°C$ and $S = 35$.

[d] At $T = 25°C$.

Atmospheric CO_2

When measuring the CO_2 content of a gas sample of the atmosphere, it is usually reported as the mole fraction, xCO_2, or simply as the CO_2 concentration. If values were reported in terms of the partial pressure of CO_2, the values would rapidly decrease with height because the partial pressure depends on the total pressure which decreases as a function of height. In contrast, the mole fraction of CO_2 may be fairly constant at different altitudes. Obviously, the mole fraction and the partial pressure are quite different quantities and even at the surface, where the total pressure is approximately 1 atm, they are not the same.[18]

At a given mole fraction, the partial pressure of CO_2 at the surface depends, for example, on the local atmospheric pressure that varies from

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[18] Note that in many publications the terms partial pressure and mole fraction of CO_2 and their units are used interchangeably which may cause confusion.

place to place. The partial pressure of CO_2 is lower in areas of low pressure and higher in areas of high pressure because the total pressure changes accordingly. In addition, if the mole fraction is determined in dry air, the calculated partial pressure of two samples with the same $x\mathrm{CO}_2$ depends on the local *in situ* humidity because the partial pressure of H_2O contributes to the total pressure. In order to avoid such complications, atmospheric CO_2 is reported in terms of mole fraction. Note, however, that from a marine perspective, the thermodynamically important quantity is the partial pressure. Only in dry air and at standard pressure, the partial pressure is numerically equal to the mole fraction.

Surface seawater $p\mathrm{CO}_2$

With respect to the CO_2 of the surface ocean, the quantity that matters is the partial pressure, or more precisely the fugacity, see next section. Consider, for example, the exchange of CO_2 between ocean and atmosphere. The quantity that drives this physical process is the partial pressure and not the mole fraction.

The CO_2 partial pressure of a seawater sample is usually determined by equilibrating a large volume of seawater with a small volume of gas. Then the mole fraction of CO_2 in the gas phase is determined from which the partial pressure is calculated. Most of the measurements are made at a temperature that is higher or lower than the *in situ* temperature. Because $p\mathrm{CO}_2$ varies strongly with temperature, large corrections of up to 150 μatm may have to be applied in order to calculate $p\mathrm{CO}_2$ at *in situ* conditions (Figure 1.4.18). This problem can be minimized if measurements are made close to the *in situ* temperature (Wanninkhof and Thoning, 1993; Körtzinger, 1999). In addition, a correction for water vapor pressure has to be applied if measurements are made in dry air (Appendix C.2).

In summary, the calculation of $p\mathrm{CO}_2$ from $x\mathrm{CO}_2$ involves several steps which include corrections due to (1) differences between *in situ* sea surface temperature and equilibration temperature, (2) the water vapor pressure at the equilibration temperature, and (3) the barometric pressure (e.g. Broecker and Takahashi, 1966; Copin-Montegut, 1988; DOE, 1994). The uncertainties in $p\mathrm{CO}_2$ associated with the analytical procedures and the corrections can be on the order of 10 μatm for discrete systems but may be reduced to about 2 μatm for continuous systems (Wanninkhof and Thoning, 1993; Körtzinger, 1999). These uncertainties are likely to be much larger than those arising from the difference between partial pressure and fugacity

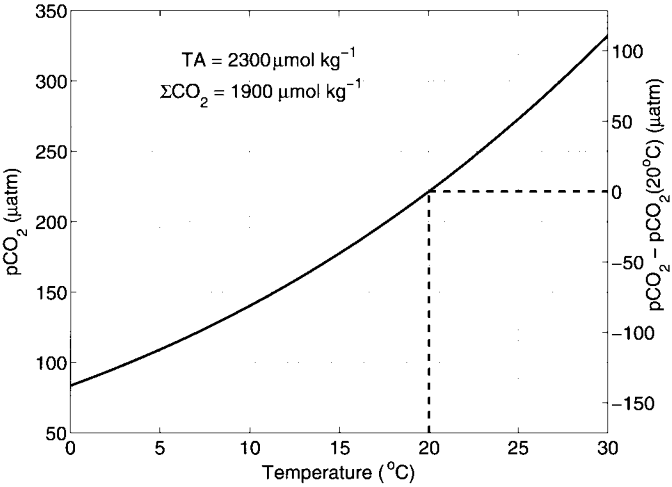

Figure 1.4.18: Seawater $p\mathrm{CO}_2$ as a function of temperature (T). If measurements are made at 20°C (so-called discrete systems), large corrections may have to be applied to calculate $p\mathrm{CO}_2$ at *in situ* T (cf. Goyet et al., 1993). The problem is less severe in so-called continuous systems where equilibration and *in situ* T are similar.

(~ 1 μatm, see next section).

When the atmospheric $p\mathrm{CO}_2$ is calculated from the measured mole fraction of CO_2 in dry air, similar corrections have to be applied. The corrections involve the barometric pressure and the water vapor pressure at *in situ* temperature.

The bottom line of this section is as follows. In order to determine the amount of CO_2 in a gas sample, the mole fraction is measured. The partial pressure, which is thermodynamically important, is calculated from the mole fraction using several corrections. The mole fraction of a gas is numerically only equal to its partial pressure, when the total pressure is 1 atm.

1.4.2 Fugacity

> **"What is the difference between partial pressure and fugacity?"**
> (question posed at a meeting)
> **"It's the same number!"**
> (answer by a well-known marine chemist; this is almost true)

> **"In most natural applications which do not require accuracies greater than $\sim$ 0.7%, the fugacity ... may be taken as equal to the partial pressure." (Weiss, 1974).**

Partial pressure is a concept appropriate for ideal gases. According to Dalton's law, the total pressure of an ideal gas mixture is given by the sum of the partial pressures of the gases, where the partial pressure of a perfect gas is the pressure it would exert if it occupied the container alone. The chemical potential of gas species i, μ_i, reads:

$$\mu_i = \mu_i^0 + RT \ln p_i \quad \text{(ideal gas)} \tag{1.4.61}$$

where μ_i^0 is the standard potential, R is the gas constant, T is the absolute temperature, and p_i is the partial pressure. For real gases Dalton's law is an approximation and the chemical potential is strictly given by:

$$\mu_i = \mu_i^0 + RT \ln f_i \quad \text{(real gas)} \tag{1.4.62}$$

where f_i is the fugacity of gas species i. Eqs. (1.4.61) and (1.4.62) are of the same form where fugacity has taken the role of partial pressure. Fugacity approaches the partial pressure in the limit of infinitely dilute mixtures:

$$\frac{f_i}{p_i} \to 1 \quad \text{as} \quad p \to 0. \tag{1.4.63}$$

The relationship between fugacity and partial pressure is analogous to the relationship between activity and concentration of ions in aqueous solutions (see Section 1.1.2). The activity, a, approaches the concentration, $[c]$, in the limit of infinitely dilute solutions:

$$\frac{a}{[c]} \to 1 \quad \text{as} \quad [c] \to 0. \tag{1.4.64}$$

For very accurate calculations, the fugacity of CO_2, fCO_2, may be used instead of the partial pressure. The fugacity can be calculated from its partial pressure (e.g. Körtzinger, 1999):

$$fCO_2 = pCO_2 \cdot \exp\left(p\frac{B + 2\delta}{RT}\right) \tag{1.4.65}$$

where fCO_2 and pCO_2 are in μatm, the total pressure, p, is in Pa (1 atm = 101325 Pa), the first virial coefficient of CO_2, B, and parameter δ are in $\text{m}^3\ \text{mol}^{-1}$, $R = 8.314$ J K^{-1} mol^{-1} is the gas constant and the absolute temperature, T, is in K. B has been determined by Weiss (1974):

$$\begin{aligned} B(\text{m}^3\,\text{mol}^{-1}) &= \Big(-1636.75 + 12.0408\,T - 3.27957 \cdot 10^{-2}\,T^2 \\ &\quad +3.16528 \cdot 10^{-5}\,T^3\Big)\ 10^{-6}. \end{aligned} \tag{1.4.66}$$

