The carbon dioxide system in seawater: Equilibrium chemistry and measurements

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1.1 Introduction

The world's oceans can be thought of as a dilute solution of sodium bicarbonate (together with other acid-base species at still lower concentrations) in a saltwater background. In the surface waters of the North Atlantic, for example, the concentration of total dissolved inorganic carbon (the sum of the concentrations of the three coexisting species: bicarbonate ion, carbonate ion, and unionised dissolved carbon dioxide) is only about 2 mmol kg^{-1}. About 90% of this is present as bicarbonate ion, the proportion of carbonate ion is about a factor of 10 less (~10%), and that of unionised carbon dioxide yet another factor of 10 less (<1%). As a result of the equilibria between these various species (see below), seawater is buffered (weakly) with respect to changes in hydrogen ion (present at much lower concentrations: $<10^{-8}$ μmol kg^{-1}).

Over the past twenty years, accurate measurement of the seawater carbon dioxide system has become a high priority for scientists who have worked to understand just how much of the carbon dioxide (CO_2) created by man's activities has ended up in the ocean, where it is distributed, and how it has changed the chemistry of the oceans. The chemical changes associated with the increase of CO_2 in the oceans are often referred to as *ocean acidification*. As we work to design suitable experiments to understand the biological and ecological consequences of such changes, it is important that the chemistry of CO_2 be well characterised in the various laboratory experiments and field observations that are undertaken. Achieving this requires an understanding of the basic solution chemistry underlying ocean acidification, as well as of the relative merits of the various analytical techniques available to the investigator.

Unfortunately – from the point of view of someone desiring simplicity – in addition to carbon dioxide there are other acid-base systems in seawater that complicate things, particularly in systems that are not typical of the open surface ocean, with its low nutrient levels and relatively low amounts of dissolved organic material. The approach I shall take in this chapter is to introduce first a somewhat simplified view of acid-base chemistry in seawater involving only the primary seawater acid-base systems: carbonic acid, boric acid and water. These will be discussed in some detail, and used to introduce the classical oceanographic analytical parameters for carbon dioxide studies in seawater: total dissolved inorganic carbon, total alkalinity, pH, and $p(CO_2)$ – the partial pressure of carbon dioxide that is in equilibrium with a water sample (Box 1.1). The concept of calcium carbonate saturation state will also be introduced.

Once this basic seawater chemistry has been presented – and assimilated – it will be appropriate to revisit a number of these topics and to introduce further complexity, so as to clarify how these various concepts can be applied appropriately in the seawater systems that are of interest to investigators in ocean acidification. Finally, I shall present a brief discussion of some of the current techniques available for the measurement of the various parameters of the seawater carbon dioxide system, and will indicate their advantages and disadvantages. The advantages and disadvantages of using alternate combinations of parameters to provide a complete description of the composition of a particular seawater sample will also be discussed.

As will become clear, at this time it is not as straightforward as one might wish to characterise the state of a particular seawater sample's carbonate chemistry and to assign a well-constrained measurement uncertainty. Investigators who wish to do high quality work in ocean acidification, but who have little previous experience in seawater CO_2 measurements, would do well to collaborate with a scientist with experience in this area and who has access to a working laboratory that can perform the necessary measurements with the required quality.

Box 1.1: Terminology and units for parameters relevant to the carbonate system

Hans-Otto Pörtner, Andrew Dickson and Jean-Pierre Gattuso

Research in ocean acidification brings together various scientific disciplines such as chemistry, geology, biogeochemistry, ocean physics and various sub-disciplines of biology and ecology (biological oceanography, marine ecology and ecological physiology, biochemistry, physiological chemistry and molecular biology). Each of these disciplines generally investigates ocean acidification from its own point of view, building on its own traditions with the goal of providing the highest possible accuracy under the constraints of each field. Ideally, efficient communication should use a unified set of terms and units in scientific presentations, discussions and publications and when differences exist, they must be clearly documented and understood. A large number of terms and units are used to describe the physicochemical properties of the carbonate system in seawater and in the biological material and fluids that interact with seawater (Table). Marine chemistry uses them to quantify changes in seawater acid-base composition. Acid-base physiology uses similar terms to estimate the quantities of protons or base equivalents moving between water and organism as well as between body compartments causing changes in body fluid composition (e.g. Pörtner *et al.*, 1991). The aim of this box is to alert readers to parameters (e.g. pH, dissolved inorganic carbon) that are defined differently in marine chemistry (see chapter 1) and physiology (see chapter 9) and to describe the main terms and units used in this guide.

pH is the parameter that causes most difficulties. Marine chemistry has developed the total hydrogen ion concentration scale. It requires buffers prepared in synthetic seawater for calibration (Hansson, 1973; Dickson *et al.*, 2007). This scale includes the effect of sulfate ion in its definition. From a physiological perspective, the use of a free hydrogen ion concentration scale would be more appropriate than the total scale as it does not include sulfate protonation in its definition. It is possible to convert a pH value from the total scale to the free scale and vice versa (Zeebe & Wolf-Gladrow, 2001) in seawater of a known salinity, and software tools are available to achieve this (Lavigne & Gattuso, 2010). The free scale could also be used to express pH of the extracellular fluids of marine invertebrates. However, neither the total scale nor the free scale can be used straightforwardly for pH determinations in intracellular fluids and in extracellular fluids of vertebrates, which have ionic strengths of about one third of that of seawater. The conventional NBS pH scale is therefore commonly used in physiology for such measurements.

The sum of the concentrations of all inorganic carbon species is termed "total dissolved inorganic carbon" (DIC or C_T) in the field of marine chemistry and "total CO_2" (C_{CO_2}) in the field of physiology. These terms are not always synonymous, especially in body fluids where C_{CO_2} may also include inorganic CO_2 species bound to protein. Furthermore, different (though related) titration procedures are used to determine total alkalinity (by use of strong acid) in seawater and titratable acid(ity) (by use of strong base) in physiological fluids like urine. In tissues and blood, the CO_2/bicarbonate buffer system is distinguished from non-bicarbonate buffers, when analysing the "titration" of the latter by accumulating CO_2, by metabolic influences, or during proton-equivalent ion exchange.

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Table: Main parameters describing the physicochemistry of seawater and body fluids and their differences in the fields of marine chemistry and physiology. The notation and units used in this guide are also shown. Alternate notations or units are given in parentheses.

	Marine chemistry		Physiology	
Parameter	Notation	Unit	Notation	Unit
pH[1]	Total scale	-	NBS or NIST scale[2]	-
Partial pressure of CO_2	$p(CO_2)$ (pCO_2, P_{CO_2}, $p(CO_2)$)	µatm	P_{CO_2}	kPa (mm Hg, Torr, µatm)
CO_2 solubility	K_0	mol kg^{-1} atm^{-1}	α_{CO_2}	mmol l^{-1} mm Hg^{-1} (kPa^{-1})
Dissolved inorganic carbon or total CO_2	DIC (C_T, $\sum CO_2$, T_{CO_2})	mol kg^{-1}	C_{CO_2}	mol l^{-1}
Bicarbonate concentration	$[HCO_3^-]$	mol kg^{-1}	$[HCO_3^-]$	mol l^{-1}
Carbonate concentration	$[CO_3^{2-}]$	mol kg^{-1}	$[CO_3^{2-}]$	mol l^{-1}
Ammonium concentration	$[NH_4^+]$	mol kg^{-1}	$[NH_4^+]$	mol l^{-1}
Total alkalinity	A_T (TA, AT, ALK)	mol kg^{-1}	-	-

1 Whenever a pH is defined, it is necessary to remember that it implicitly is based on a concentration unit, for hydrogen ion, although the pH value itself has the dimension 1.

2 The free scale can be a suitable alternative.

1.2 Basic chemistry of carbon dioxide in seawater

1.2.1 Introduction

Seawater is unique among natural waters in that its relative composition is well defined (see e.g. Millero *et al.*, 2008) and dominated (>99.3% by mass) by a fairly limited number of major ions (Figure 1.1). The various acid-base species discussed in this chapter are in the remaining 0.7%, with carbonic acid and boric acid species predominating. As we shall see, this distinction between the *major* ions, that can be considered to make up a background ionic medium, and the various reacting species, that are present at relatively low concentrations, is an important convenience when discussing acid-base chemistry in seawater.

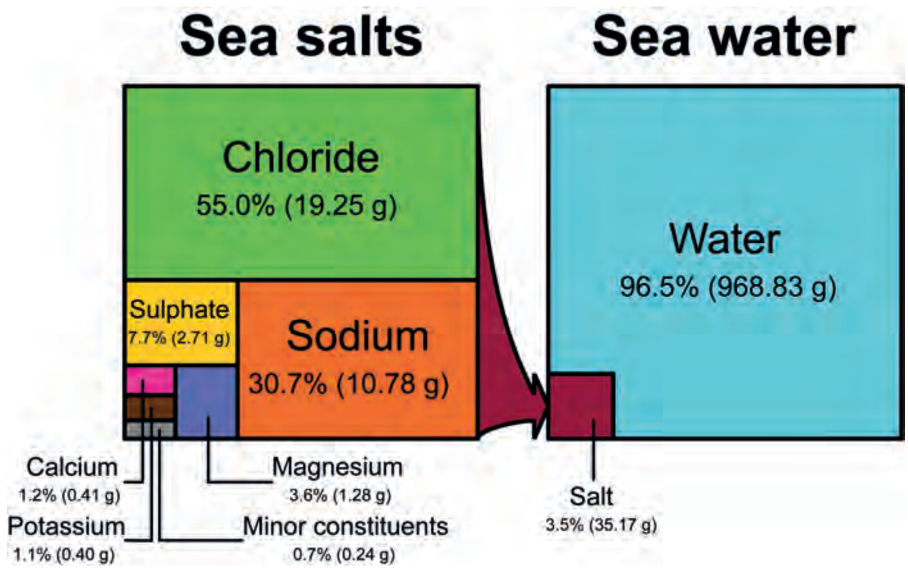

Figure 1.1 Composition of reference seawater (Millero *et al.*, 2008) showing quantities in relation to 1 kg of seawater. Modified from http://commons.wikimedia.org/wiki/File:Sea_salt-e-dp_hg.svg

1.2.2 Acid-base equilibria in seawater

When carbon dioxide dissolves in water, it hydrates to yield carbonic acid, H_2CO_3. This reaction is slow relative to the ionisation of H_2CO_3 and it is possible to distinguish between simple dissolved carbon dioxide, $CO_2(aq)$, and the hydrated species, H_2CO_3 (see e.g. Soli & Byrne, 2002). This kinetic process is relevant in some physiological systems and is catalysed by the enzyme carbonic anhydrase. At equilibrium, the concentration of carbonic acid, $[H_2CO_3]$, is only about 1/1000 of the concentration of dissolved carbon dioxide, $[CO_2(aq)]$ and has no special significance to the acid-base equilibria since both are uncharged (Butler, 1998). Here the total concentration of the two unionised species: $[H_2CO_3] + [CO_2(aq)]$, will be abbreviated as the concentration of the hypothetical aqueous species CO_2^*: $[CO_2^*]$.[1] In acid solutions (pH < 5) CO_2^* is the dominant carbon dioxide species in solution, however at higher pHs it ionises to form bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions.

