Measurement of Seawater pH: A Theoretical and Analytical Investigation

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MEASUREMENT OF SEAWATER pH: A THEORETICAL AND ANALYTICAL INVESTIGATION

By

Jason F. Waters

A DISSERTATION

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MEASUREMENT OF SEAWATER pH: A THEORETICAL AND ANALYTICAL INVESTIGATION

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The emission of anthropogenic carbon is leading to the influx of additional CO₂ to the atmosphere and global ocean. While the flux of anthropogenic CO₂ from the atmosphere to the ocean may be leading to the mitigation of global climate change, it is also leading to the decline of global ocean pH – a process referred to as Ocean Acidification. The net effects Ocean Acidification will have on physical, biogeochemical, and ecological processes are currently not well constrained, but there is significant research interest in evaluating the effects of decreased pH on ocean processes. Seawater pH is the essential measurement required to analyze these changes, but there is no universally accepted definition of pH for ionic media. This absence leads to increased confusion in the measurement of seawater pH, which can lead to decreased inter-comparability of the pH and related carbon system measurements.

This dissertation focuses on advancement of the theoretical and analytical aspects of seawater pH, which is achieved through: 1) development of a semi-autonomous system for the spectrophotometric measurement of pH and total alkalinity in seawater, 2) re-evaluation of the standard potential for the free pH concentration scale and bisulfate dissociation constant in seawater, 3) analytical comparisons of pH determined with unpurified colorimetric pH indicators over a of range salinities and initial solution pH values, and 4) determination of the rates of increase in anthropogenic CO₂ and decrease
in ocean pH. Such progressions will lead to greater understanding and comparability of ocean pH and carbon measurements, thus advancing future research in chemical, physical, and biological processes related to Ocean Acidification.
To my wife, Traci, for your love, support, and superior mastery of grammar;
and to my parents, for everything.

This dissertation is dedicated to the memory of Ms. Gay Ingram.
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Chapter 1.

Introduction

1.1 Anthropogenic Global Change

Presently, there is a general consensus within the scientific community that increased concentrations of CO₂ in the atmosphere and oceans is causing and will continue to cause global climate change. The atmosphere and global oceans are susceptible to changes caused by increased concentrations of CO₂, but the overall effects of the increased CO₂ in the ocean and atmosphere systems are not fully known. Consequently, there are significant research efforts - including those presented here - dedicated to monitoring current trends, predicting future conditions, and determining the overall effects these changes will have on chemical, ecological, and physical processes and systems.

1.1.1 Anthropogenic CO₂

Over the past 200 years, the partial pressure of atmospheric carbon dioxide has been increasing largely due to fossil fuel combustion and land use changes [Solomon et al., 2007]. Current atmospheric carbon dioxide levels are approximately 400 µatm, representing an increase of ~120 µatm since the Industrial Revolution. Estimates indicate that only half of the emitted anthropogenic CO₂ emissions are currently stored in the atmosphere; the remaining emissions are stored in the global ocean and the terrestrial biosphere [Sabine et al., 2004]. Because the ocean covers over two-thirds of the Earth’s surface, the oceanic uptake of anthropogenic CO₂ is a key process mitigating the potential warming effects of storing excess anthropogenic CO₂ in the atmosphere.

Current estimates indicate ocean storage accounts for approximately 40% of the total anthropogenic emissions of CO₂, and the ocean’s capacity to store CO₂ is controlled by biological (soft-tissue and calcification), physical (interior export) and chemical (solubility) processes [Zeebe et al., 2008]. However, the oceanic uptake of anthropogenic CO₂ causes significant
changes in ocean carbon chemistry and may ultimately lead to cessation or significant decrease in the inorganic storage of anthropogenic CO$_2$ in the ocean [Sabine et al., 2004].

1.1.2 Ocean Acidification

In the ocean and other natural waters, pH is largely controlled by carbon dioxide (CO$_2$) concentrations. In the atmosphere, CO$_2$ has a single chemical form; however, in seawater there are four inorganic carbon species that can exist: CO$_2$(g), CO$_2^*$ (aq), HCO$_3^-$ (aq), and CO$_3^{2-}$(aq), where

\[ CO_2^*(aq) = CO_2(aq) + H_2CO_3(aq). \]  

CO$_2^*$ (aq) is a hypothetical species used to describe the sum of the concentrations of CO$_2$(aq) and H$_2$CO$_3$(aq) and is defined by convention. The use of the CO$_2^*$ species is due to the analytical difficulties in distinguishing CO$_2$(aq) from H$_2$CO$_3$(aq), and vice-versa [Dickson et al., 2007]. If CO$_2$(aq) and H$_2$CO$_3$(aq) can be explicitly defined, then the following equilibrium equations hold:

\[ CO_2(g) \rightleftharpoons CO_2(aq), \]  

\[ CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq). \]

\[ H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq), \]  

\[ HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq). \]

The relative concentrations of the inorganic carbon species are related to the solution pH and can be determined from chemical equilibria (e.g. equations (1.1)).