The parameter δ is the cross virial coefficient:

$$\delta(\text{m}^3\,\text{mol}^{-1}) = (57.7 - 0.118\,T)\ 10^{-6} \tag{1.4.67}$$

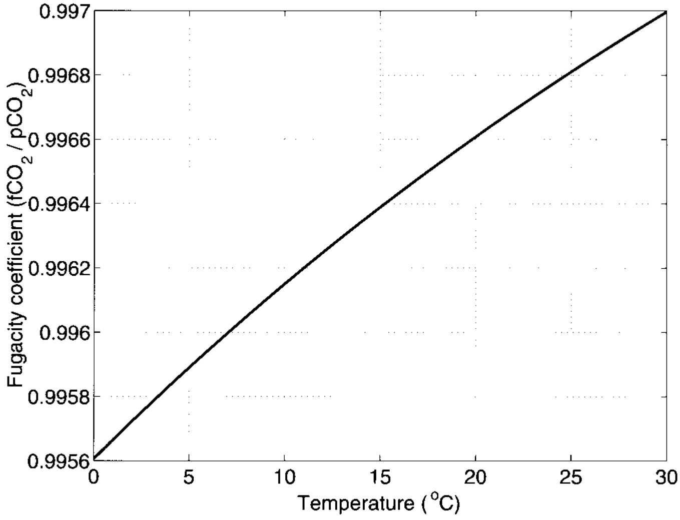

Figure 1.4.19: The fugacity coefficient, $f\text{CO}_2$ / $p\text{CO}_2$, as a function of temperature. The fugacity is about 3 to 4‰ smaller than the partial pressure. At $p\text{CO}_2$ = 360 μatm, the difference is about 1 μatm.

The fugacity coefficient, i.e. the ratio of fugacity and partial pressure of CO_2, varies between ~ 0.996 and ~ 0.997 over the range $0° \leq T_c \leq 30°\text{C}$ at 1 atm (Figure 1.4.19). At $p\text{CO}_2 = 360$ μatm, the difference is therefore about 1 μatm.

The fugacity of a pure gas can be calculated from its equation of state (Appendix C.3). The calculation of fugacity for gas mixtures is beyond the scope of this book (compare, for example, Guggenheim (1967) or Weiss (1974) and references therein). The relationship between chemical potential, fugacity, and partial pressure at the air-sea interface is discussed in Appendix C.4.

In summary, CO_2 in the gas phase can be characterized as mole fraction, $x\text{CO}_2$ (μmol mol^{-1}), which is also often denoted as concentration or mixing ratio (ppmv). The mole fraction or the partial pressure, $p\text{CO}_2$ (μatm), may be used depending on the application. The mole fraction of CO_2 in the gas phase is determined analytically and $p\text{CO}_2$ is calculated from it using several corrections. The values of the mole fraction in dry air (in μmol mol^{-1}) and the partial pressure (in μatm) are the same numbers, provided that the partial pressure also refers to dry air at a pressure of 1 atm. The fugacity, $f\text{CO}_2$ (μatm), and the partial pressure, $p\text{CO}_2$ (μatm), are almost the same numbers (a few per mil difference).

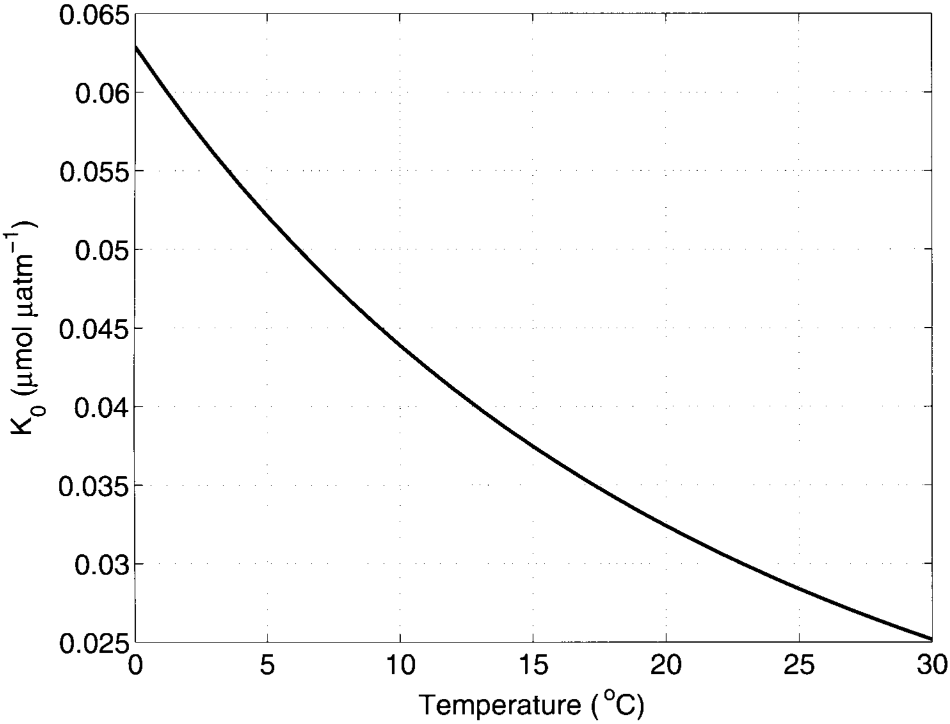

Figure 1.5.20: The solubility of CO_2, K_0, as a function of temperature at $S = 35$.

1.5 The Revelle factor

In order to demonstrate some properties of the carbonate system, we will answer the following question: *How does DIC change in response to increasing atmospheric CO_2 concentrations?*

The CO_2 concentration in surface waters, $[CO_2]$, currently increases due to invasion of CO_2 from the atmosphere. The increase of atmospheric CO_2 is a result of anthropogenic CO_2 emissions as, for instance, burning of fossil fuel releases CO_2. It is very important to note in this context that invasion of CO_2 does not change the total alkalinity in seawater (cf. Section 1.2). In equilibrium, the net exchange of CO_2 between air and sea is zero. This is the case when the partial pressure of CO_2 in the atmosphere, pCO_2, equals the partial pressure of CO_2 in the surface ocean, PCO_2, which is related to the concentration of CO_2 by Henry's law:

$$[CO_2] = K_0(T,S) \cdot PCO_2 \qquad (1.5.68)$$

where $K_0(T, S)$ is the mainly temperature-dependent solubility (Figure 1.5.20). Note that for very accurate studies the fugacity may be used (see Section 1.4 and Appendix A.3). The CO_2 concentration in seawater increases proportionally to the increase of CO_2 in the atmosphere. But what happens to the other components of the carbonate system? Before addressing this question we will remind the reader of *p*H-buffering.

1.5.1 Titration of a weak acid by a strong base: *p*H-buffering

When a strong base is added to pure water (*p*H = 7) the *p*H of the solution will strongly increase (dashed line in Figure 1.5.21). However, when the initial solution contains a weak acid, the *p*H-response to the addition of a strong base is quite different: the *p*H increase is much less. Addition of OH^- leads to a more complete dissociation of the weak acid. The resulting H^+ ions combine with OH^- ions and form water. The system is buffered. This stabilization of a dynamic equilibrium against an outside perturbation can be regarded as another example of Le Chatelier's principle (Atkins, 1990): A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance.