[1] This corresponds to defining the standard states of $CO_2(aq)$ and of H_2CO_3 using the so-called *hydrate convention* (Pitzer & Brewer, 1961).

Thus when carbon dioxide dissolves in seawater it can be considered to react with the water in accordance with the following series of chemical equilibria (Figure 1.2):

$$CO_2(g) = CO_2^*(aq) ; \quad (1.1)$$

$$CO_2^*(aq) + H_2O(l) = H^+(aq) + HCO_3^-(aq) ; \quad (1.2)$$

$$HCO_3^-(aq) = H^+(aq) + CO_3^{2-}(aq) ; \quad (1.3)$$

the notations (g), (l), (aq) refer to the state of the species, i.e. a gas, a liquid, or in aqueous solution respectively. Equation (1.1) refers to the solubility equilibrium of carbon dioxide between air and seawater; equations (1.2) and (1.3) are consecutive acid dissociation reactions of dissolved carbon dioxide. Two other important acid-base equilibria in seawater are the dissociation of boric acid and the self-ionisation of water:

$$B(OH)_3(aq) + H_2O(l) = H^+(aq) + B(OH)_4^-(aq) ; \quad (1.4)$$

$$H_2O(l) = H^+(aq) + OH^-(aq) . \quad (1.5)$$

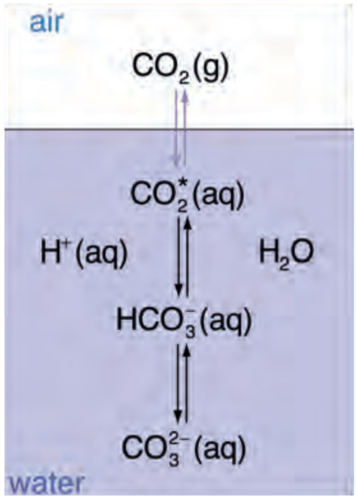

Figure 1.2 The chemical equilibria of the carbon dioxide system in seawater.

The equilibrium relationships between the concentrations of these various species can then be written in terms of the equilibrium constants:

$$K_0 = [CO_2^*] / f(CO_2) ; \quad (1.6)$$

$$K_1 = [H^+][HCO_3^-] / [CO_2^*] ; \quad (1.7)$$

$$K_2 = [H^+][CO_3^{2-}] / [HCO_3^-] ; \quad (1.8)$$

$$K_B = [H^+][B(OH)_4^-] / [B(OH)_3] ; \quad (1.9)$$

$$K_W = [H^+][OH^-] . \quad (1.10)$$

In these equations, $f(CO_2)$ is the fugacity of carbon dioxide in the gas phase (see Standard Operating Procedure (SOP) 24 in Dickson *et al.*, 2007) and brackets represent total stoichiometric concentrations[2] of the particular chemical species enclosed between them, expressed as moles per kilogram of solution. The use of fugacity in equation (1.6) allows the same equilibrium constant to be used for a wide variety of gas phase compositions (Weiss, 1974). In practice, most applications in ocean acidification studies will involve air containing carbon dioxide that is in equilibrium with the seawater at a total pressure of about 1 atmosphere. This air will thus also contain water vapour that is at its equilibrium concentration (its vapour pressure, approximately). Weiss & Price (1980) defined an alternate relationship, F such that

$$F = [CO_2^*] / x'(CO_2) ; \quad (1.11)$$

where $x'(CO_2)$ is the mole fraction of CO_2 present in dry air (i.e. after drying to remove the water vapour), and the appropriate corrections for non-ideality have been included implicitly. There are many situations where it is more practical to use this equation directly rather than calculating the correct $f(CO_2)$ value.

These equilibrium constants[3] are functions of the temperature, pressure and salinity of the seawater and have been measured at one atmosphere pressure in a variety of studies (see Millero, 2007). Recommended values are given in Table 1.1 as a function of salinity and temperature.

2 The *total* stoichiometric concentration of a species is the sum of the concentrations of the *free* species itself, together with the concentrations of all complexes that are formed between that species and the components of the ionic medium (for seawater: H_2O, Na^+, Mg^{2+}, K^+, Ca^{2+}, Cl^-, & SO_4^{2-}).

3 Strictly, equilibrium expressions such as equations (1.6) to (1.10) should be expressed in terms of activities rather than total stoichiometric concentrations so as to be *equilibrium constants*. However, as activity coefficients remain approximately constant for small amounts of reacting species in a background ionic medium, these expressions are valid and correspond to *ionic medium* equilibrium constants where the corresponding standard states are based on a seawater medium of a specified composition (Dickson *et al.*, 1981). Note that the activity of water is assumed to be unity.

Table 1.1 Expressions for calculating equilibrium constants (on the total hydrogen ion scale) as a function of salinity (S) and temperature (T, in Kelvin) (Weiss & Price, 1980; Millero, 1995; Dickson *et al.*, 2007).

Note: $I/m^\circ = \frac{19.924S}{1000 - 1.005S} \approx 0.02S$; $k^\circ = 1\ \text{mol kg}^{-1}$.

Equilibrium constant expression	Equation in text
$\ln(K_0/k^\circ) = 93.4517\left(\frac{100}{T}\right) - 60.2409 + 23.3585\ln\left(\frac{T}{100}\right) + S\left(0.023517 - 0.023656\left(\frac{T}{100}\right) + 0.0047036\left(\frac{T}{100}\right)^2\right)$	(1.6)
$\log(K_1/k^\circ) = \frac{-3633.86}{T} + 61.2172 - 9.67770\ln(T) + 0.011555S - 0.0001152S^2$	(1.7)
$\log(K_2/k^\circ) = \frac{-471.78}{T} - 25.9290 + 3.16967\ln(T) + 0.01781S - 0.0001122S^2$	(1.8)
$\ln\left(\frac{K_B}{k^\circ}\right) = \frac{-8966.90 - 2890.53S^{1/2} - 77.942S + 1.728S^{3/2} - 0.0996S^2}{T} + (148.0248 + 137.1942S^{1/2} + 1.62142S) + (-24.4344 - 25.085S^{1/2} - 0.2474S)\ln(T) + 0.053105S^{1/2}T$	(1.9)
$\ln\left(K_W/(k^\circ)^2\right) = \frac{-13847.26}{T} + 148.9652 - 23.6521\ln(T) + \left(\frac{118.67}{T} - 5.977 + 1.0495\ln(T)\right)S^{1/2} - 0.01615S;$	(1.10)
$\ln\left(\frac{F}{\text{atm}\ k^\circ}\right) = 218.2968\left(\frac{100}{T}\right) - 162.8301 + 90.9241\ln\left(\frac{T}{100}\right) - 1.47696\left(\frac{T}{100}\right)^2 + S\left(0.025695 - 0.025225\left(\frac{T}{100}\right) + 0.0049867\left(\frac{T}{100}\right)^2\right)$	(1.11)
$\lg K_{sp}(\text{aragonite}) = -171.945 - 0.077993T + 2903.293/T + 71.595\lg(T) + (-0.068393 + 0.0017276T + 88.135/T)S^{0.5} - 0.10018S + 0.0059415S^{1.5}$	(1.14)
$\lg K_{sp}(\text{calcite}) = -171.9065 - 0.077993T + 2839.319/T + 71.595\lg(T) + (-0.77712 + 0.0028426T + 178.34/T)S^{0.5} - 0.07711S + 0.0041249S^{1.5}$	(1.15)
$\ln(K'_S/k^\circ) = \frac{-4276.1}{T} + 141.328 - 23.093\ln(T) + \left(\frac{-13856}{T} + 324.57 - 47.986\ln(T)\right)\times\left(\frac{I}{m^\circ}\right)^{1/2} + \left(\frac{35474}{T} - 771.54 + 114.723\ln(T)\right)\times\left(\frac{I}{m^\circ}\right) - \frac{2698}{T}\left(\frac{I}{m^\circ}\right)^{3/2} + \frac{1776}{T}\left(\frac{I}{m^\circ}\right)^2 + \ln(1 - 0.001005S),$	(1.30)
$\ln(K_F/k^\circ) = \frac{874}{T} - 9.68 + 0.111S^{1/2}$	(see 1.41)
$\ln(K_{Si}/k^\circ) = \frac{-8904.2}{T} + 117.385 - 19.334\ln(T) + \left(\frac{-458.79}{T} + 3.5913\right)(I/m^\circ)^{1/2} + \left(\frac{188.74}{T} - 1.5998\right)(I/m^\circ) + \left(\frac{-12.1652}{T} + 0.07871\right)(I/m^\circ)^2 + \ln(1 - 0.001005S);$	(1.45)
$\ln(K_{1P}/k^\circ) = \frac{-4576.752}{T} + 115.525 - 18.453\ln(T) + \left(\frac{-106.736}{T} + 0.69171\right)S^{1/2} + \left(-\frac{0.65643}{T} - 0.01844\right)S;$	(1.46)
$\ln(K_{2P}/k^\circ) = \frac{-8814.715}{T} + 172.0883 - 27.927\ln(T) + \left(\frac{-160.340}{T} + 1.3566\right)S^{1/2} + \left(\frac{0.37335}{T} - 0.05778\right)S,$	(1.47)
$\ln(K_{3P}/k^\circ) = \frac{-3070.75}{T} - 18.141 + \left(\frac{17.27039}{T} + 2.81197\right)S^{1/2} + \left(\frac{-44.99486}{T} + 0.09984\right)S;$	(1.48)
$\ln K_{NH3} = -6285.33/T + 0.0001635T - 0.25444 + (0.46532 - 123.7184/T)S^{0.5} + (-0.01992 + 3.17556/T)S$	(1.49)

1.2.3 The saturation state of calcium carbonate minerals in seawater

There are three primary biogenic carbonate-containing mineral phases that occur in seawater: aragonite, calcite, and magnesian calcite. Aragonite and calcite are naturally occurring polymorphs of calcium carbonate with differing crystal lattice structures and hence solubilities, aragonite being about 1.5 times more soluble than calcite at 25°C. Magnesian calcite is a variety of calcite with magnesium ions randomly substituted for the calcium ions in a disordered calcite lattice. At low mole fractions of magnesium (<4%) the solubility of this phase is lower than that of calcite, whereas at high mole fractions (>12%) the solubility is greater than that of aragonite (see Figure 1.3).