As the ocean stores greater amounts of anthropogenic CO$_2$, concentrations of the acidic proton will increase. This process is commonly referred to as Ocean Acidification; however, the term acidification can be misleading. As ocean pH decreases with the further consump-
tion of global fossil fuel reserves, chemical equilibria will shift towards a higher acidity, but seawater is expected to remain slightly alkaline; see Figure 1.1. The buffering of the ocean against changes in pH is a result of the natural background concentrations of the carbonate (CO$_3^{2-}$) and bicarbonate ions (HCO$_3^-$). As concentrations of the acidic proton increase, protonation of the carbonate ion occurs, thus reducing the concentration of the acidic proton and decreasing the rates of acidification.

Figure 1.1: Upper: The expected emissions of anthropogenic CO$_2$ in GtC yr$^{-1}$. Lower: The expected change in atmospheric pCO$_2$ (green) and ocean surface pH$_{SW}$ (red). From: Millero et al. [2009a]; originally adapted from Caldeira and Wickett [2003]

Ocean Acidification is expected to impact both physical and biological systems. Of the many potential impacts, one of the most studied is the decrease in carbonate mineral saturation states ($\Omega$),

$$\Omega = \frac{[CO_3^{2-}] [Ca^{2+}]}{K_{sp}},$$

(1.2)
where $[\text{CO}_3^{2-}]$ is the concentration of the carbonate ion, $[\text{Ca}^{2+}]$ is the concentration of calcium ion, and $K_{sp}^*$ is the stoichiometric solubility product for the carbonate mineral polymorph. The changes in saturation states are related to a decrease in the concentration of $\text{CO}_3^{2-}$, and it has been shown that a decrease in the saturation state will have a direct impact on calcification rates of many marine organisms [Kleypas et al., 1999; Gattuso et al., 1998; Langdon et al., 2000; Langdon and Atkinson, 2005; Yates and Halley, 2006; Cooper et al., 2008; Tanzil et al., 2009].

The changes in inorganic ion speciation at low ocean pH will also affect sound absorption and trace metal availability. In the ocean, sound speed absorption is affected by the pH-dependent borate speciation. In seawater, boron exists as either boric acid ($\text{B(OH)}_4^-$), or borate ($\text{B(OH)}_3^-$. The bulky, ionized $\text{B(OH)}_4^-$ is weakly associated with water molecules in solution, and can be temporarily compressed by a passing sound wave. This compression attenuates the propagation of sound waves within the solution. Under less alkaline conditions, the concentrations of $\text{B(OH)}_4^-$ will decrease and lead to an increase in sound wave propagation. The effects this will have on marine mammals and industrial interests are not yet fully evaluated [Hester et al., 2008].

Ocean Acidification will also affect thermodynamic and kinetic processes of metals in the ocean [Byrne et al., 1988a; Millero et al., 2009a]. Under increasingly acidic conditions, the concentrations of some inorganic (mainly $\text{CO}_3^{2-}$ and $\text{OH}^-$) and organic ligands will decrease [Millero et al., 2009a; Louis et al., 2009]. This suggests there will be an increase in free metal ion concentrations within the oceans, which could potentially affect the availability of nutrient-type trace metals, or the toxicity of other metals in marine environments.

1.2 The Ocean Inorganic Carbon System

In order to study and evaluate the potential effects of anthropogenic carbon storage and Ocean Acidification on physical, biogeochemical, and ecological systems, the global ocean carbon system must be well constrained through direct evaluation. These evaluations have classically been achieved with research cruises in which the hydrographic data necessary to constrain
Figure 1.2: Monthly measured CO$_2$ parameters in the upper 25m from the the Hawaii Ocean Time-series (HOT). The nDIC and nCO$_3^{2-}$ are DIC and CO$_3^{2-}$ normalized to a salinity of 35, and the pH$_{sws}$, pCO$_2$ and nCO$_3^{2-}$ are calculated from DIC and TA.