Consider a volume V_A of a weak acid ($HA \rightleftharpoons H^+ + A^-$) with concentration $[A_0]$ that will be titrated with a strong base ($BOH \rightleftharpoons B^+ + OH^-$) of concentration $[B_0]$. We will calculate the *p*H after adding the volume V_B of the strong base. Conservation of electric charge leads to

$$[B^+] + [H^+] = [A^-] + [OH^-] \tag{1.5.69}$$

The total number of A groups (in HA and A^-) is constant. The concentration decreases, however, due to the addition of the strong base (V_B):

$$[HA] + [A^-] = \frac{[A_0]V_A}{V_A + V_B}. \tag{1.5.70}$$

The concentration of the base group B^+ in the titration volume reads (for a strong base: $[BOH] \approx 0$):

$$[B^+] = \frac{[B_0]V_B}{V_A + V_B}. \tag{1.5.71}$$

In addition we may exploit the equilibrium relations

$$K_A^* = \frac{[H^+][A^-]}{[HA]} \tag{1.5.72}$$

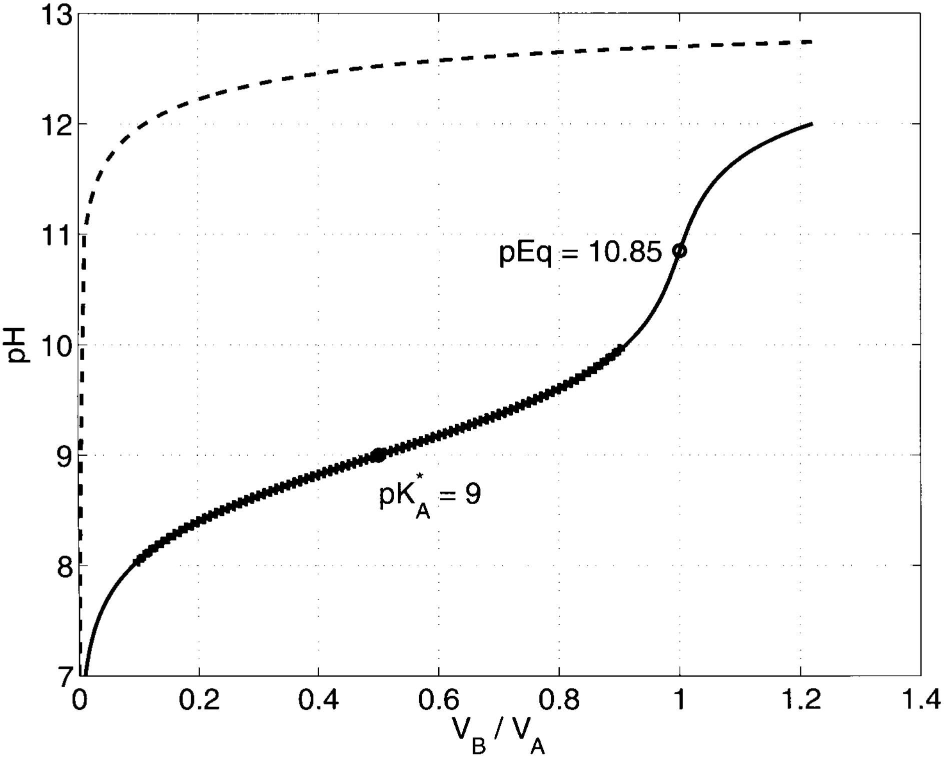

Figure 1.5.21: Titration of a weak acid ($pK^*_\mathrm{A} = 9$, $[A_0] = 0.1$ mol kg^{-1}) with a strong base ($[B_0] = 0.1$ mol kg^{-1}). The exact relation between pH and V_B/V_A, Eq. (1.5.76), can be approximated (in the range $0.1 < V_B/V_A < 0.9$; thick line) by the Henderson-Hasselbalch equation (1.5.77) which gives an explicit expression for pH as a function of V_B/V_A. The dashed line shows the titration curve for an unbuffered solution (pure water). pEq is the equivalence point defined as the pH at which $V_B = V_A$.

and

$$K^*_\mathrm{w} = [\mathrm{H}^+][\mathrm{OH}^-]. \tag{1.5.73}$$

Eliminating [HA] between Eq. (1.5.70) and Eq. (1.5.72) and solving for $[\mathrm{A}^-]$ yields

$$[\mathrm{A}^-] = \frac{[\mathrm{A}_0]V_A}{V_A + V_B}\frac{K^*_\mathrm{A}}{K^*_\mathrm{A} + [\mathrm{H}^+]}. \tag{1.5.74}$$

Replacing the various terms in Eq. (1.5.69) by the expressions given in Eqs. (1.5.71), (1.5.73), and (1.5.74) leads to an equation for $[\mathrm{H}^+]$:

$$\frac{[\mathrm{B}_0]V_B}{V_A + V_B} + [\mathrm{H}^+] = \frac{[\mathrm{A}_0]V_A}{V_A + V_B}\frac{K^*_\mathrm{A}}{K^*_\mathrm{A} + [\mathrm{H}^+]} + \frac{K^*_\mathrm{w}}{[\mathrm{H}^+]}. \tag{1.5.75}$$

Unfortunately, Eq. (1.5.75) is a cubic equation in $[\mathrm{H}^+]$ which is very awkward to solve. However, it can be solved readily for V_B as a function of $[\mathrm{H}^+]$:

$$\boxed{\frac{V_B}{V_A} = \frac{(K_\mathrm{A}^* + [\mathrm{H}^+])\,(K_\mathrm{w}^* - [\mathrm{H}^+]^2) + K_\mathrm{A}^*[\mathrm{A}_0][\mathrm{H}^+]}{(K_\mathrm{A}^* + [\mathrm{H}^+])([\mathrm{B}_0][\mathrm{H}^+] + [\mathrm{H}^+]^2 - K_\mathrm{w}^*)}\,. \qquad (1.5.76)}$$

Thus one can find the volume of base needed to achieve any pH; this is sufficient to produce the solid line in Figure 1.5.21. The exact relation between pH and V_B/V_A, Eq. (1.5.76), can be approximated (in the range $0.1 < V_B/V_A < 0.9$) by the Henderson-Hasselbalch equation

$$p\mathrm{H} = pK_\mathrm{A}^* - \log \frac{[\mathrm{A}_0]V_A - [\mathrm{B}_0]V_B}{[\mathrm{B}_0]V_B}\,. \qquad (1.5.77)$$

Exercise 1.11 (*)

Derive the equation for the unbuffered titration curve (Figure 1.5.21).

Exercise 1.12 (**)

Which approximations have to be made in order to obtain the Henderson-Hasselbalch equation (1.5.77)? Is the Henderson-Hasselbalch equation applicable at $V_B/V_A = 1$? Hint: start with Eq. (1.5.72).

1.5.2 CO$_2$-buffering

When $\mathrm{CO_2}$ dissolves in seawater, the $\mathrm{CO_2}$ concentration in solution changes only slightly because the system is buffered by $\mathrm{CO_3^{2-}}$ ions. In case of pH-buffering discussed in the previous section, the $\mathrm{OH^-}$ ions are neutralized by the $\mathrm{H^+}$ ions provided by the weak acid. In case of $\mathrm{CO_2}$-buffering, the $\mathrm{CO_2}$ is scavenged by the $\mathrm{CO_3^{2-}}$ ions according to the reaction:

$$\mathrm{CO_2} + \mathrm{CO_3^{2-}} + \mathrm{H_2O} \rightarrow 2\mathrm{HCO_3^-}\,. \qquad (1.5.78)$$

However, a small part of the resulting $\mathrm{HCO_3^-}$ will dissociate into $\mathrm{CO_3^{2-}}$ and $\mathrm{H^+}$ and therefore lower the pH ($\mathrm{CO_2}$ is a weak acid!). In the following, we will derive a quantitative expression for this $\mathrm{CO_2}$-buffering, called the Revelle factor.