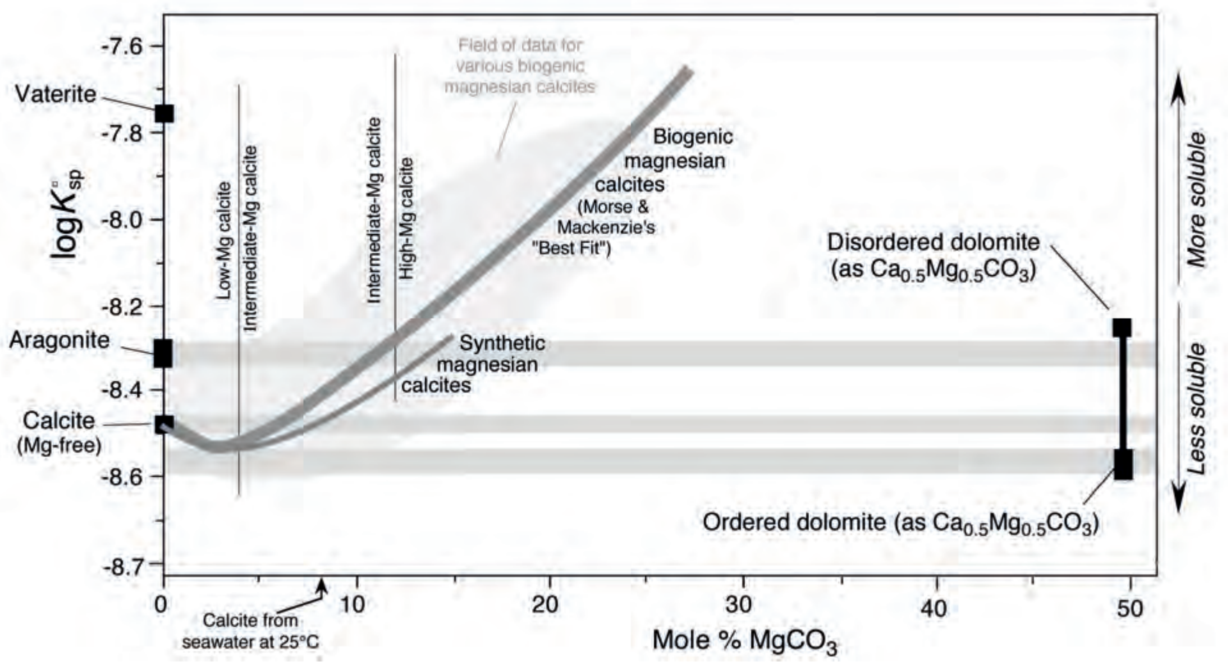

Figure 1.3 The influence of the mole fraction of magnesium on the solubility of magnesian calcites (after a slide by L.B. Railsback -- http://www.gly.uga.edu/railsback/FundamentalsIndex.html). The values of $\log K^{\circ}_{sp}$ are the thermodynamic values (S = 0) at 25°C; the stoichiometric equilibrium constants in seawater (S = 35) are about 130 times (~2.1 log units) larger.

The dissolution equilibria for calcite and aragonite can be written as

$$CaCO_3(s) = Ca^{2+}(aq) + CO_3^{2-}(aq) ; \tag{1.12}$$

where (s) indicates the solid phase. The corresponding equilibrium constant is the solubility product

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] ; \tag{1.13}$$

where the effect of the different crystal structure of the particular solid phase is now implicit in the solubility product itself. Strictly, aragonite and calcite have different standard Gibbs free energies, thus even when ionic medium standard states are used; the solubility products for the two minerals will have different values. It is necessary to indicate the mineral of interest explicitly, e.g.

$$K_{sp}(\text{aragonite}) = [Ca^{2+}][CO_3^{2-}] ; \tag{1.14}$$

$$K_{sp}(\text{calcite}) = [Ca^{2+}][CO_3^{2-}] . \tag{1.15}$$

Clearly these equations cannot both hold true simultaneously. Aragonite is often referred to as a metastable form of calcium carbonate as it is not the form that would be expected at complete thermodynamic equilibrium.

Nevertheless it is often convenient to treat the solubility of aragonite in seawater as though it were a stable phase and to apply equation (1.14) to investigate its saturation state – equation (1.17) below.

Magnesian calcites can be problematic. Their solubility is not unique, nor do they necessarily form or dissolve congruently (i.e., maintaining the same molar ratio throughout the formation or dissolution process). As a result, they do not have unique solubility products (see Figure 1.3). Nevertheless, it is sometimes useful to define *apparent* solubility products for these minerals in seawater (i.e., with essentially fixed proportions of magnesium and calcium ions) as

$$K'_{sp}(\text{mag. calcite}) = [Ca^{2+}][CO_3^{2-}]; \quad (1.16)$$

the exact value of K'_{sp}(mag. calcite) at any particular salinity and temperature will then depend on the mole fraction of magnesium in the solid (see e.g. Busenberg & Plummer, 1989).

The most common use of such solubility products – particularly in ocean acidification research – is to calculate the saturation state of seawater with respect to a particular calcium carbonate mineral X. The saturation state, $\Omega(X)$, is defined by the expression:

$$\Omega(X) = [Ca^{2+}][CO_3^{2-}] / K_{sp}(X). \quad (1.17)$$

This expresses the ratio between the observed ion product, $[Ca^{2+}][CO_3^{2-}]$, and its expected value were the solution to be in equilibrium with the particular calcium carbonate mineral. If $\Omega(X) = 1$, the solution is in equilibrium with that mineral phase, if $\Omega(X) > 1$ the solution is supersaturated with respect to that particular mineral phase, and if $\Omega(X) < 1$ it is undersaturated. Insofar as the kinetics of dissolution (and formation) of such minerals have been shown to be functions of saturation state (see e.g. Morse & Arvidson, 2002; Morse *et al.*, 2007) this is a useful parameter for studies of calcification and dissolution.

1.2.4 Analytical parameters for the carbon dioxide system in seawater

It is usually not practical to measure the individual concentrations of each of these acid-base species in seawater directly so as to get a complete description of the composition of a particular seawater sample. Typically, the concentrations are inferred from a combination of analytical measurements made on the particular sample, together with published values for the various equilibrium constants (Table 1.1) as well as published information about the boron to salinity ratio of seawater (Table 1.2).

Table 1.2 Reference composition of seawater (Millero *et al.*, 2008) at a practical salinity of 35.* The DIC is 0.0019663 mol kg^{-1}; the total concentration of boron is 0.0004151 mol kg^{-1}. To calculate the composition at another salinity, $[Y]_S = [Y]_{35} \times (S/35)$, where Y refers to species that are dependent on salinity such as calcium ion concentration or total boron.

Constituent	Concentration mol kg^{-1}
Sodium	0.4689674
Magnesium	0.0528171
Calcium	0.0102821
Potassium	0.0102077
Strontium	0.0000907
Chloride	0.5458696
Sulphate	0.0282352
Bicarbonate	0.0017177

Constituent	Concentration mol kg^{-1}
Bromide	0.0008421
Carbonate	0.0002390
Borate	0.0001008
Fluoride	0.0000683
Hydroxide	0.0000080
Boric acid	0.0003143
Dissolved carbon dioxide	0.0000096

*The concentrations of the various acid-base species were estimated assuming that the pH = 8.1 (on the seawater scale), and that the A_T = 2300 μmol kg^{-1}. The atmospheric CO_2 fugacity was chosen as 33.74 Pa = 333 μatm, i.e. appropriate for the time period the original salinity/conductivity relationship was characterised (see Millero *et al.*, 2008 – p. 59).

Salinity and temperature: It is always important to measure salinity and temperature. The various equilibrium constants are all functions of salinity and temperature (see Table 1.1), and the composition of the solution that is inferred from the various other analytical measurements will depend on these values.

Total dissolved inorganic carbon: The total dissolved inorganic carbon of a seawater sample:

$$\mathrm{DIC} = [\mathrm{CO_2^*}] + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}]; \tag{1.18}$$

can be measured directly by acidifying the sample, extracting the resulting unionised carbon dioxide, and measuring its amount. The result is expressed in moles per kilogram of solution, and is independent of the temperature (and pressure) of the sample.

Total alkalinity: The total alkalinity of a sample of seawater is a type of mass-conservation expression for hydrogen ion relative to a chosen zero value. For simple, open-ocean surface seawater it can be approximated by the expression:

$$A_\mathrm{T} \approx [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] - [\mathrm{H^+}]\,. \tag{1.19}$$

The total alkalinity of a seawater sample is estimated using some form of acidimetric titration. Again, the result is expressed in moles per kilogram of solution and is independent of the temperature (and pressure) of the sample. Thus although the concentration of each of the individual species making up alkalinity changes when the temperature or pressure changes, the particular linear combination of these concentrations given in equation (1.19) remains constant.

Hydrogen ion concentration: The hydrogen ion concentration in seawater is reported as a pH:

$$\mathrm{pH} = -\lg[\mathrm{H^+}]\,. \tag{1.20}$$

where $\lg x = \log_{10} x$ (Thompson & Taylor, 2008)[4]. Here hydrogen ion concentration is also expressed on a total scale (footnote 2) in moles per kilogram of solution. The pH of a seawater sample can be measured by one of two techniques: a potentiometric technique using an electrode that is sensitive to hydrogen ion together with a suitable reference electrode, and a spectrophotometric technique in which an indicator dye – a dye for which the acid and base forms have different colours – is added to the solution and the pH inferred from the resulting absorbance spectrum. Note that the pH of a particular sample of seawater depends upon its temperature (and pressure). If either of these is changed, the pH will change.

p(CO$_2$): The partial pressure of carbon dioxide in air in equilibrium with a seawater sample (at a specified temperature) is a measure of the degree of saturation of the sample with CO_2 gas. The $p(CO_2)$ of a particular seawater sample is a strong function of temperature, changing about 4.2% per Kelvin.