Ocean processes are analyzed. A significant deficiency of these hydrographic programs is the limited temporal resolution in which ocean dynamics are observed. To overcome this deficiency, ocean time series stations are organized to analyze the hydrographic data on monthly time scales. These time series programs have proven to be crucial in documenting the seasonal and net annual changes in ocean surface chemistry due to the influx of anthropogenic carbon; see Figure 1.2.

With the exception of CO$_2(g)^i$, the carbon species cannot be measured directly and must be calculated from a set of interdependent and measurable parameters. In natural waters, the inorganic carbon system can be defined by four analytical parameters: total dissolved inorganic CO$_2$ (DIC), total alkalinity (TA), pH, and the fugacity of CO$_2$ (fCO$_2$). There are various methods outlined for measuring each of the carbon parameters in seawater. A set

---

$^i$Recently analytical methods for direct determination of CO$_3^{2-}$ (aq) [Byrne and Yao, 2008; Martz et al., 2009] were developed, but measurements have not been implemented in the ocean.
of standard methodologies has been proposed and published by the Department of Energy [Dickson et al., 2007].

1.2.1 Total Dissolved Inorganic Carbon

DIC is the concentration sum of the three aqueous\(^\text{ii}\) carbonate species: CO\(_2^+\), HCO\(_3^-\), and CO\(_3^{2-}\)

\[
\text{TCO}_2 = \text{[CO}_2^+\text{]} + \text{[HCO}_3^-\text{]} + \text{[CO}_3^{2-}\text{]}. \quad (1.3)
\]

DIC is analytically determined by the acidification of a known mass of sample to a pH where all the inorganic carbon species are converted to CO\(_2\). The CO\(_2\) is then extracted, dried, and coulometrically titrated [Johnson et al., 1985, 1987, 1993], or measured by non-dispersive infrared analysis [O’Sullivan and Millero, 1998; Kaltin et al., 2005]. Systems appropriate for the field measurement of DIC, using liquid core waveguides and low power spectrophotometers, have also been developed [Byrne et al., 2002; Wang et al., 2007].

1.2.2 Total Alkalinity

TA is defined as the measure of the proton deficit in a solution with respect to a defined zero level of protons [Dickson, 1981; Peng et al., 1987; Wolf-Gladrow et al., 2007]. Essentially, TA is a measure of the water mass buffer capacity, where larger TA values are more able to withstand rapid changes in pH. In seawater the TA is explicitly defined as [Dickson, 1981]

\[
\text{TA} = \text{[HCO}_3^-\text{]} + 2\text{[CO}_3^{2-}\text{]} + \text{[B(OH)}_3^-\text{]} + \text{[SiO(OH)}_3^-\text{]} + \text{[HPO}_4^{2-}\text{]} + 2\text{[PO}_4^{3-}\text{]} \\
+ \text{[OH}^-\text{]} + \text{[HS}^-\text{]} + 2\text{[S}_2^-\text{]} + \text{[NH}_3\text{]} - \text{[H}^+\text{]} - \text{[HSO}_4^-\text{]} - \text{[HI}^-\text{]} - \text{[H}_3\text{PO}_4\text{]}. \quad (1.4)
\]

A widely used analytical method for measuring TA is by full-curve potentiometric titration [Millero et al., 1993a; Dickson et al., 2007]. The TA is determined using either a Gran Function [Gran, 1950, 1952] or by a least-squares fit of the full titration data to determine the standard electrode potential (\(E^*\)), pK\(_1\), pH, TA, and DIC of the sample.

\(^\text{ii}\)Unless another phase is explicitly specified, the aqueous phase (aq) should be assumed for all ions.
An alternative method to the full titration procedure is the single point titration. With
the single point method, a given mass of sample is acidified with a known mass of acid and
purged of the CO$_2$ produced during the acidification. The TA is then calculated from the final
pH of the solution, determined using either potentiometry [Anderson and Robinson, 1946] or
spectrophotometry [Breland and Byrne, 1993; Clayton et al., 1995; Roche and Millero, 1998;
Yao and Byrne, 1998]. Potentiometric titrations generally require calibration to assess the
potential drift in the $E^*$ of the electrodes. However, calibration of the glass electrodes can be
avoided by using a non-linear least squares regression technique [Dickson et al., 2007].