To analyze the problem we first reduce the system of equations (1.1.7), (1.1.9) – (1.1.11), and (1.2.31) in that we express DIC and TA as functions of

$h := [\mathrm{H}^+]$ and $s := [\mathrm{CO}_2]$ (note that the abbreviations are used here only to simplify the expressions):

$$\mathrm{DIC} = s\left(1 + \frac{K_1^*}{h} + \frac{K_1^* K_2^*}{h^2}\right) \tag{1.5.79}$$

$$\mathrm{TA} = s\left(\frac{K_1^*}{h} + 2\frac{K_1^* K_2^*}{h^2}\right) + \frac{B_T K_\mathrm{B}^*}{K_\mathrm{B}^* + h} + \frac{K_\mathrm{W}^*}{h} - h. \tag{1.5.80}$$

The change of DIC and TA is given by the total differentials:

$$d\mathrm{DIC} = D_s ds + D_h dh \tag{1.5.81}$$

$$d\mathrm{TA} = A_s ds + A_h dh \tag{1.5.82}$$

where[19]

$$D_s := \left(\frac{\partial \mathrm{DIC}}{\partial s}\right)_h = 1 + \frac{K_1^*}{h} + \frac{K_1^* K_2^*}{h^2} \tag{1.5.83}$$

$$D_h := \left(\frac{\partial \mathrm{DIC}}{\partial h}\right)_s = -s\left(\frac{K_1^*}{h^2} + 2\frac{K_1^* K_2^*}{h^3}\right) \tag{1.5.84}$$

$$A_s := \left(\frac{\partial \mathrm{TA}}{\partial s}\right)_h = \frac{K_1^*}{h} + 2\frac{K_1^* K_2^*}{h^2} \tag{1.5.85}$$

$$A_h := \left(\frac{\partial \mathrm{TA}}{\partial h}\right)_s = -s\left(\frac{K_1^*}{h^2} + 4\frac{K_1^* K_2^*}{h^3}\right) - \frac{K_\mathrm{B}^* B_T}{(K_\mathrm{B}^* + h)^2} - \frac{K_\mathrm{W}^*}{h^2} - 1. \tag{1.5.86}$$

We know the change of CO_2 from Henry's law. When CO_2 invades the surface ocean, the pH decreases. To calculate the change in hydrogen ion concentration we make use of the differential of alkalinity. The uptake of CO_2 from the atmosphere does not change alkalinity ($d\mathrm{TA} = 0$) and therefore

$$\begin{aligned}\frac{dh}{ds} &= -A_s A_h^{-1} \\ &= \frac{\left(\frac{K_1^*}{h} + 2\frac{K_1^* K_2^*}{h^2}\right)}{1 + \frac{K_\mathrm{W}^*}{h^2} + \frac{B_T K_\mathrm{B}^*}{(K_\mathrm{B}^* + h)^2} + s\left(\frac{K_1^*}{h^2} + 4\frac{K_1^* K_2^*}{h^3}\right)}\end{aligned} \tag{1.5.87}$$

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[19] D_s is the partial derivative of DIC with respect to the carbon dioxide concentration, s, while the H^+ concentration, h, is kept constant (indicated by the index h at the foot of the right bracket).

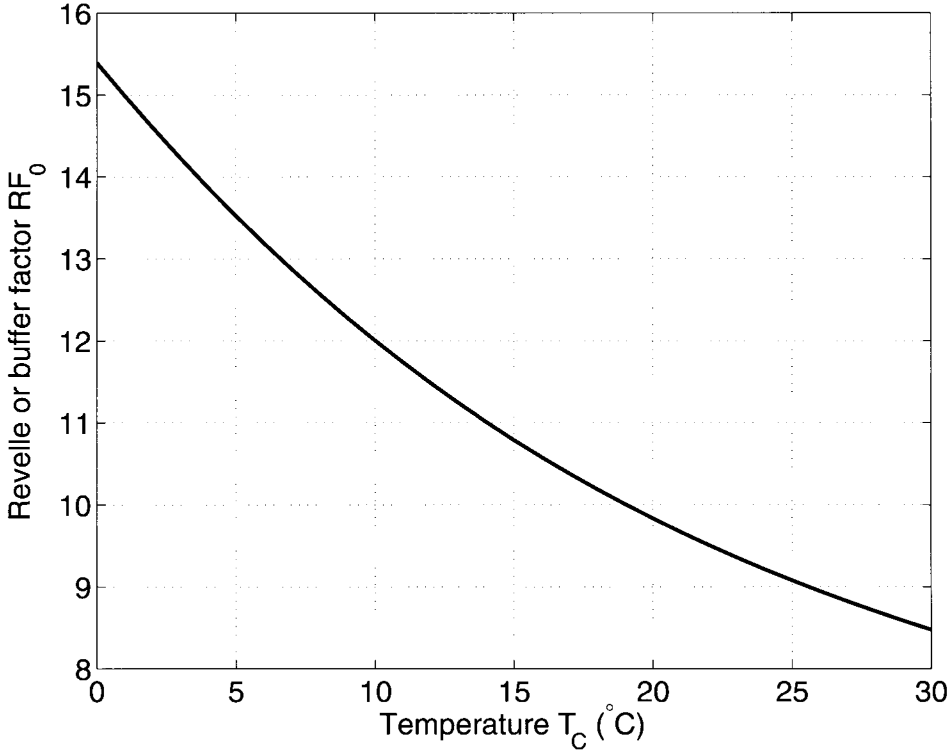

Figure 1.5.22: The Revelle factor RF_0 as a function of temperature ($S = 35$, $p\text{CO}_2 = 360\ \mu\text{atm}$, $\text{TA} = 2300\ \mu\text{mol kg}^{-1}$).

and

$$
\begin{aligned}
\frac{d\text{DIC}}{ds} &= \left[D_s - D_h A_s A_h^{-1}\right] \\
&= \frac{4\dfrac{K_1^* K_2^*}{h^2} + \dfrac{K_1^*}{h} + \dfrac{(K_1^*)^2 K_2^*}{h^3} + \dfrac{h}{s}}{4\dfrac{K_1^* K_2^*}{h^2} + \dfrac{K_1^*}{h} + \dfrac{h}{s}\left[1 + \dfrac{K_\text{w}^*}{h^2} + \dfrac{B_T K_\text{B}^*}{(K_\text{B}^* + h)^2}\right]} \\
&\quad + \frac{\left(1 + \dfrac{K_1^* K_2^*}{h^2} + \dfrac{K_1^*}{h}\right)\left(1 + \dfrac{K_\text{w}^*}{h^2} + \dfrac{B_T K_\text{B}^*}{(K_\text{B}^* + h)^2}\right)}{4\dfrac{K_1^* K_2^*}{h^2} + \dfrac{K_1^*}{h} + \dfrac{h}{s}\left[1 + \dfrac{K_\text{w}^*}{h^2} + \dfrac{B_T K_\text{B}^*}{(K_\text{B}^* + h)^2}\right]} .
\end{aligned}
\tag{1.5.88}
$$

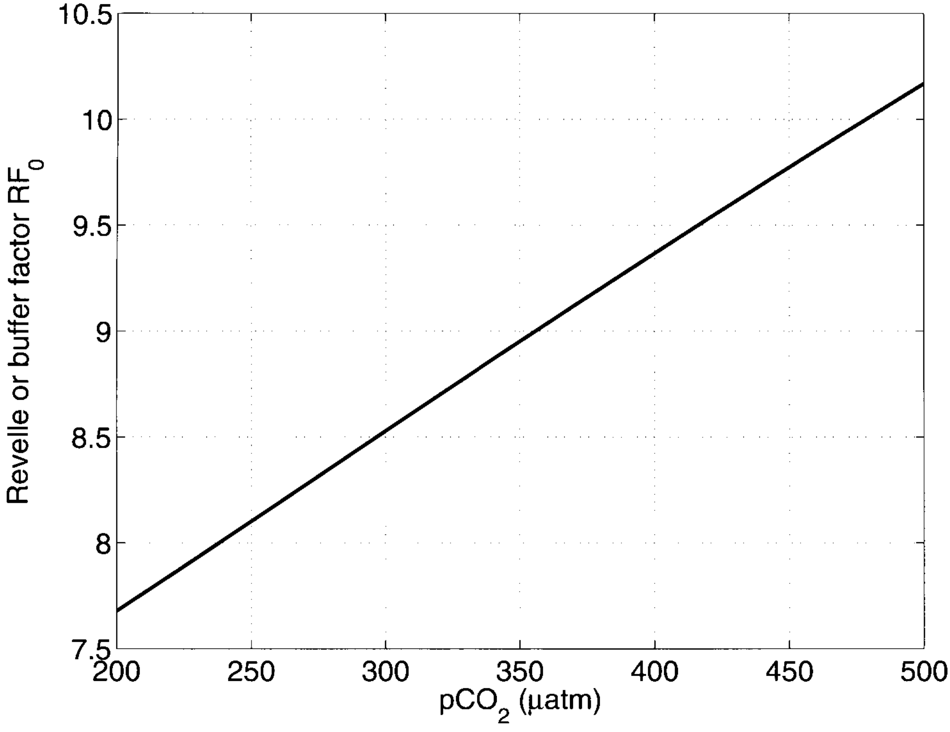

Figure 1.5.23: The Revelle factor RF_0 as a function of $p\text{CO}_2$ ($T_c = 25°\text{C}$, $S = 35$, TA $= 2300$ μmol kg^{-1}). With increasing partial pressure of CO_2 the Revelle factor increases and thus the buffering capacity of the ocean decreases.