The partial pressure of a gas in a mixture is given by the expression:

$$\mathrm{p(CO_2)} = x(\mathrm{CO_2})\,p, \tag{1.21}$$

where $x(CO_2)$ is the mole fraction of the CO_2 in the gas phase (air), and p is the total pressure. If these are known – usually from direct measurements on the gas phase – it is possible to estimate the corresponding fugacity of CO_2 (see SOP 24 in Dickson *et al.*, 2007). This can then be used with the solubility constant, K_0, in equation (1.6) to calculate the concentration of dissolved, unionised carbon dioxide, $[\mathrm{CO_2^*}]$. The units for fugacity are the same as for pressure, and must correspond to those used to define K_0.

Commonly it is not the $p(CO_2)$ that is measured directly, but rather the mole fraction of CO_2 in air that was in equilibrium with a water sample and which was subsequently dried before measurement. In that case, the function F presented in equation (1.11) often provides a more convenient way to calculate $[\mathrm{CO_2^*}]$ provided that the total pressure is approximately 1 atm. In the inverse case, where seawater is equilibrated with dry air containing a known mole fraction of CO_2 at a total pressure of 1 atm, the same expression may prove useful.

4 Strictly $\mathrm{pH} = -\log_{10}\{[\mathrm{H^+}]/(\mathrm{mol\ kg^{-1}})\}$ so as to allow the taking of the logarithm. This nicety will not be adhered to in this chapter.

There are a variety of approaches to measuring each of these parameters. At this time, the oceanographic community studying the carbon cycle in the open ocean environment has made available a *Guide to Best Practices for Ocean CO_2 Measurements* (Dickson *et al.*, 2007) that describes the present state-of-the-art techniques for each of these CO_2 parameters.

1.2.5 Calculation of carbon species concentrations in seawater

It is conventional to provide thermodynamic information about acid-base reactions that are written as acid dissociations – e.g. equations (1.2) to (1.5); however, these are not the only possible ways to write the various reactions. Although it is possible to write many balanced chemical reactions relating the seven individual acid-base species mentioned above (CO_2^*, HCO_3^-, CO_3^{2-}, $B(OH)_3$, $B(OH)_4^-$, H^+ and OH^-), the equilibrium constant for every one of these possible reactions can be calculated from a knowledge of the four simple acid dissociation constants, (1.7) to (1.10). For example, a particularly convenient formulation that encapsulates the equilibrium relationship between the concentrations of the various carbon dioxide species is

$$CO_2^* + CO_3^{2-} + H_2O = 2HCO_3^- : \tag{1.22}$$

notations in parentheses indicating the state of the various species (g, l, aq, s) are omitted from now on to simplify the various expressions.

An examination of this equation tells us essentially what happens as the dissolved carbon dioxide concentration increases (for example by dissolution of CO_2 from the atmosphere). The additional carbon dioxide reacts with carbonate ion to form bicarbonate ion. The net effect is to increase the concentrations of dissolved carbon dioxide and bicarbonate ion, while decreasing the concentration of carbonate ion. The extent to which this occurs (at any particular salinity and temperature) can be inferred from the equilibrium constant corresponding to reaction (1.22), which in turn can be derived from equations (1.7) and (1.8):

$$K = K_1 / K_2 = [HCO_3^-]^2 / ([CO_2^*][CO_3^{2-}])\,. \tag{1.23}$$

In Figure 1.4a, I have used equation (1.23) to construct a contour plot indicating how the concentrations of bicarbonate ion ($[HCO_3^-]$) in seawater media can be viewed as a function of the concentration of dissolved carbon dioxide ($[CO_2^*]$) and of carbonate ion ($[CO_3^{2-}]$) at S = 35 and t = 25°C (T = 298.15 K). The x-axis is also marked in terms of $f(CO_2)$, which is directly proportional to $[CO_2^*]$— equation (1.6).

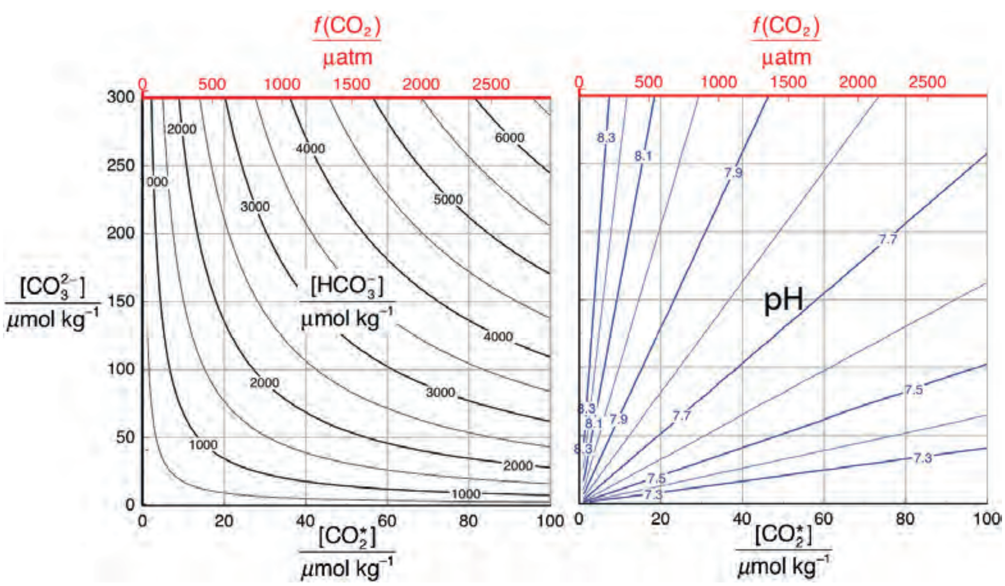

Figure 1.4a Plot of contours of constant bicarbonate concentration (µmol kg^{-1}) as a function of $[CO_2^*]$ and $[CO_3^{2-}]$. **1.4b**. Plot of contours of constant pH as a function of $[CO_2^*]$ and $[CO_3^{2-}]$.

Another convenient reaction relates carbonate ion directly to the dissolved carbon dioxide:

$$CO_2^* + H_2O = 2H^+ + CO_3^{2-} . \tag{1.24}$$

The equilibrium constant for this reaction is then the product of K_1 and K_2:

$$K_1 K_2 = [H^+]^2[CO_3^{2-}]/[CO_2^*] . \tag{1.25}$$

Examination of this expression shows that the concentration ratio $[CO_3^{2-}]/[CO_2^*]$ is a function of the hydrogen ion concentration and thus of the pH – equation (1.20). This is shown in Figure 1.4b.

If one picks a particular point on these graphs, i.e. specifying $[CO_2^*]$ and $[CO_3^{2-}]$, all the other information about the concentrations of the other acid-base species is necessarily defined in terms of the various equilibrium constants (which in turn depend on the salinity and temperature). For example, $[HCO_3^-]$ can be calculated from equation (1.23) and $[H^+]$ from equation (1.25). Then once $[H^+]$ is known, $[OH^-]$ can be calculated from equation (1.10) and the ratio $[B(OH)_4^-]/[B(OH)_3]$ from equation (1.9). We also know the total boron concentration in the seawater: $[B(OH)_4^-]+[B(OH)_3]$, which varies in direct proportion to the salinity (Table 1.2), so the individual concentrations of $[B(OH)_4^-]$ and $[B(OH)_3]$ can be estimated. Note too that each of the analytical parameters mentioned above: DIC, A_T, pH and p(CO_2), can in turn be estimated once these various concentrations are known.

In general therefore, the composition of the carbon dioxide system in any seawater sample is specified completely once one knows the salinity and temperature (and hence the values for all the various equilibrium constants), together with two other concentration-related parameters (in addition to the total boron/salinity ratio). These other concentration-related parameters are typically chosen from those mentioned above: DIC, A_T, pH and p(CO_2). The advantages and disadvantages of choosing a particular pair are discussed later in this chapter.

If one also wishes to estimate the saturation state – equation (1.17) – with regard to a particular calcium carbonate mineral, in addition to the appropriate solubility product, one also needs the concentration of calcium ion. For unmodified seawaters this too can be estimated from the salinity (Table 1.2).

There are a variety of programs available to do these calculations. Perhaps the most widely known is CO2SYS which was originally made available as a DOS executable (Lewis & Wallace, 1998), but which is now also available as Excel macros or as MATLAB code at http://cdiac.ornl.gov/oceans/co2rprt.html. Other similar programs are available, for example csys, a series of MATLAB files based on the book by Zeebe & Wolf-Gladrow (2001), is available at http://www.soest.hawaii.edu/oceanography/faculty/zeebe_files/CO2_System_in_Seawater/csys.html; seacarb, a series of functions written in R (Lavigne & Gattuso, 2010), is available at http://cran.at.r-project.org/web/packages/seacarb/index.html; and SWCO2, a package available from Keith Hunter at http://neon.otago.ac.nz/research/mfc/people/keith_hunter/software/swco2/.

When doing such calculations, with or without a standard package, there are two important considerations. First, it is desirable to use the best available values for the equilibrium constants. However, it may not always be clear from a particular program, just which constants have been selected for use. The expressions given in Table 1.1 are those recommended in the recently published *Guide to best practices for ocean CO_2 measurements* (Dickson *et al.*, 2007) and are on the *total* hydrogen ion concentration scale. Second, if pH measurements are made, it is essential that the pH be defined in the same way it was for the equilibrium constants. This is discussed in more detail below.