1.2.3 The Partial Pressure or Fugacity of CO$_2$

The pCO$_2$ of a water sample is a measure of the partial pressure of CO$_2$(g) in solution, and in
accordance with Henry’s Law, is related to the CO$_2^*$ species by

$$pCO_2 = \frac{CO_2^*}{K_0}, \quad (1.5)$$

where $K_0$ is the gas solubility, or Henry’s Law, constant for CO$_2$ in seawater. When the pCO$_2$
is corrected for the non-ideal behavior of a real gas in solution, it is reported as the fugacity
of CO$_2$ (fCO$_2$). In seawater, correction for the non-ideal behavior of the gas in solution is
generally less than 3 μatm [Pierrot et al., 2009].

The pCO$_2$ of seawater is not measured directly in the solution; instead, a water sample is
equilibrated with a head-space gas, which is generally achieved using shower-head type equi-
libration. A shower-head equilibrator forces a water stream through a filter, converting the
stream to finer droplets and the dissolved gases in these droplets equilibrate with the head-
space gas of the equilibrator. Once gaseous equilibrium occurs, the pCO$_2$ of the head-space
gas is equal to dissolved pCO$_2$, and the head-space gas is analyzed to determine the sam-
ple pCO$_2$. Analysis of the pCO$_2$ is generally achieved using non-dispersive infrared analysis
[Wanninkhof and Thoning, 1993] or gas chromatography [Neill et al., 1997]. These methods
determine the mole fraction of CO$_2$ in the head-space, which is converted to pCO$_2$ using the
measured atmospheric pressure. The measured pCO$_2$ can be converted to the fCO$_2$ if the sample salinity and measurement temperature are known. Spectrophotometric detection of pCO$_2$ can be achieved with methods similar to those of spectrophotometric DIC, except the pCO$_2$ samples are not acidified before analysis [Wang et al., 2003].

1.2.4 pH

The measurement of pH is a common water quality test, but is rarely made with the sole purpose of constraining the relative concentration of the hydrogen ion in solution. Instead, pH is important because of the information it can provide on other equilibrium processes within a solution. The pH can control nutrient and metal concentrations or biological availability in natural waters and can also be used to predict the solubilities of certain minerals in solution, or to influence intra-cellular functions. In fact, pH controls such a wide variety of processes that pH is referred to as the “master” variable for physical and biological processes in the ocean [Bates, 1982; Millero, 1986; Clayton et al., 1995].

In pure or dilute solutions, pH is a measure of the activity of the hydrogen ion. However, the convention used to define chemical activity does not accurately estimate activity coefficients for solutions with an ionic strength greater than approximately 0.1 mol kg$^{-1}$. Therefore, this scale should not be used in natural waters with nominal salinities greater than $\sim 5$. In seawater, pH should instead be measured on a concentration scale. This convention is often not well understood and as a result can lead to confusion when measuring pH in seawater. This confusion often stems from the multitude of different scales that can be applied to define pH on a concentration scale. Currently, pH can be presented on three different pH concentration scales – the free, total, or seawater pH scale – which are reported with three different concentration units: molarity (mol L$^{-1}$), molality (mol kg$^{-1}$H$_2$O), or molinity (mol kg$^{-1}$soln). Within the ocean pH range, the concentration scales are defined as the free proton concentration:

$$\text{pH}_F = -\log\{[H^+]\},$$  
(1.6a)
the total proton concentration:

\[ \text{pH}_T \approx -\log ([H^+] + [HSO_4^-]), \]  

(1.6b)

and the seawater proton concentration:

\[ \text{pH}_{\text{SWS}} \approx -\log ([H^+] + [HSO_4^-] + [HF]). \]  

(1.6c)

In combining the pH scales with the mole-concentrations, one is left with at least nine ways in which seawater pH can be reported; currently none of these scales are universally promoted as a standard definition of pH in seawater.

Despite the lack of a standard definition, the pH of seawater is traceable to standard methods. When properly calibrated, seawater pH is traceable to the electrical potential of HCl in artificial seawater solutions measured using the standard hydrogen and silver-silver chloride electrodes [Khoo et al., 1977; Dickson, 1990; Campbell et al., 1993]. Using the measured standard potentials of HCl, the hydrogen/silver-silver chloride electrode system is used to determine the pH of amine buffers in artificial seawater solutions [Hansson, 1973; Bates and Erickson, 1986; Bates and Calais, 1981; Czerminski et al., 1982; Ramette et al., 1977; Millero et al., 1993b; Dickson, 1993; DelValls and Dickson, 1998]. It is not possible to make these standard measurements in real seawater due to interference caused by interactions between F⁻ and Br⁻ with Ag⁺ in the silver-silver chloride half-cell. As the pH of real seawater solutions cannot be directly measured with a hydrogen electrode, the artificial seawater buffer solutions are used as standards for the potentiometric and spectroscopic determination of pH in seawater solutions [Dickson, 1993; Millero et al., 1993b]. Due to the ionic background of seawater, the methodologies, outlined below, for these measurements deviate somewhat from methods used in dilute solutions.