The right-hand side of Eq. (1.5.87) is always positive, i.e. with increasing CO_2 concentration the hydrogen ion concentration increases and the pH decreases: the water becomes more acidic. As a consequence the concentration ratios of CO_2, HCO_3^-, and CO_3^{2-} change: while the portions of CO_2 and HCO_3^- increase, the portion of CO_3^{2-} decreases (compare Figure 1.1.2). The DIC concentration increases with increasing CO_2 concentration (all terms of the right-hand side of Eq. (1.5.88) are positive). However, the increment is not proportional to the increment of $[\text{CO}_2]$. This effect is quantified by the differential Revelle[20] or buffer factor RF_0:

$$\boxed{RF_0 := \left(\frac{d[\text{CO}_2]}{[\text{CO}_2]} \bigg/ \frac{d\text{DIC}}{\text{DIC}}\right)_{\text{TA}\,=\,\text{const.}} \qquad (1.5.89)}$$

---

[20] Roger Revelle (1909-1991)

where the index 0 indicates that the alkalinity is constant. The Revelle factor for more general conditions is discussed in Section 1.6.2.

In other words, the Revelle factor is given by the ratio of the relative change of CO_2 to the relative change of DIC. Typical values of RF_0 in the ocean are between 8 and 15 (see Figures 1.5.22 and 1.5.23), depending on the atmospheric CO_2 concentration and seawater temperature (Broecker et al., 1979). Thus, the relative change of CO_2 is larger than the relative change of DIC by about one order of magnitude. As a consequence, a doubling of atmospheric CO_2 leads to a change of DIC by only 10% ($\simeq$ 200 μmol kg^{-1}), provided that all other parameters including temperature are kept constant.

In summary, the carbonate system in seawater comprises only a few components (CO_2, HCO_3^-, CO_3^{2-}, H^+, OH^-) which are relevant for buffering. In addition, boron compounds ($B(OH)_3$, $B(OH)_4^-$) also serve as a *p*H buffer and have to be taken into account in quantitative calculations. The response of the system due to uptake of CO_2 is not easily predictable and differentials of DIC and TA have been used to derive an expression for the Revelle factor. Using the Revelle factor, one calculates that when the ocean takes up CO_2, the relative increase in DIC is approximately only one tenth of the relative increase in dissolved CO_2.

Exercise 1.13 (**)

Derive Eqs. (1.5.79) and (1.5.80).

1.6 Worked out problems

In this section, some problems are discussed which shall illustrate the properties of the carbonate system. The discussion includes important topics such as the formation of calcium carbonate, the Revelle factor as a function of biological processes, air-sea gas exchange, and changes of atmospheric CO_2 concentrations on glacial-interglacial time scales and in the future. Another worked out problem that deals with the manipulation of seawater chemistry for the purpose of culture experiments with phytoplankton can be found in Appendix C.5.

1.6.1 Formation of $CaCO_3$ leads to higher CO_2 levels

As already mentioned in the introduction, formation of $CaCO_3$ increases the concentration of CO_2. In this section three different ways of reasoning will be given to explain this counterintuitive behavior.

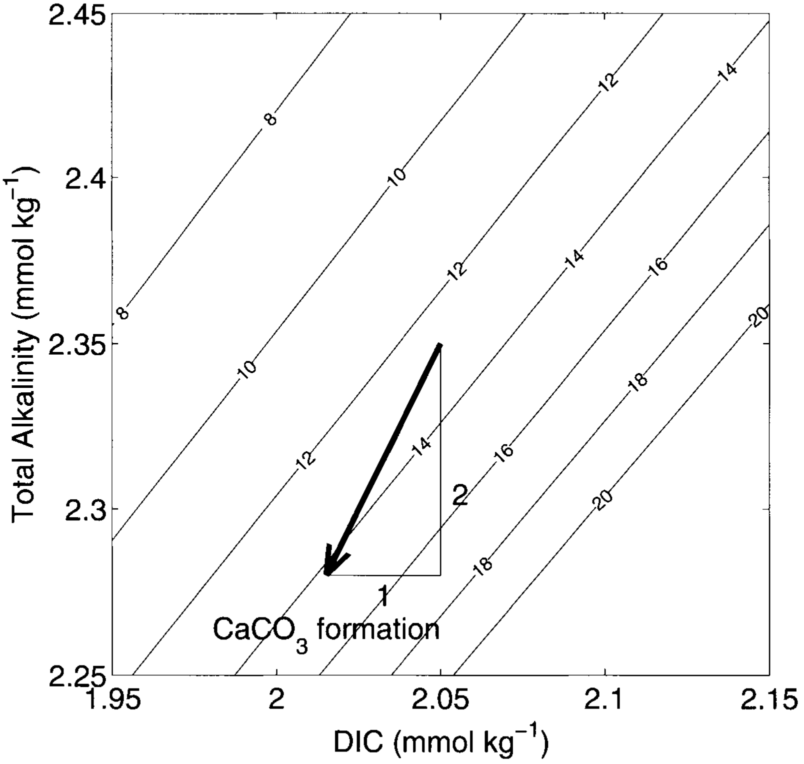

Figure 1.6.24: Isocontours of [CO_2] in μmol kg^{-1} as a function of DIC and TA (T_c = 25°C, S = 35). The arrow shows the path during calcification: for the change of DIC by one unit, the alkalinity changes by two units. As a result, the concentration of CO_2 increases.

The first is not much more than a donkey-bridge. Consider the chemical reaction

$$Ca^{2+} + 2\,HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \tag{1.6.90}$$

in which two bicarbonate ions are consumed and one CO_2 molecule is produced for each $CaCO_3$ molecule precipitated. There are several possible interpretations of this reaction equation:

- $CaCO_3$ formation results in production of CO_2. This is correct. Consider the backward reaction of (1.6.90). Carbonic acid and other acids can be neutralized by $CaCO_3$. For example, tons of lime have been added to acidified lakes in order to restore their pH by neutralizing sulfuric acid (Mackenzie and Mackenzie, 1995). This procedure is analogous to taking sodium bicarbonate tablets to treat heartburn. The inverse reaction must liberate CO_2.

- For each mole of $CaCO_3$ formed the amount of CO_2 in the water increases by one mole. This is wrong because of buffering: most of the newly formed CO_2 will be converted to bicarbonate. Note that per mole $CaCO_3$ formed, indeed 1 mole CO_2 is produced. However, as this CO_2 is mainly converted to HCO_3^-, the concentration of CO_2 in the water does not increase by 1 mole. Reaction scheme (1.6.90) is therefore incomplete.
- TA and DIC are reduced by 2 and 1 units, respectively, for each unit of $CaCO_3$ formed. This is correct.
- Organisms use bicarbonate for $CaCO_3$ formation. This might be correct; for sure carbonate alkalinity is consumed.

For the second way of reasoning consider the isocontours of $[CO_2]$ as a function of DIC and alkalinity (Figure 1.6.24); the values have been calculated with formulas derived in Appendix B. The arrow describes the shift in the carbonate system in response to calcification. For each unit of $CaCO_3$ produced, DIC is reduced by one unit and alkalinity by two units. According to this ratio the arrow crosses the isocontours from lower to higher CO_2 concentrations.

In the next subsection the change of concentration will be calculated explicitly (third way of reasoning).