1.3 The definition and measurement of pH in seawater

1.3.1 Introduction

Unfortunately, as noted by Dickson (1984), the field of pH scales and the study of acid-base reactions in seawater is one of the more confused areas of marine chemistry. The primary intent of measuring pH is to use it together with appropriated acid-dissociation constants (and other information – see section 1.2.5 above) to calculate the speciation of the various acid-base systems in seawater. For a particular acid-dissociation, e.g.

$$HB = H^+ + B^- ; \tag{1.26}$$

the corresponding equilibrium expression can be written in the form

$$\mathrm{pH} + \lg K(\mathrm{HB}) = \lg\{[\mathrm{B}^-]/[\mathrm{HB}]\}. \tag{1.27}$$

If the pH scale is changed, changing the numerical value of pH, the corresponding value of the equilibrium constant must also change, and by the same amount, to ensure that the right hand side of this equation remains constant. It is thus essential that the pH is defined on the same pH scale as that of all acid-dissociation constants that are used with it.

The pH of seawater is best defined in terms of the concentration of hydrogen ion on the total hydrogen ion concentration scale (strictly the activity of hydrogen ion referenced to an *ionic medium* standard state, see footnote 3), and that is the approach recommended here. The equilibrium constants recommended in Dickson *et al.* (2007) and provided in this chapter (Table 1.1) are also defined using this pH scale.

1.3.2 The total hydrogen ion concentration scale

A key feature underlying the study of acid-base chemistry in seawater is the (often implicit) use of ionic medium standard states making it practical to define equilibrium constants that are based on concentration products, e.g., equations (1.7) to (1.10). The pH is defined as

$$\mathrm{pH} = -\lg[\mathrm{H}^+]; \tag{1.28}$$

where the square brackets again imply *total* concentration, that is the sum of the concentration of the *free* species itself, together with the concentrations of all complexes that are formed between that species and the components of the ionic medium (for seawater: H_2O, Na^+, Mg^{2+}, K^+, Ca^{2+}, Cl^-, and SO_4^{2-}).

In the case of hydrogen ion, such complexes occur with water (there are no unhydrated protons present in aqueous solution), and with sulphate ion to form the hydrogen sulphate anion: HSO_4^-. This interaction is usually written as the dissociation:

$$\mathrm{HSO_4^-} = \mathrm{H^+} + \mathrm{SO_4^{2-}}; \tag{1.29}$$

with the associated equilibrium constant,

$$K'_\mathrm{S} = [\mathrm{H}^+]_\mathrm{F}[\mathrm{SO_4^{2-}}]/[\mathrm{HSO_4^-}]. \tag{1.30}$$

The term $[\mathrm{H}^+]_\mathrm{F}$ indicates that here the hydrogen ion concentration is the *free* concentration (i.e., including only the hydrated forms of the ion), and the prime indicates that the equilibrium constant is defined accordingly. Thus one might expect the total hydrogen ion concentration to be expressed as:

$$[\mathrm{H}^+] = [\mathrm{H}^+]_\mathrm{F} + [\mathrm{HSO_4^-}]. \tag{1.31}$$

Substituting equation (1.30) in this, gives

$$[\mathrm{H}^+] = [\mathrm{H}^+]_\mathrm{F}(1 + [\mathrm{SO_4^{2-}}]/K'_\mathrm{S}). \tag{1.32}$$

The term in parentheses is essentially constant at pH > 5. To ensure that $[\mathrm{H}^+] \propto [\mathrm{H}^+]_\mathrm{F}$ even at lower pH's such as are found in an alkalinity titration or other solutions that have high acid levels, Dickson (1990) proposed that the *total* hydrogen ion scale for seawater be defined as

$$[\mathrm{H}^+] = [\mathrm{H}^+]_\mathrm{F}(1 + S_\mathrm{T}/K'_\mathrm{S}); \tag{1.33}$$

where S_T is the total amount of sulphate ion present in the seawater and this is the current definition. At pH >5, equations (1.32) and (1.33) are essentially equivalent.

1.3.3 Measuring total hydrogen ion concentration using a pH cell

The standard potentiometric technique (Dickson, 1993; Dickson *et al.*, 2007) uses the pH cell:

$$\begin{array}{c|c||c|c} \text{reference} & \text{KCl solution} & \text{test} & \text{electrode reversible} \\ \text{electrode} & (c \geq 1\ \text{mol dm}^{-3}) & \text{solution} & \text{to H}^+(\text{aq}) \end{array}\;; \tag{A}$$

where typically the electrode reversible to hydrogen ion is a glass electrode, often in a combination format with the associated reference electrode. The pH of a sample is then defined in terms of electromotive force measurements on the sample itself (X) and on a standard buffer solution (S) of assigned pH:

$$\mathrm{pH(X)} = \mathrm{pH(S)} - \frac{E_\mathrm{X} - E_\mathrm{S}}{RT \ln 10 / F}. \tag{1.34}$$

In this equation pH(X) and pH(S) are the pHs of the sample and standard buffer, respectively; E_X and E_S are the corresponding e.m.f.s obtained with cell (A) on these solutions; T is the measurement temperature (note that both sample solution and standard buffer *must* be at the same temperature); and R and F are the gas and Faraday constants, respectively. The primary standard buffer for the measurement of total hydrogen ion concentrations in seawater media is based on 2-amino-2-methyl-1,3-propanediol (Tris) in synthetic seawater, and its pH values are assigned using Harned cells – cells with hydrogen and silver/silver chloride electrodes (DelValls & Dickson, 1998; Nemzer & Dickson, 2005).

Although it is practical to make up one's own Tris buffers in accordance with the recipe given by Nemzer & Dickson (2005), it is not particularly straightforward and requires some care to ensure values that are in good agreement (0.005) with those published by DelValls & Dickson (1998). It is recommended that such "home-made" buffers be calibrated against a primary standard buffer wherever practical.

A further complication with using such buffers is that, ideally, the salinity of the buffer matches the salinity of the sample being tested. This is rarely the case, however it has been shown that if the salinity is relatively close (within 5) of the buffer (usually prepared with a nominal salinity of 35), then the likely error is less than 0.01 in pH (Whitfield *et al.*, 1985).

If this electrode-based technique is used to measure pH, the overall uncertainty for the pH measurement is probably less than 0.02 for seawater measurements in the pH range 7.5-8.5, provided that the electrode slope is Nernstian or nearly so (>99%). If the quality of the electrode has not been assessed independently this uncertainty can be larger, but as the pH(S) of Tris buffer is about 8.1, the errors will not be very large within the usual seawater pH range (7.5-8.5).

1.3.4 Measuring total hydrogen ion concentration using an indicator dye

The spectrophotometric approach to pH measurement involves adding a small amount of a solution of a pH indicator dye to the seawater sample (e.g. Clayton & Byrne, 1993; Dickson *et al.*, 2007). The dye is an acid-base compound such as *m*-cresol purple whose second dissociation:

$$\mathrm{HI^-} = \mathrm{H^+} + \mathrm{I^{2-}}; \tag{1.35}$$

occurs at around seawater pH thus ensuring that both species are present in measurable amounts. The expression for the acid-dissociation constant for this dye

$$K(\mathrm{HI^-}) = [\mathrm{H^+}][\mathrm{I^{2-}}]/[\mathrm{HI^-}]; \tag{1.36}$$

can be rewritten as

$$\mathrm{pH} = -\lg K(\mathrm{HI^-}) + \lg\{[\mathrm{I^{2-}}]/[\mathrm{HI^-}]\}. \tag{1.37}$$

The spectrophotometric approach uses the fact that the acid and base forms of the indicator have substantially different absorbance spectra. Thus the information contained in the spectrum for the indicator dye in the seawater solution is sufficient to estimate the second term on the right hand side of equation (1.37). The total absorbance at a particular wavelength λ,

$$A_\lambda = \varepsilon_\lambda(\mathrm{HI^-})[\mathrm{HI^-}] + \varepsilon_\lambda(\mathrm{I^{2-}})[\mathrm{I^{2-}}]; \tag{1.38}$$

where $\varepsilon_\lambda(\mathrm{HI^-})$ and $\varepsilon_\lambda(\mathrm{I^{2-}})$ are the extinction coefficients at that wavelength of the acid and base forms of the dye, respectively.

Typically absorbance information from two wavelengths (1) and (2) suffices to compute the pH:

$$\mathrm{pH} = -\lg K(\mathrm{HI}^-) + \lg\left(\frac{A_1/A_2 - \varepsilon_1(\mathrm{HI}^-)/\varepsilon_2(\mathrm{HI}^-)}{\varepsilon_1(\mathrm{I}^{2-})/\varepsilon_1(\mathrm{HI}^-) - (A_1/A)\varepsilon_2(\mathrm{I}^{2-})/\varepsilon_2(\mathrm{HI}^-)}\right). \quad (1.39)$$

These two wavelengths are usually chosen to correspond to the absorbance maxima for the base (1) and acid (2) forms of the dye. This choice of wavelengths is at once the most sensitive to pH changes as well as forgiving of minor deviations in wavelength reproducibility. The properties of the indicator dye *m*-cresol purple: equilibrium constant[5] and extinction coefficient ratios, have been described by Clayton & Byrne (1993). This method is also calibrated by assigning the value of $K(\mathrm{HI}^-)$, in solutions of known [H^+], ideally using primary standard buffers certified using a Harned Cell.

For the most accurate measurements, it is important to allow for the pH change resulting from the dye addition (Clayton & Byrne, 1993; Dickson *et al.*, 2007). This is usually minimised by adjusting the pH of the dye stock solution to be similar to that of the samples being measured. Unfortunately, it has also been suggested recently that these dyes, when obtained commercially, may have small amounts of coloured impurities that can vary from lot to lot. This will affect the apparent extinction coefficient ratios and can contribute as much as 0.01 to the overall uncertainty of the resulting pH data (Yao *et al.*, 2007). Thus the appropriate overall uncertainty estimate for spectrophotometric pH measurements is probably about 0.01 in pH.

1.3.5 Other pH scales (that are not recommended for use)

Two other pH scales have been used for seawater measurements in the past:

1. The so-called NBS scale (more correctly now referred to as the IUPAC scale) was based originally on recommendations and primary buffer standards from the US National Bureau of Standards (NBS), renamed the National Institute of Standards and Technology in 1988.
2. The seawater pH scale (SWS) which includes fluoride ion in the ionic medium (in addition to sulphate) and thus includes the species HF in the definition of the SWS hydrogen ion concentration:

$$[\mathrm{H}^+]_{\mathrm{SWS}} = [\mathrm{H}^+]_{\mathrm{F}} + [\mathrm{HSO}_4^-] + [\mathrm{HF}]; \quad (1.40)$$

or, more strictly,

$$[\mathrm{H}^+]_{\mathrm{SWS}} = [\mathrm{H}^+]_{\mathrm{F}}(1 + S_{\mathrm{T}}/K'_{\mathrm{S}} + F_{\mathrm{T}}/K'_{\mathrm{F}}); \quad (1.41)$$

where F_{T} is the total concentration of fluoride ion in the seawater, and K'_{F} is the dissociation constant for HF with hydrogen ion concentration expressed as the *free* concentration.