**Potentiometry** — In seawater, potentiometric pH measurements are made using hydrogen sensitive glass/reference electrodes calibrated using a seawater buffer. The precision of
potentiometric systems can be as good as $\pm 0.001 - 0.003$ units of pH [Millero et al., 1993b]. The sample pH, $\text{pH}_X$, is defined to be relative to the standard pH of the buffer, $\text{pH}_S$, calibrated with the standard hydrogen electrode by

$$\text{pH}_X = \frac{\text{pH}_S - (E_X - E_S)}{k},$$

(1.7)

where $E_S$ is the electrical potential of the standard buffer solution measured with the glass electrode, $E_X$ is the electrical potential of the unknown sample, and $k$ is the Nernst slope ($k = \{RT \ln(10)/F\}$ [Bates and Guggenheim, 1960].

**Spectroscopy** — More precise measurements ($\pm 0.0004$ pH units) can be made using spectroscopic methods with pH-sensitive colorimetric indicators [Robert-Baldo et al., 1985; Byrne et al., 1988b; King and Kester, 1989; Clayton and Byrne, 1993; Zhang and Byrne, 1996; Yao and Byrne, 1998; Ohline et al., 2007; Millero et al., 2009b]. These indicators are of the generic chemical form

$$\text{H}_2\text{I} \rightleftharpoons \text{HI}^- \rightleftharpoons \text{I}^{2-}.$$  

(1.8)

Each of the acid/base indicator species has unique color and molar absorptivity, which are exploited to determine the solution pH. For indicators calibrated by Byrne and co-workers [Robert-Baldo et al., 1985; Byrne et al., 1988b; King and Kester, 1989; Clayton and Byrne, 1993; Zhang and Byrne, 1996; Yao and Byrne, 1998], pH is determined from the indicator acid dissociation constant and the measured ratio of the peak absorbencies of the $\text{HI}^-$ and $\text{I}^{2-}$ species. Recently, a full spectrum modeling technique was developed, which uses the measured absorbencies over the entire visible spectrum. This technique is reported to result in a lower standard deviation of duplicate samples when compared with the three-point ratio technique [Ohline et al., 2007]. However, the use of the peak absorbency method only relies on the region of the absorbance spectra which is most
sensitive to changes in absorbance, versus the full spectrum which averages high sensitivity changes with lower sensitive changes [Byrne, 2012].

1.2.5 CO₂ Parameters - Internal Consistency

When two or more of the inorganic CO₂ parameters are measured on the same sample, the remaining parameter(s) and the individual concentrations of the inorganic carbon species can be calculated. The calculations are completed using the acid dissociation constants and acid-base equilibrium relationships for H₂CO₃ [Park, 1969; Dickson et al., 2007; Millero, 2007]. This over-determination of the CO₂ system allows for the calculation of the internal consistency, or apparent accuracy, of a set of inorganic CO₂ measurements. The internal consistency is determined by comparing the measured and calculated values of each of the parameters and is useful when examining the reliability of the inorganic carbon measurements [Millero, 2007].

1.2.5.1 Stoichiometric H₂CO₃ Dissociation Constants

Calculation of the internal consistency requires the acid dissociation constants for equations (1.1d - 1.1e) are known. Acid-base equilibrium in seawater is complicated by the non-ideal behavior of ions in electrolyte solutions. This non-ideal behavior causes the thermodynamic properties, such as acid dissociation, of an electrolyte to vary in a non-linear manner. These deviations are corrected by using ion activities instead of ion concentrations and requires the estimation of ion activity coefficients, which is not always practical or possible [Dickson, 1984]. The use of ion activities in seawater is largely avoided by using a proton concentration scale and stoichiometric thermodynamic constants (Kᵢ⁺) defined by ion concentrations. For CO₂⁺, the dissociation constants are defined as

\[
K₁⁺ = \frac{[H⁺][HCO₃⁻]}{[CO₂⁺]}, \quad (1.9a)
\]

\[
K₂⁺ = \frac{[H⁺][CO₃²⁻]}{[HCO₃⁻]}. \quad (1.9b)
\]
The stoichiometric thermodynamic constants are only valid at a given chemical composition of seawater and must be evaluated as a function of salinity and temperature. It is also necessary to ensure these stoichiometric coefficients are on a common scale with the measured pH.