1.6.2 The Revelle factor as a function of rain ratio

The Revelle or buffer factor, RF, has been introduced already in Section 1.5.2 in the context of changing atmospheric CO_2 concentrations. The buffer factor RF is defined as the ratio of the relative change in $[CO_2]$ to the relative change in DIC:

$$RF := \frac{d[\mathrm{CO_2}]}{[\mathrm{CO_2}]} \bigg/ \frac{d\mathrm{DIC}}{\mathrm{DIC}}. \tag{1.6.91}$$

In Section 1.5.2, RF has been calculated for the case when the alkalinity is kept constant and was denoted by RF_0. Now the Revelle factor will be discussed for more general conditions including $CaCO_3$ precipitation.

Dissolved inorganic carbon is removed or exported from the upper mixed layer of the ocean either as $CaCO_3$ or as particulate organic carbon (POC).

The ratio of these two forms is called the rain rate ratio, or for short the rain ratio, r:

$$r := \frac{\text{rate of CaCO}_3\text{ export}}{\text{rate of POC export}} \tag{1.6.92}$$

(see, for example, Heinze et al., 1991, p. 402).[21] This ratio may vary between zero and infinity, whereas the rain ratio parameter γ, defined by

$$\gamma := \frac{\text{rate of CaCO}_3\text{ export}}{\text{rate of carbon export (POC plus CaCO}_3\text{)}} \tag{1.6.93}$$

is in the range between zero and one. For $\gamma = 0$, there is only POC export and no $CaCO_3$ export, for $\gamma = 1$ there is only $CaCO_3$ export and no POC export. The quantities r and γ are related by

$$r = \frac{1}{1-\gamma} \quad \text{and} \quad \gamma = \frac{r}{1+r}. \tag{1.6.94}$$

Consider the change in DIC and TA due to the production of $CaCO_3$ and POC. Let U be the export of carbon per time interval. The change of DIC reads:

$$d\mathrm{DIC} \;=\; D_s ds + D_h dh = -U dt \tag{1.6.95}$$

where $D_s ds + D_h dh$ is the total differential of DIC; D_s and D_h are the partial derivatives of DIC with respect to $[CO_2]$ and $[H^+]$, respectively (Eqs. 1.5.83 and 1.5.84), and ds and dh are the infinitesimal changes in $[CO_2]$ and $[H^+]$, respectively. Only the part γU which is in the form of $CaCO_3$ reduces TA:

$$d\mathrm{TA} \;=\; A_s ds + A_h dh = -2\gamma U dt \tag{1.6.96}$$

The factor two stems from the fact that TA changes by two units for each unit of DIC change. The partial derivatives of DIC and TA are given by Eqs. (1.5.83) - (1.5.86).

From Eqs. (1.6.95) and (1.6.96) the Revelle factor can be calculated. Multiplying (1.6.95) by 2γ ($\gamma \neq 0$) leads to

$$2\gamma(D_s ds + D_h dh) = A_s ds + A_h dh \tag{1.6.97}$$

which may be solved for dh

$$dh = \frac{A_s - 2\gamma D_s}{2\gamma D_h - A_h} ds. \tag{1.6.98}$$

---

[21] Some authors use the inverse of r as the rain rate ratio.

Eliminating dh in Eq. (1.6.95) leads to

$$d\mathrm{DIC}/ds = D_s + D_h \frac{A_s - 2\gamma D_s}{2\gamma D_h - A_h}. \tag{1.6.99}$$

Note that Eq. (1.6.99) also contains the special case where only CO_2 is taken up (set $\gamma = 0$ and compare with Eq. (1.5.88)).

The Revelle factor as a function of the rain ratio parameter γ reads:

$$\begin{aligned} RF &:= \frac{ds}{s} \Big/ \frac{d\mathrm{DIC}}{\mathrm{DIC}} \\ &= \frac{\mathrm{DIC}\,(2\gamma D_h - A_h)/s}{D_s\,(2\gamma D_h - A_h) + D_h\,(A_s - 2\gamma D_s)} \\ &= \frac{\mathrm{DIC}}{s} \frac{2\gamma D_h - A_h}{D_h A_s - D_s A_h} \end{aligned} \tag{1.6.100}$$

Some remarks are in order.

- The Revelle factor is a linear function of the rain ratio parameter γ:

$$\begin{aligned} RF(\gamma) &= c_0 + c_1\gamma \\ c_0 &= -\frac{\mathrm{DIC}}{s} \frac{A_h}{D_h A_s - D_s A_h} \\ c_1 &= \frac{\mathrm{DIC}}{s} \frac{2D_h}{D_h A_s - D_s A_h} \end{aligned}$$

- For $\gamma = 0$, the Revelle factor for constant alkalinity, RF_0, is recovered from Eq. (1.6.100) which has been derived in Section 1.5.

- The denominator $D_h A_s - D_s A_h$ is always positive:

$$\begin{aligned} D_h A_s - D_s A_h &= \frac{sK_1^*}{h^2}\left(1 + 4\frac{K_2^*}{h} + \frac{K_1^* K_2^*}{h^2}\right) \\ &\quad + \left(1 + \frac{K_1^*}{h} + \frac{K_1^* K_2^*}{h^2}\right)\left(\frac{K_\mathrm{B}^* B_T}{(K_\mathrm{B}^* + h)^2} + \frac{K_\mathrm{W}^*}{h^2} + 1\right) \end{aligned}$$

- The Revelle factor is
  - positive for $\gamma < \dfrac{A_h}{2D_h}$
  - zero for $\gamma = \gamma^{(0)} := \dfrac{A_h}{2D_h}$

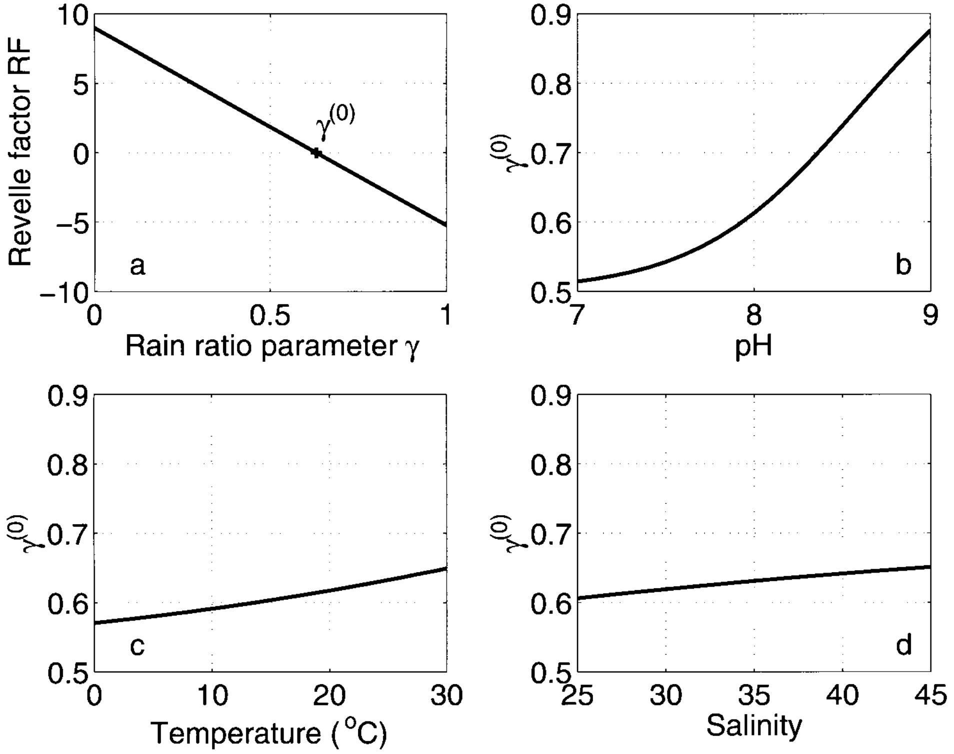

Figure 1.6.25: Revelle factor at $T_c = 25°$, $S = 35$, DIC $= 2000$ μmol kg^{-1}, $p\text{CO}_2 =$ 360 μatm. (a) The Revelle factor, RF, as a function of the rain ratio parameter γ ($\gamma = 0$: no CaCO$_3$, only organic carbon; $\gamma = 1$: only CaCO$_3$, no organic carbon; see text). RF vanishes at the rain ratio parameter $\gamma^{(0)} \approx 0.63$. (b) $\gamma^{(0)}$ as a function of pH, (c) temperature, and (d) salinity.

$$- \text{ negative for } \gamma > \frac{A_h}{2D_h}$$

A typical value for $A_h/2D_h$ is 0.63 at $T_C = 25°\text{C}$, $S = 35$, DIC $= 2000$ μmol kg^{-1}, $p\text{CO}_2 = 360$ μatm (Figure 1.6.25). Export of carbon with a rain ratio parameter $\gamma = 0.63$ does not change [CO$_2$]; at lower rain rate ratios ($\gamma < 0.63$) [CO$_2$] decreases (dominance of POC production), whereas at higher ratios ($\gamma > 0.63$) [CO$_2$] increases (dominance of alkalinity decrease due to CaCO$_3$ production). The variations of $\gamma^{(0)}$ with pH, temperature, and salinity are shown in Figure 1.6.25.