The uncertainty inherent in using the IUPAC scale for seawater measurements may be as large as 0.05 in pH, even for careful measurements. For the seawater scale, the errors will be approximately the same as for the total scale, provided that measurements are made in a similar fashion. It will however be important to assure oneself that indeed the standard buffer or the indicator dye's p*K* have been assigned values on this scale. Note that if it is necessary to calculate the amount of hydrogen fluoride in a particular sample, it can be estimated from knowledge of the total hydrogen ion concentration, the total fluoride concentration (proportional to salinity) and the corresponding equilibrium constant.

Whatever pH scale is employed, it is essential that it be used with equilibrium constants defined on the same scale. If one were to use pH measurements on the IUPAC scale with the constants of Table 1.1 (on the total hydrogen ion scale) an additional systematic error of about 0.15 pH units would be incurred at 25°C (pH ≈ pH(NBS) – 0.15). For seawater scale pH measurements, the error is about 0.01 units (pH ≈ pH(SWS) + 0.01).

5 The paper of DelValls & Dickson (1998) suggests that the buffer used by Clayton & Byrne (1993) to estimate $K(\mathrm{HI}^-)$ may have been assigned an inappropriate pH. This has not yet been confirmed. Recent work in my laboratory, however, suggests an additional systematic error may largely counteract the proposed original error.

1.4 Implications of other acid-base equilibria in seawater on seawater alkalinity

1.4.1 Natural seawater

In addition to the various species detailed above, i.e. those from carbon dioxide, boric acid or water, natural seawater can contain a number of other acid-base species in significant amounts. The most common are a variety of minor nutrient species that also have acid-base behaviour (e.g. silicate, phosphate, and ammonia):

$$\mathrm{Si(OH)_4 = H^+ + SiO(OH)_3^-};\tag{1.42}$$

$$\mathrm{H_3PO_4 = H^+ + H_2PO_4^- = 2H^+ + HPO_4^{2-} = 3H^+ + PO_4^{3-}};\tag{1.43}$$

$$\mathrm{NH_4^+ = H^+ + NH_3}.\tag{1.44}$$

The dissociation constants for these various equilibria are thus

$$K_{\mathrm{Si}} = [\mathrm{H^+}][\mathrm{SiO(OH)_3^-}]/[\mathrm{Si(OH)_4}];\tag{1.45}$$

$$K_{\mathrm{1P}} = [\mathrm{H^+}][\mathrm{H_2PO_4^-}]/[\mathrm{H_3PO_4}];\tag{1.46}$$

$$K_{\mathrm{2P}} = [\mathrm{H^+}][\mathrm{HPO_4^{2-}}]/[\mathrm{H_2PO_4^-}];\tag{1.47}$$

$$K_{\mathrm{3P}} = [\mathrm{H^+}][\mathrm{PO_4^{3-}}]/[\mathrm{HPO_4^{2-}}];\tag{1.48}$$

$$K_{\mathrm{NH3}} = [\mathrm{H^+}][\mathrm{NH_3}]/[\mathrm{NH_4^+}].\tag{1.49}$$

Although ammonia is typically present at very low amounts (< 1 µmol $\mathrm{kg^{-1}}$) in oxygenated seawater and can usually be ignored, the other species are present at significant concentrations in deep water, and can be upwelled to the surface in various regions. In addition, there is the potential for additional organic acid-base species to be present, especially in enclosed systems with significant biological activity (Hernández-Ayon *et al.*, 2007; Kim & Lee, 2009).

The net effect is to add additional species into the expression for the total alkalinity of seawater which is rigorously defined (Dickson, 1981) as ". . . the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \le 10^{-4.5}$ at 25°C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in 1 kilogram of sample." Thus

$$\begin{aligned} A_{\mathrm{T}} = {} & [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] + [\mathrm{HPO_4^{2-}}] \\ & + 2[\mathrm{PO_4^{3-}}] + [\mathrm{SiO(OH)_3^-}] + [\mathrm{NH_3}] + [\mathrm{HS^-}] + \ldots \\ & - [\mathrm{H^+}]_{\mathrm{F}} - [\mathrm{HSO_4^-}] - [\mathrm{HF}] - [\mathrm{H_3PO_4}] - \ldots \end{aligned}\tag{1.50}$$

where the ellipses stand for additional minor acid or base species that are either unidentified or present in such small amounts that they can be safely neglected. $[\mathrm{H^+}]_{\mathrm{F}}$ is the *free* concentration of hydrogen ion. Wolf-Gladrow *et al.* (2007) provide a detailed discussion of the origins of this expression and its application to biogeochemical processes.

For natural seawater these additional components do not usually complicate the *measurement* of total alkalinity, the value of which can be determined fairly accurately even if the existence of such species is ignored. However, it will affect significantly the *use* of this measured total alkalinity in inferring the composition of the seawater solution (section 1.2.5). One way to think about this is to consider how much each acid-base system contributes to the total alkalinity of a particular sample. Thus the "phosphate alkalinity" $([\mathrm{HPO_4^{2-}}] + 2[\mathrm{PO_4^{3-}}] - [\mathrm{H_3PO_4}])$ in most samples (pH range 7–8) is approximately equal to the total concentration of phosphate in the sample, whereas for silicate the "silicate alkalinity" $([\mathrm{SiO(OH)_3^-}])$ depends strongly on pH, and at pH 8 will be about 3% of the total silicate concentration (less at lower pH's). Ignoring such contributions from these minor acid-base systems is thus equivalent to the alkalinity value being in error by the corresponding amount.

Essentially any computation involving total alkalinity requires (as with borate) that the total concentrations and the various equilibrium constants of all these other acid base systems be known so that they can be accounted for (see Table 1.2). If they are not well known there will be an inherent uncertainty in the computed speciation.

In the case of substantial organic contributions to the alkalinity such information may well not be available, and total alkalinity, though measurable, may not be fully interpretable.

1.4.2 Modified seawater media – implications for alkalinity

Often when culturing organisms in the laboratory, it will be common to have high concentrations of these nutrient species (and possibly of ammonia and of various organic acid-base species). If this is indeed the case, it is unlikely that measurements of total alkalinity will provide the information desired about the sample's carbon dioxide speciation without significant (and possibly a prohibitive amount of) extra work. This is particularly true if other acid-base species are deliberately added to the culture medium (for example the use of HEPES to control pH). It will then almost certainly be impossible to infer anything useful from a total alkalinity measurement and other techniques must be used.

1.5 Choosing the appropriate measurement techniques

1.5.1 Introduction

As was discussed in section 1.2.5, there are no analytical methods that measure directly the individual concentrations of all the various acid-base species that are present in seawater. These concentrations are usually inferred from measurements of salinity, temperature, and at least two of the analytical parameters introduced in section 1.2.4, in addition to the various other equilibrium constants, etc. The question for an investigator then becomes: which two parameters should I choose to measure? Furthermore, what measurement techniques should I use to estimate them?

A key aspect of making appropriate choices is that the measurements chosen be *fit for purpose*, that is, able to achieve the goals: uncertainty, convenience, speed, cost, etc., of the ocean acidification study being undertaken. An important first step is to define clearly the purpose for which the measurements are being made and to specify the associated constraints on the uncertainty required of the analytical measurements as well as other necessary considerations.

1.5.2 Available measurement techniques

In the 1990s a group of US investigators decided to document the techniques that they were using for open ocean studies of the carbon dioxide system in seawater. The resulting handbook (DOE, 1994) was made available through CDIAC as a printed book, as well as electronically. Recently an effort was made to update this information. This resulting document was published as the *Guide to best practices for ocean CO_2 measurements* (Dickson *et al.*, 2007) by PICES; it is available on the web at: http://cdiac.ornl.gov/oceans/Handbook_2007.html.

This *Guide* provides detailed standard operating procedures for each of the current state-of-the-art techniques for measuring the various parameters of the seawater carbon dioxide system. Unfortunately, none of these techniques can be described as routine. Each requires trained analytical staff to perform the technique described, and much of the instrumentation described in the *Guide* is not commercially available. In fact most such instrumentation in use is, to some degree or another, "home-built" and it involves a significant cost to acquire (or build) a working instrument (including the necessary training of personnel). Furthermore, these instruments have not usually been optimised for ease of use or even ease of maintenance.

The combined standard uncertainty of these various techniques has – as yet – not been evaluated fully, but it is fair to say that on the whole the techniques detailed in the *Guide* are aimed at getting the best possible quality of measurement data for the carbon dioxide system in seawater. Furthermore, many of them have been used extensively in multiple laboratories and there is – within the user community – a reasonable understanding of their uncertainty, as well as of their advantages and disadvantages.

In addition to the techniques outlined in the *Guide*, a few other approaches (see Table 1.3) are worthy of consideration as being of appropriate quality for ocean acidification studies while being – perhaps – more cost-effective. Instrumentation for some of these techniques is now available commercially (typically from individual scientists who have established companies to build and sell such instrumentation), but – as a result of the limited market for such instrumentation – none of them is available as a "turnkey" system, nor is there a well-developed support infrastructure providing the necessary training or instrument servicing. Furthermore, at this time such techniques have rarely been described with the level of detail outlined in the *Guide* nor have they been independently and rigorously tested.

Table 1.3 Methods for the measurement of parameters of the carbon dioxide system in seawater (also see notes below).

Total dissolved inorganic carbon	
A.	Acidification / vacuum extraction / manometric determination
B.	Acidification / gas stripping / coulometric determination
C.	Acidification / gas stripping / infrared detection
D.	Closed-cell acidimetric titration
Total alkalinity	
E.	Closed-cell acidimetric titration
F.	Open-cell acidimetric titration
G.	Other titration systems
pH	
H.	Electrometric determination with standard Tris buffer
I.	Spectrophotometric determination using *m*-cresol purple
$x'(CO_2)$ / $p(CO_2)$	
J.	Direct infrared determination of $x'(CO_2)$

A. This method is used in my laboratory for the certification of reference materials.

B. This is the method described in SOP 2 of Dickson *et al.* (2007). A system for implementing this (VINDTA 3C) is available from Marianda (http://www.marianda.com)

C. This approach has been described in various publications (e.g. Goyet & Snover, 1993). Systems for implementing it are available from Apollo SciTech, Inc. (http://apolloscitech.com), and from Marianda (AIRICA: http://www.marianda.com).