Stoichiometric dissociation constants for CO$_2^+$ have been made in artificial seawater [Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993] and real seawater solutions [Mehrbach et al., 1973; Mojica Prieto and Millero, 2002; Millero et al., 2006]. Due to discrepancies between the measured values of K$_2^+$ in artificial and real seawater, which may be due to interaction between CO$_2^-$ and boron in real seawater [McElligott and Byrne, 1997; Mojica Prieto and Millero, 2002], it is recommended that the real seawater stoichiometric dissociation constants are used. Millero [2010] has compiled the measurements made in real seawater [Mehrbach et al., 1973; Mojica Prieto and Millero, 2002; Millero et al., 2006], and recommends these compiled values as the acid dissociation constants are in good agreement and have been extrapolated to pure water for use in estuaries and rivers.

1.3 Dissertation Overview

As discussed in the preceding sections, one of the changes caused by the emission of anthropogenic carbon is a decrease in ocean pH. Significant research efforts are dedicated to monitoring the change in pH and the effects it will have on ocean processes [e.g. Byrne et al., 1988a; Raven et al., 2005; González-Dávila et al., 2007; Dore et al., 2009; Doney et al., 2009; Millero et al., 2009a]. However, pH measurements in seawater can be confusing and difficult to compare. In fact, ocean pH has been described as “one of the more confused areas of marine chemistry” [Dickson, 1984], and the existence of multiple methods used to define pH is criticized for contributing to incomparability amongst measurements [Orr et al., 2009]. A similar criticism for the existence of multiple measures of “pH” for seawater was made over 30 years ago [Culberson, 1981]

At present three pH scales [NBS, free proton, and total proton scale] are in use for sea water pH measurements. Considering the small
number of marine chemists and the large expanse of the ocean, this
is two too many.

Instead of rectifying this problem an additional pH scale, the seawater proton scale, has since
been added!

This dissertation attempts to advance our ability to make repeatable measurements of pro-
cesses related to Ocean Acidification by re-evaluating the free proton concentration scale and
suggesting the implementation of a single pH scale that can be universally applied to the
marine sciences. In addition, the dissertation also quantifies and compares the rates of acidifi-
cation in the open ocean, describes the development and testing of a instrument for the semi-
autonomous spectroscopic determination of pH and TA, and compares the relative accuracies
of various colorimetric pH indicators used in the determination of ocean pH.

1.3.1 Chapter Overview

Chapter 2 — A semi-autonomous system for the spectrophotometric measurement of TA
and pH is described. Results from both laboratory and ship-based performance evalua-
tions are presented. A manuscript based on this chapter is in preparation for submission
for peer-reviewed publication.

Chapter 3 — A Pitzer activity coefficient model is validated against the measured mean ac-
tivity coefficient of HCl in artificial seawater [Khoo et al., 1977; Dickson, 1990; Camp-
bell et al., 1993] and the chemical model is used to evaluate the free proton scale stan-
dard potential. The standard potential is necessary to evaluate seawater pH buffers cal-
ibrated on the free proton concentration scale. The re-evaluated standard potential is
used to derive new equations for the pH of equi-molar buffers in artificial seawater as a
function of temperature and salinity. The new buffer equations can be used to calibrate
pH measurements in seawater on the free proton concentration scale. At the time this
dissertation was submitted, a manuscript based on this chapter was under review for
publication in Marine Chemistry.
Chapter 4 — Spectrophotometric pH measurements are made with different indicators and compared in solutions that span the natural ranges salinity and pH of the upper ocean. These measurements are used to estimate a practical accuracy for spectrophotometric pH measurements made with impure and pure pH indicators.

Chapter 5 — The decadal storage of anthropogenic CO$_2$ and acidification is assessed for the South Pacific. The change in anthropogenic CO$_2$ determined from the ‘extended’ multiple linear regression is compared with calculations from the time-transit distribution method. The mean decadal change in anthropogenic CO$_2$ and decrease in ocean surface pH are also compared with similar estimates and measurements. This chapter has been previously published as: Waters J. F., Millero F. J. and Sabine C. L. (2011) Changes in South Pacific anthropogenic carbon. *Global Biogeochemical Cycles*, 25:GB4011. doi:10.1029/2011GB003988.

Chapter 6 — An overall summary and concluding remarks for the dissertation.
Chapter 2.