Exercise 1.14 (**)

In the calculations given above the (small) change in alkalinity due to assimilation of nitrate has been neglected. How can this effect be taken into account?

1.6.3 Equilibration time for air-sea gas exchange

At the air-sea interface, gases are exchanged between atmosphere and ocean. On seasonal time scales, the troposphere is well mixed whereas only the oceanic mixed layer (and not the deep ocean) is involved in the exchange process, except for regions of strong vertical convection or upwelling. The equilibration of partial pressure of O_2 between the atmosphere is governed by the equation:

$$\begin{aligned} \frac{d[O_2]^{\mathrm{oce}}}{dt} &= \frac{k_{\mathrm{ge}}}{d_{\mathrm{ML}}\ \alpha_{O_2}} \left(pO_2{}^{\mathrm{atm}} - pO_2{}^{\mathrm{oce}}\right) \\ &= \frac{k_{\mathrm{ge}}}{d_{\mathrm{ML}}} \left([O_2]^{\mathrm{atm}} - [O_2]^{\mathrm{oce}}\right) \end{aligned} \tag{1.6.101}$$

where $k_{\mathrm{ge}} = 4.2$ m d^{-1} is the gas exchange coefficient (derived from radiocarbon measurements, Siegenthaler (1986)), $d_{\mathrm{ML}} = 50$ m is the typical depth of the mixed layer, and α_{O_2} is the solubility of O_2 in seawater. The partial pressure and concentration of O_2 are denoted by pO_2 and $[O_2]$, respectively; superscripts 'atm' and 'oce' refer to the values in the atmosphere and ocean. Note that the relations $[O_2]^{\mathrm{atm}} = pO_2{}^{\mathrm{atm}}/\alpha_{O_2}$ and $[O_2]^{\mathrm{oce}} = pO_2{}^{\mathrm{oce}}/\alpha_{O_2}$ have been used.

The characteristic time constant, or equilibration time, can be defined as:

$$\tau_{O_2} := \left([O_2]^{\mathrm{atm}} - [O_2]^{\mathrm{oce}}\right) \left(\frac{d[O_2]^{\mathrm{oce}}}{dt}\right)^{-1} = \frac{d_{\mathrm{ML}}}{k_{\mathrm{ge}}} \approx 12 \text{ d.}$$

After the time span τ_{O_2} the perturbation $\left([O_2]^{\mathrm{atm}} - [O_2]^{\mathrm{oce}}\right)_{t=0}$ has decreased to 37% ($\simeq 1/e$) of its initial value.

The equilibration time for CO_2 is much longer because CO_2 is a small part (roughly 0.5%) of the dissolved inorganic carbon (DIC) which buffers changes in CO_2 concentration and thereby slows down equilibration. The change in DIC is driven by partial pressure differences of CO_2 between air and water:

$$\begin{aligned} \frac{d\mathrm{DIC}}{dt} &= \left(\frac{d\mathrm{DIC}}{d[CO_2]^{\mathrm{oce}}}\right) \left(\frac{d[CO_2]^{\mathrm{oce}}}{dt}\right) \\ &= \frac{k_{\mathrm{ge}}}{d_{\mathrm{ML}}} \left([CO_2]^{\mathrm{atm}} - [CO_2]^{\mathrm{oce}}\right) \end{aligned}$$

The equilibration time for CO_2 is defined analogously to that for oxygen:

$$\begin{aligned} \tau_{CO_2} &:= \left([CO_2]^{atm} - [CO_2]^{oce}\right)\left(\frac{d[CO_2]^{oce}}{dt}\right)^{-1} \\ &= \frac{d_{ML}}{k_{ge}}\left(\frac{d\mathrm{DIC}}{d[CO_2]^{oce}}\right) \\ &= \underbrace{\frac{d_{ML}}{k_{ge}}}_{\approx 12\ \mathrm{d}}\ \underbrace{\frac{\mathrm{DIC}}{[CO_2]^{oce}}}_{\approx 200}\ \underbrace{\frac{1}{\mathrm{RF}_0}}_{\approx 0.1} \approx 240\ \mathrm{d} \end{aligned} \tag{1.6.102}$$

where RF_0 is the Revelle factor at constant TA (Eq. (1.5.89)). The factor (d_{ML}/k_{ge}) is similar for all gases. The quotient $\mathrm{DIC}/[CO_2]^{oce}$, which is unique for CO_2, expresses the fact that CO_2 dissociates in seawater and hence builds up a large reservoir of dissolved inorganic carbon. In summary, the extraordinary long equilibration time of CO_2 as opposed to O_2 (about 20 times longer) is due to the large concentration of DIC which can only be exchanged via a bottleneck, namely the low concentration of CO_2.

Exercise 1.15 (**)

How does the equilibration time τ_{CO_2} vary with pCO_2 while TA is kept constant?

Exercise 1.16 (**)

Find an interpretation of the factor $1/\mathrm{RF}_0$ in Eq. (1.6.102).

1.6.4 Glacial to interglacial changes in CO_2

The atmospheric CO_2 concentration at the last glacial maximum (LGM; ~ 18,000 years before present) has been about 100 ppmv lower compared to the year 1800 (preindustrial value ≃ 280 ppmv). Can this change be explained simply by a change in the ocean surface temperature?

Based on the results of box models (Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk; 1984), Broecker and Peng (1998) argue that the atmospheric CO_2 concentration depends on the state of the surface ocean in subpolar regions where most of the deep water is formed. The sea surface temperatures in these regions were most likely about 1 K lower during the last glacial. The cooling by 1 K leads to a decrease of CO_2 by about 20 ppmv. During the LGM the mean salinity was ~3% higher because large amounts of fresh water were deposited in ice sheets in North America, Scandinavia and northern Russia (the sea level was more than 100 m below the current level). This increase of salinity compensates almost half of the CO_2 decrease due to cooling. If we assume