D. This method is not recommended. If the electrode used is non-Nernstian, a significant error is introduced in the estimation of DIC.

E. This method is described as SOP 3a of Dickson *et al.* (2007). A system for implementing this (VINDTA 3S) is available from Marianda (http://www.marianda.com).

F. This method is used in my laboratory for the certification of reference materials (Dickson *et al.*, 2003). It is described as SOP 3b of Dickson *et al.* (2007), and also as ISO 22719:2008 "Water quality – Determination of total alkalinity in seawater using high precision potentiometric titration."

G. A number of titration systems are now available for this: from the Kimoto Electric Co. (http://www.kimoto-electric.co.jp/english/product/ocean/alkali.html), from Apollo SciTech, Inc. (http://apolloscitech.com), and from Langdon Enterprises (clangdon920@yahoo.com). Although all are described as capable of good repeatability, their reproducibility and uncertainty are unknown.

H. This requires a high-quality pH meter (readable to 0.1 mV, 0.001 in pH) and access to certified Tris buffers. (The method is described in SOP 6a of Dickson *et al.*, 2007).

I. This method is described in SOP 6b of Dickson *et al.* (2007), however see Yao *et al.* (2007).

J. This method is described in SOP 5 of Dickson *et al.* (2007), and requires a significant amount of seawater such as a flowing stream of seawater: e.g., the system marketed by General Oceanics: http://www.generaloceanics.com/genocean/8050/8050.htm. If however, it is desired to make the measurement on a discrete sample of seawater, the uncertainty is increased to between 0.5 and 1.0%. One such method is described in SOP 4 of Dickson *et al.* (2007); another in a paper by Neill *et al.* (1997).

In Table 1.4, I provide estimates of the measurement uncertainty for the various primary analytical parameters. These are only for guidance, the magnitudes of these uncertainties depend not only on the measurement technique employed, but also on the metrological traceability of the measured results, as well as on the implementation of the technique in a particular laboratory (skill of analysts, quality assurance program, etc.); thus the measurement uncertainty value should be estimated separately by each individual laboratory.

Table 1.4 Estimated measurement uncertainties for the measurement of parameters of the carbon dioxide system in seawater (for a single measurement on a sample of surface seawater). RM: Reference materials.

Parameter	Reference method	State-of-the-art (using RMs)*	Other techniques (using RMs)	Without using RMs†
Total alkalinity	1.2 μmol kg^{-1}	2-3 μmol kg^{-1}	4-10 μmol kg^{-1}	?
Total dissolved inorganic carbon	1.0 μmol kg^{-1}	2-3 μmol kg^{-1}	4-10 μmol kg^{-1}	?
pH	0.003‡	~0.005‡	0.01-0.03	?
$x'(CO_2)$ / $p(CO_2)$	1.0 μatm	~2 μatm	5-10 μatm	?

*The methods described in Dickson *et al.* (2007), performed by an experienced laboratory with well-trained analysts, and with a good quality assurance program in place.

†If appropriate reference materials are not used, it is usually not practical to assign a measurement uncertainty.

‡These levels of uncertainty in pH require that the apparent dye extinction coefficient ratios be appropriate to the particular lot of dye being used (see discussion in Yao *et al.* (2007)).

1.5.3 Quality assurance of measurements

Quality assurance constitutes the system by which an analytical laboratory can assure outside users that the analytical results they produce are of proven and known quality (Dux, 1990). A formal quality assurance program will be required for the carbon dioxide measurements performed in association with ocean acidification studies. A quality assurance program consist of two separate related activities (Taylor, 1987):

Quality control: The overall system of activities whose purpose is to control the quality of a measurement so that it meets the needs of users. The aim is to ensure that data generated are of known accuracy to some stated, quantitative, degree of probability, and thus provides quality that is satisfactory, dependable, and economic.

Quality assessment: The overall system of activities whose purpose is to provide assurance that quality control is being done effectively. It provides a continuing evaluation of the quality of the analyses and of the performance of the associated analytical systems.

These are discussed in detail in the books of Taylor (1987) and of Dux (1990), and a brief description appropriate to ocean carbon dioxide measurements is given in Chapter 3 of Dickson *et al.* (2007). In particular, effective quality control requires at a minimum the following:

- Suitable and properly maintained equipment and facilities,
- Well documented measurement procedures (SOPs),
- Regular and appropriate use of reference materials to evaluate measurement performance,
- Appropriate documentation of measurements and associated quality control information.

As noted above, regular use of reference materials is the preferred approach to evaluating measurement quality. Reference materials are stable substances for which one or more properties are established sufficiently well to calibrate a chemical analyser or to validate a measurement process (Taylor, 1987). Ideally, such materials are based on a matrix similar to that of the samples of interest, in this case seawater. The most useful reference materials are those for which one or more of the properties have been *certified* as accurate, preferably by the use of a definitive method in the hands of two or more analysts.

The US National Science Foundation has, since 1988, supported my laboratory at the Scripps Institution of Oceanography to produce and distribute such reference materials for the quality control of ocean CO_2 measurements (see Table 1.5). They should be used regularly to ensure the quality of measurements performed in support of ocean acidification studies.

Table 1.5 Availability of reference materials for the quality control of carbon dioxide measurements in seawater. RM: Reference materials.

Analytical measurement	Desired accuracy†	Uncertainty††	Availability
Total dissolved inorganic carbon	± 1 μmol kg^{-1}	± 1 μmol kg^{-1}	Since 1991[(a)]
Total alkalinity	± 1 μmol kg^{-1}	± 1 μmol kg^{-1}	Since 1996[(b)]
pH	± 0.002	± 0.003	Since 2009[(c)]
Mole fraction of CO_2 in dry air	± 0.5 μmol/mol	± 0.1 μmol/mol	Since 1995[(d)]

†These values are based on considerations outlined in the report of SCOR Working Group 75 (SCOR, 1985). They reflect the desire to measure changes in the CO_2 content of seawater that allow the increases due to the burning of fossil fuels to be observed.

††Estimated standard uncertainties for the reference materials described here.

(a)Sterilised natural seawater, certified using a definitive method based on acidification, vacuum extraction, and manometric determination of the CO_2 released. Available from UC San Diego (http://andrew.ucsd.edu/co2qc/).

(b)Certified using a definitive method based on an open-cell acidimetric titration technique (Dickson *et al.*, 2003). Available from UC San Diego (http://andrew.ucsd.edu/co2qc/).

(c)Standard buffer solutions based on Tris in synthetic seawater (Nemzer & Dickson, 2005). Available from UC San Diego (http://andrew.ucsd.edu/co2qc/).

(d)Cylinders of air certified by non-dispersive infrared spectrometry. Available from NOAA/ESRL, Boulder, CO (http://www.esrl.noaa.gov/gmd/ccgg/refgases/stdgases.html). However, gas mixtures certified to a lesser accuracy can be obtained from a variety of manufacturers.

1.5.4 Error propagation and its implications

Although, mathematically (in a system without any uncertainties) the use of different combinations of analytical parameters should provide equivalent information, in practice that is not the case. The inherent measurement uncertainties propagate through all further computations aimed at estimating other aspects of the carbon dioxide system in a particular seawater sample. Furthermore, such results will include additional measurement uncertainties associated with the various equilibrium constants, and with other information such as the boron/salinity ratio, the total concentration of phosphate, etc.

The general relationship between the combined standard uncertainty $u_c(y(x_1, x_2, \ldots, x_n))$ of a value y and the uncertainties of the independent parameters $x_1, x_2, \ldots, x_n$ on which it depends is:

$$u_c(y(x_1, x_2, \ldots, x_n)) = \sqrt{\sum_{i=1,n} \left(\frac{\partial y}{\partial x_i}\right)^2 u(x_i)^2} \tag{1.51}$$

where $y(x_1, x_2, \ldots, x_n)$ is a function of several parameters (Ellison *et al.*, 2000), and $u(x_i)$ is the uncertainty in x_i. The various partial derivatives $(\partial y / \partial x_i)$ can be estimated either algebraically (where convenient) or numerically. This is the approach that should be used to estimate the combined measurement uncertainty of an analytical measurement (see Ellison *et al.*, 2000).

In the case of the calculation of some aspect of the carbonate system (e.g. $[CO_3^{2-}]$) from various combinations of the possible analytical parameters, alternate approaches are *not* necessarily equivalent. Dickson and Riley (1978) first pointed out the implications of uncertainties in the various analytical parameters (and in the equilibrium constants) in detail. They chose to rewrite equation (1.51) in terms of the *relative uncertainties*:

$$\frac{u_c(y(x_1,x_2,\ldots,x_n))}{y} = \sqrt{\sum_{i=1,n}\left(\frac{\partial y}{y}\Big/\frac{\partial x_i}{x_i}\right)^2\left(\frac{u(x_i)}{x_i}\right)^2}, \qquad (1.52)$$

and their Table II provides values of the sensitivity coefficients $\{(\partial y / y)/(\partial x_i / x_i)\}$ for a surface seawater. It is important to note that the values of these sensitivity coefficients, and similarly of the partial differentials $(\partial y / \partial x_i)$, are not constant but depend on the approximate composition of the seawater itself. For particular ocean acidification experiments (whose CO_2 levels are likely to be significantly different from that of the seawaters used in Dickson and Riley) one should plan to estimate them numerically using a program such as CO2SYS.

The uncertainties in the values of the equilibrium constants and other ancillary data such as the boron to salinity ratio are often forgotten. Furthermore, it is usually not straightforward to use CO2SYS (or other easily available software) to estimate the likely contribution of these additional uncertainties. In that case, values provided by Dickson and Riley (1978) provide reasonable estimates of the sensitivity coefficients with respect to K_1 and K_2 (except perhaps when using the measurement pair A_T and DIC).

Table 1.6 Estimated relative uncertainties* in calculating $[CO_2^*]$ and $[CO_3^{2-}]$ (or saturation state) resulting from the measurement uncertainties in Table 1.4, and based on the sensitivity parameters calculated by Dickson & Riley (1978) for surface seawater. The uncertainties for the various equilibrium constants are assumed to be 0.01 in $\log_{10}(K_1)$; 0.02 in $\log_{10}(K_2)$; and 0.002 in $\log_{10}(K_0)$. RM: Reference materials.