A Semi-Autonomous System for the Spectrophotometric Determination of pH and Total Alkalinity

2.1 Background

During the mid-1990s, the anthropogenic ocean carbon inventory was estimated to be $118\pm19$ Pg C [Sabine et al., 2004], representing $\sim 40\%$ of the anthropogenic CO$_2$ produced by the combustion of fossil fuels and land use changes [Solomon et al., 2007; Sabine et al., 2010]. To further assess the decadal variability and trends in ocean carbon uptake and storage, repeat hydrographic programs are organized on cruise tracks where the anthropogenic inventory has been previously determined. The anthropogenic carbon inventory is generally derived directly using the measured carbon data [Sabine et al., 2004; Wallace, 1995], or can also be derived using transient tracers, such as chlorofluorocarbons or sulfur hexaflouride [Haine and Hall, 2002; Hall et al., 2002, 2004]. When evaluating the anthropogenic inventory from carbon measurements, it is necessary to know the dissolved inorganic carbon (DIC). Total alkalinity (TA) and either pH or the fugacity of CO$_2$ ($f$CO$_2$) can alternatively be measured and used to calculate the DIC with acid dissociation constants [Millero, 2007]. The currently recommended analytical techniques for TA [Millero et al., 1993a; Dickson et al., 2007] and DIC [Johnson, 1992; Dickson et al., 2007] provide the required precision for differentiating the anthropogenic signal from the natural background CO$_2$. However, they require rigorous operator control and have time intensive set up and calibration routines. This has largely limited high quality observations of Ocean Acidification rates to global ship-board surveys [Byrne et al., 2010; Waters et al., 2011] and ocean time-series stations [González-Dávila et al., 2007; Dore et al., 2009]. Recently, the development of systems for measuring TA or DIC with no required operator control was highlighted to be of “vital importance” as a research priority for monitoring Ocean Acidification [Orr et al., 2009].
Of the four carbon parameters, only two of the parameters are required to constrain the carbon system, but not all combinations of measured carbon inputs provide accurate estimates of the remaining CO$_2$ parameters. When accuracy is required for constraining the CO$_2$ system, the combination of pH-$f$CO$_2$ should be avoided as the respective errors associated with the calculated TA and DIC are $\pm 21$ and $\pm 18 \mu$mol kg$^{-1}$ [Millero, 2007]. Input of TA-DIC also has a relatively high associated error and can lead to calculated values of pCO$_2$ up to 30% under saturated [Hoppe et al., 2012]. This is attributed to the high uncertainty in $K'_2$ [Millero, 2007]; however, propagation of the error associated with $K'_2$ may not be enough to fully explain under saturations of this magnitude [Hoppe et al., 2012]. In order to achieve high accuracy in the calculated CO$_2$ parameters, calculations should be made with pH-TA, or $f$CO$_2$-TA (providing estimates of DIC accurate to within approximately 1 – 2%), or the TA can also be calculated with the same relative accuracy from the input of DIC with either pH, or $f$CO$_2$. If calculated pH is required, it can be determined with high accuracy, better than $\pm 0.003$ units in pH, when determined from $f$CO$_2$-TA or $f$CO$_2$-DIC. Calculated $f$CO$_2$ can also be determined with high accuracy, to within $\sim 2 \mu$atm, from pH and either TA or DIC [Millero, 2007]. When only 2 of the 4 carbon parameters are measured, it is recommended that either pH or $f$CO$_2$ be paired with either DIC or TA for the highest accuracy in the resulting calculations of the remaining CO$_2$ parameters.

Despite the larger relative error introduced in the calculated pH and $f$CO$_2$, DIC and TA are recommended for ship-based surveys when only two of the carbon parameters are measured [Orr et al., 2009]. This recommendation is largely because of the Certified Reference Material (CRM) program for ocean CO$_2$ measurements [Dickson et al., 2003], where the periodic analysis of a CRM allows for the assessment of the accuracy for DIC and TA measurements. However, with the recent purification of the colorimetric pH indicator meta-cresol purple (mCP) [Liu et al., 2011], spectrophotometric pH measurements have the potential to be as accurate as the pH buffer solutions used in seawater pH calibrations [e.g. DelValls and Dickson, 1998; Nemzer and Dickson, 2005]. Using purified pH indicators, it should now be
possible to accurately and precisely constrain the carbon dioxide system using pH and either TA or DIC.