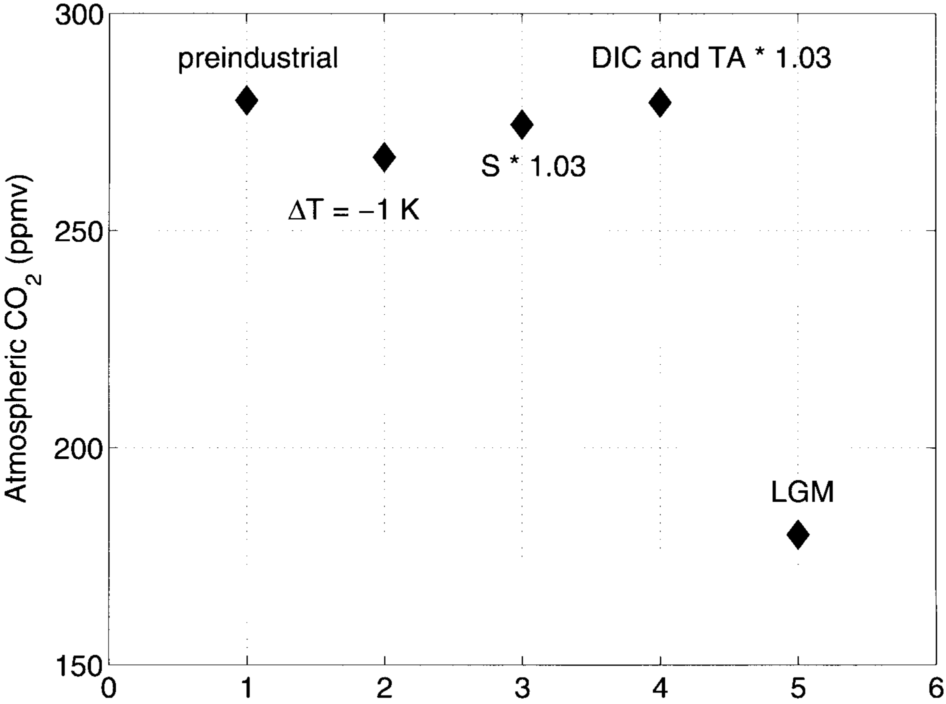

Figure 1.6.26: Changes in atmospheric CO_2 due to changes in temperature, salinity, DIC, and TA (preindustrial values: CO_2= 280 ppmv, DIC = 2000 μmol kg^{-1} at T_c = 10°C and S = 35). The glacial-interglacial change in atmospheric CO_2 (from 180 ppmv at the LGM to 280 ppmv in preindustrial time) cannot be explained simply by changes in temperature and sea level.

that DIC and TA were also higher by 3%, which is an oversimplification of the glacial situation, the change due to cooling is almost compensated (Figure 1.6.26).

Thus the glacial-interglacial change in atmospheric CO_2 cannot be explained simply by differences in temperature and sea level. During the past two decades several scenarios have been proposed for the state of the glacial ocean (see, for instance, Broecker (1982), Berger and Keir (1984), Boyle (1988), Broecker and Peng (1989), Heinze et al. (1991), Broecker and Henderson (1998), Sigman and Boyle (2000)) but none of these hypotheses appears to be without contradictions to accepted facts. While the composition of the paleoatmosphere can be determined quite well from air contained in gas bubbles in glacial ice, there is no such tool for the ocean. Furthermore, whereas the atmosphere is fairly homogeneous due to short mixing time scales on the order of years, the ocean is rather inhomogeneous and

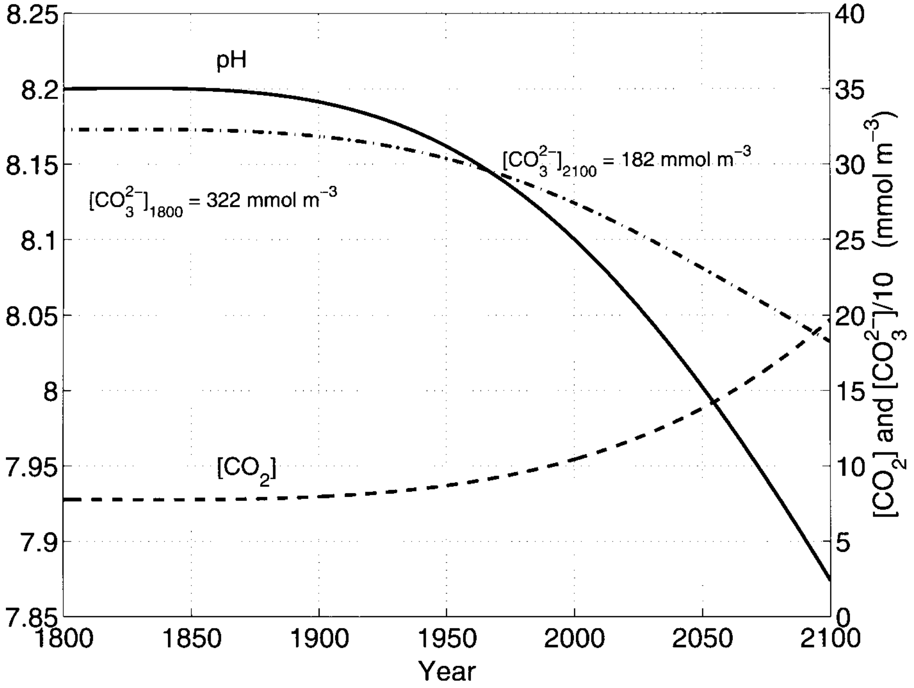

Figure 1.6.27: Changes of CO_2, CO_3^{2-}, and pH in the surface ocean calculated according to the business as usual scenario IS92a ($T_c = 25°C$, $S = 35$).

has mixing time scales of the order of thousand years. The reconstruction of the state of the paleocean is therefore much more intricate. One has to rely on so-called paleoproxies which are used to approximate the inhomogeneous distributions of temperature, salinity, nutrients, carbonate system parameters and other variables of the past ocean. Some of those proxies will be discussed in Chapter 3.

1.6.5 Future CO_2 emissions and change in pH

The atmospheric CO_2 concentration has increased from the preindustrial value of 280 ppmv to a value of 364 ppmv in 1997 (Indermühle et al., 1999). According to a business as usual scenario, the CO_2 concentration will reach 700 ppmv in the year 2100 (Scenario IS92a; IPCC, 1995). What are the consequences of this rapid increase for the ocean?

The carbonate system in the surface ocean will follow the forcing by the atmosphere with a time lag of less than one year (compare Section 1.6.3

on air-sea equilibration time). The mean surface ocean *p*H today is already about 0.1 units lower than the preindustrial value. In the future, the *p*H and the concentration of carbonate ions will further decrease due to the invasion of CO_2 from the atmosphere (Figure 1.6.27).

These changes may have important consequences for growth, calcification rates, and isotopic composition of marine plankton and corals. For instance, regarding $CaCO_3$ production in the surface ocean, it is to be expected that marine calcification in corals (e.g. Gattuso et al., 1999; Kleypas et al., 1999; Langdon et al., 2000), foraminifera (Wolf-Gladrow et al., 1999b), and coccolithophorids (Riebesell et al., 2000; Zondervan et al., 2001) will decrease in the future. As atmospheric CO_2 concentrations increase, CO_2 concentrations in the surface ocean increase as well, leading to a reduction of the $CaCO_3$ saturation state in surface seawater. Calcification rates in marine organisms have been found to be sensitive to changes of the saturation state and, as a result, showed reduced production of $CaCO_3$ at higher CO_2 concentrations. On a global scale, this is a potential negative feedback effect on atmospheric pCO_2 which has been estimated to lead to an additional storage of $\sim$6 to $\sim$32 Gt C in the surface ocean until the year 2100 (Riebesell et al., 2000; Zondervan et al., 2001).

Chapter 2

Kinetics

In Chapter 1, the properties of the carbonate system in thermodynamic equilibrium were studied. It was demonstrated how those properties can be used to understand changes of the seawater chemistry resulting from processes such as the invasion of anthropogenic CO_2 into the ocean or from the formation of $CaCO_3$. Equilibrium properties of the carbonate system are applicable to the description of those processes because the characteristic time and length scales involved are on the order of months to years and meters to kilometers. On small length and time scales, however, disequilibrium of the carbonate system has to be taken into account. It will be shown in Section 2.4 that the time required to establish chemical equilibrium is on the order of a minute. Consequently, processes faster than this cannot be adequately described by equilibrium concepts. One example is the transport or the supply of chemical substances on length scales where chemical conversion and diffusion are the dominant mechanisms ($\lesssim 10^{-3}$ m). This is the case, e.g. within the diffusive boundary layer at the ocean-atmosphere interface (air-sea gas-exchange) or within the microenvironment of larger marine plankton.

In this chapter some basic features of chemical kinetics and their mathematical description are introduced (Section 2.1). Then the values and the temperature dependence of the rate constants of the carbonate system are summarized (Section 2.3). The kinetics of the carbonate system are described in detail (Section 2.4), including an analysis of the time scales involved in the relaxation of the system towards equilibrium. In this context, the stable carbon isotopes ^{12}C, ^{13}C, and ^{14}C are also considered (Section 2.5). Finally, diffusion-reaction equations in plane and in spherical geometry are discussed (Section 2.6).