Pair of parameters	Relative uncertainty	Reference methods	State-of-the-art (using RMs)*	Other techniques (using RMs)
pH, A_T	$u_c([CO_2^*])/[CO_2^*]$ $u_c([CO_3^{2-}])/[CO_3^{2-}]$	2.6% 3.6%	2.9% 3.7%	6.1-8.7% 5.1-6.5%
pH, DIC	$u_c([CO_2^*])/[CO_2^*]$ $u_c([CO_3^{2-}])/[CO_3^{2-}]$	2.4% 4.1%	2.6% 4.2%	5.6-8.0% 5.7-7.3%
A_T, DIC	$u_c([CO_2^*])/[CO_2^*]$ $u_c([CO_3^{2-}])/[CO_3^{2-}]$	4.9% 0.6%	5.4% 1.7%	5.8-9.3% 2.2-5.5%
pH, $p(CO_2)$	$u_c([CO_2^*])/[CO_2^*]$ $u_c([CO_3^{2-}])/[CO_3^{2-}]$	0.6% 5.3%	0.8% 5.7%	1.5-2.9% 10.6-15.0%
A_T, $p(CO_2)$	$u_c([CO_2^*])/[CO_2^*]$ $u_c([CO_3^{2-}])/[CO_3^{2-}]$	0.6% 3.3%	0.8% 3.3%	1.5-2.9% 3.4-3.8%
DIC, $p(CO_2)$	$u_c([CO_2^*])/[CO_2^*]$ $u_c([CO_3^{2-}])/[CO_3^{2-}]$	0.6% 4.0%	0.8% 4.1%	1.5-2.9% 4.2-4.9%

*These values are certainly not accurate to two significant figures. However, one can easily see the implications of the estimated measurement uncertainties, and can also infer the importance of the uncertainties ascribed to the various equilibrium constants (which dominate the relative uncertainty when using methods with the lowest possible uncertainty.

The principal difficulty in performing a rigorous error propagation to estimate the overall uncertainty of, for example, saturation state is that it is often not straightforward to obtain the necessary information about the uncertainties $u(x_i)$ of the various input data. The marine chemistry community has rarely attempted to estimate the combined standard uncertainty for the various measurement techniques discussed here, instead usually providing only precision information, and then often only data obtained under repeatability conditions, i.e. the variability within a single laboratory, over a short time, using a single operator, item of equipment, etc. This is necessarily a *lot* smaller than the combined standard uncertainty for a particular measurement technique (Ellison *et al.*, 2000). Table 1.4 provides (my personal) estimates of the measurement uncertainties associated with the various parameters. Table 1.6 uses these values, together with the sensitivity coefficients estimated by Dickson and Riley (1978) to calculate the relative uncertainties of $[CO_2^*]$ and $[CO_3^{2-}]$ resulting from the various possible pairs of parameters.

As can be seen, the likely relative uncertainty in estimating the concentration of unionised CO_2: $[CO_2^*]$, is always smallest if $p(CO_2)$ is measured directly, and is otherwise of an approximately similar magnitude whichever parameter pair is chosen. Also, the relative uncertainty in $[CO_3^{2-}]$ (or saturation state) is similar for different combinations, with the exception of pH and $p(CO_2)$ where it is twice as large.

1.5.5 Advantages (and disadvantages) of different parameters

There are a variety of possible metrics for choosing suitable parameter combinations to characterise the seawater composition in an ocean acidification experiment. At present, I feel it is fair to say that there is not really an *optimal* choice of parameters. Here I briefly summarise the advantages and disadvantages of each parameter (prices are for 2009 and expressed in US dollars).

Total alkalinity: Equipment for this measurement can be purchased for $10,000-20,000. It is relatively straightforward to use, though troubleshooting can be problematic. It typically has a stable calibration, and reference materials are available. Samples are easy to handle, as gas exchange is not typically a problem. The lowest uncertainty is obtained with sample sizes of about 100 ml, although it is practical to titrate samples that are as small as 15 ml without much difficulty. An analysis takes about 10–15 min in all. The most obvious disadvantage is that it is more difficult to interpret alkalinity accurately in samples with high concentrations of nutrients or of dissolved organic material. Reference materials are available.

Total dissolved inorganic carbon: Equipment for this measurement (using the infrared technique) can be purchased for $40,000-50,000. It is relatively straightforward to use and quite quick (~10 min per sample), however the calibration is, in many cases, achieved using reference materials and is not highly stable. The sample size needed for analysis is small (<10 ml), however samples must be protected from gas exchange, particularly at higher $p(CO_2)$. Reference materials are available.

pH: Equipment for spectrophotometric pH measurement can be obtained for less than $20,000. The procedure is relatively straightforward, and capable of some automation. It is necessary to minimise gas exchange when handling samples. The most obvious disadvantage at this time is the need for concern about the dye purity (Yao & Byrne, 2007), which causes the measurement uncertainty to be about 10 times its reproducibility. At this time, there are only limited amounts of pH reference materials available, though I hope my laboratory will be able to supply them in larger quantities in the future.

p(CO_2): Equipment for this measurement is typically quite expensive (about $50,000). It usually requires a flowing stream of seawater and is calibrated using cylinders of air with known CO_2 levels. It is cumbersome to set up, but can be relatively straightforward to use once running. One advantage is that such systems are usually designed to run autonomously.

At this time only pH and $p(CO_2)$ can be used for continuous measurement allowing relatively straightforward monitoring of an experiment over time. However, if the experiment is arranged such that the alkalinity of the seawater remains constant (or nearly so), one need only monitor one of these continually, though it will be desirable to measure two parameters explicitly on any discrete samples taken to characterise the experiment.

At this time, I believe that the best combination of parameters for studying the CO_2 system in open ocean water is probably total alkalinity and total carbon. It is straightforward to collect and preserve samples for later analysis, the equipment is reasonably readily available, and reference materials are also available to ensure metrological traceability. Also, there will be a close link to the extensive set of open-ocean studies that have been, and will be performed in the future.

Nevertheless, there are occasions when an alkalinity measurement will be difficult to interpret. In that case, I believe that the optimal combination of parameters is pH (measured spectrophotometrically) and total dissolved inorganic carbon (measured using infrared spectroscopy). These two parameters allow a description of the CO_2 system alone (without concern as to other co-existing acid-base systems), equipment for making the measurements is available, and reference materials are also available (though pH reference materials are in shorter supply). This pair can also be applied to study normal seawaters and may well be the best all-round choice.

1.6 Conclusions and recommendations

As can be seen from the extensive discussion above, seawater acid base chemistry is necessarily complicated. It involves a variety of different acid-base species in addition to the three forms of carbon dioxide: dissolved carbon dioxide, bicarbonate ion, and carbonate ion. Although care has gone into defining and measuring the various equilibrium constants, the uncertainty of these is still discussed extensively (see for example Millero, 1995; Millero *et al.*, 2006).

At present there are four parameters that can be reliably measured for the seawater carbon dioxide system (A_T, DIC, pH, p(CO_2)), and one of these, pH, has multiple possible definitions which in turn can result in multiple values for acid-dissociation constants (Dickson, 1984). This chapter follows the recommendation of the original *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in seawater* (DOE, 1994) and of the more recent *Guide to best practices for ocean CO_2 measurements* (Dickson *et al.*, 2007) and recommends use of the so-called *total hydrogen ion concentration scale* to define pH in seawater media. Values of equilibrium constants that correspond to this pH scale are given in Table 1.1.

The various equilibrium and mass-balance equations that describe the acid-base chemistry of seawater comprise a set of equations with a limited number of linearly independent variables (the rank of the system of equations). It is possible to obtain a complete description of the acid-base composition of a seawater sample at a particular temperature and pressure provided the following is known:

- the salinity and temperature, and hence the solubility constant of carbon dioxide in the seawater as well as the equilibrium constant for each of the acid dissociation reactions that is assumed to exist in the solution;
- the total concentrations for each of these non-CO_2 acid-base systems;
- the values for at least two of the CO_2-related parameters: A_T, DIC, pH, p(CO_2).

At this time, the analytical methods described in the *Guide to best practices for ocean CO_2 measurements* (Dickson *et al.*, 2007) are presently the best understood and have the lowest uncertainty. For studies on natural seawater, my recommendation would be to measure A_T and DIC (as samples for these can be preserved easily and the measurements made with low uncertainty). However, as was noted above, there may be samples from ocean acidification experiments where it is not possible to fully interpret an alkalinity measurement. In such cases, it is probably best to measure pH and DIC, and this combination is also acceptable for the study of ocean acidification in natural seawaters. However, in that case the uncertainty of the calculated parameters is typically dominated by the uncertainty in the (spectrophotometric) pH measurement, and a total carbon value obtained using a simpler system (such as one based on infrared measurement) is ideal.

Nevertheless, it is not – as yet – straightforward to make accurate measurements of seawater CO_2 parameters. Most of the methods require trained analysts, and in many cases equipment is not easily available. At this time, it is probably desirable for individuals studying ocean acidification to plan to work closely with a scientist with a good understanding of seawater acid-base chemistry and with access to a working laboratory that can perform the necessary measurements. Alternately, it may be practical to send samples to a central laboratory for analysis provided that such a laboratory has an appropriate quality assurance program in place, and can provide the results in a timely fashion.

As we move into the future, we need to develop robust analytical techniques that can be used conveniently for ocean acidification studies (involving in many cases smaller samples than are typical for open ocean studies). Although some such techniques already exist (Table 1.3), they still require additional efforts to document them effectively and to establish a community-wide quality assurance scheme for each technique. Such a scheme will involve:

1. writing appropriate Standard Operating Procedures for the techniques in use;
2. interlaboratory comparison exercises to assess the various figures of merit for each technique (trueness and precision);
3. regular use of certified reference materials to assist in the quality control;
4. regular laboratory performance testing using blind samples.

To date it is fair to state that few ocean acidification experiments have been conducted where scrupulous care has been directed at the – apparently straightforward – task of measuring the associated carbon dioxide chemistry. Although this may well not be the largest source of uncertainty in such experiments, it is appropriate to plan to control it effectively.

1.7 References

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