For studies focused on quantifying changes in calcification under different acidification scenarios, using pH and TA is recommended over pH and DIC [Hoppe et al., 2012]. The basis of this recommendation is two-fold: (1) TA is twice as sensitive to changes in carbonate concentrations as is DIC [Park, 1969], and (2) carbon system parameters can be measured more accurately than calculated and the measured parameters should therefore reflect the processes of interest [Dickson and Riley, 1978]. In the following chapter, a simple and convenient procedure appropriate for field-based measurements of spectrophotometric pH and TA is outlined. Trial results from laboratory and field tests are used to compare the instrument to other spectrophotometric and standard ship-board methods. The implementation of such a system could prove to be useful in future studies related to calcification under increasing acidification—decreasing pH—scenarios.

2.1.1 Measurement of pH

Spectrophotometric pH is measured using colorimetric indicators, where the absorption maximum of the deprotonated (I$^2$–) and protonated (HI$^+$) forms of the indicator are measured by spectrophotometry (Figure 2.1). The ratio of the deprotonated and protonated species are related to the peak absorption of the species ($A_i$) and the indicator molar absorptivities ($\epsilon_i$) by [Clayton and Byrne, 1993]

$$\frac{[I^2^-]}{[HI^-]} = \frac{A_{\lambda_1}/A_{\lambda_2} - \epsilon_{HI^-}/\epsilon_{HI^-}}{e_{I^2^-}/e_{HI^-} - A_{\lambda_1}/A_{\lambda_2} e_{I^2^-}/e_{HI^-}},$$

(2.1)

where $\lambda_i$ is the wavelength of maximum absorption for the given species. It is convenient to represent the wavelength absorbance ratio as $R$ and the molar absorptivity ratios as $e_i$, and the form of equation (2.1) can be simplified to

$$\frac{[I^2^-]}{[HI^-]} = \frac{R - e_1}{e_2 - R e_3}.$$

(2.2)
The spectrophotometric pH of a solution can be determined using the ratio of the indicator species and the Henderson-Hasselbalch equation

$$\text{pH} = -\log(K^*_a) + \log \left( \frac{[\text{I}^2-]}{[\text{HI}^-]} \right),$$

(2.3)

where $K^*_a$ is the indicator stoichiometric acid dissociation constant. Equation (2.2) is combined with equation (2.3) and the pH is calculated from

$$\text{pH} = -\log(K^*_a) + \log \left( \frac{R - e_1}{e_2 - R e_3} \right).$$

(2.4)

When calculating the pH from equation (2.4), it is necessary to ensure $K^*_a$ is given on the desired proton concentration scale.

![Figure 2.1: Absorbance spectrum of meta-cresol purple (mcp; pH$_{sWS}$=7.9007) and bromocresol green (BCG; pH$_t$=3.486) in CRM Batch 112. The horizontal lines are maximum absorbance wavelengths of mCP [Clayton and Byrne, 1993] and BCG [Breland and Byrne, 1993; Yao and Byrne, 1998]. The offset in the observed peak absorbance for mCP at 434 nm is due to absorbance of the I$^2-$ species.](image)
Byrne and co-workers have determined $K_a^*$ and molar absorptivity ratios for an extensive array of colorimetric indicators, which are used in the determination of pH for fresh water [Yao and Byrne, 2001], seawater [Byrne et al., 1988b; Clayton and Byrne, 1993; Zhang and Byrne, 1996; Liu et al., 2011], and acidified seawater solutions [Breland and Byrne, 1993; Yao and Byrne, 1998]. These publications have demonstrated a high reproducibility, as good as ±0.0004 units in pH, is possible using spectrophotometric and colorimetric pH indicators [e.g. Byrne et al., 1988b; Clayton and Byrne, 1993; Liu et al., 2011]. With the recent realization of purified indicators [Liu et al., 2011], it should be possible to achieve an accuracy of ±0.003 units.

### 2.1.2 Measurement of TA

An exact definition of TA in seawater is defined by Dickson [1981], but for oxygenated, oligo- orophoric seawater, it is suitable to simplify the exact definition to

$$
TA = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+] - [\text{HSO}_4^-] - [\text{HF}].
$$

(2.5)

However, in regions with abundant nutrient concentrations (ammonia, silicate, and phosphates) or reduced compounds (sulfide compounds), the full definition of TA should be considered [Dickson, 1981].

The determination of TA is based on either the single-point titration [Anderson and Robinson, 1946] or a step-wise, multiple-point titration [Millero et al., 1993a; Dickson et al., 2007]. Commonly, the titration pH is monitored using potentiometry [Anderson and Robinson, 1946; Millero et al., 1993a], but thermometric [Millero et al., 1974] and spectrophotometric [King and Kester, 1989; Breland and Byrne, 1993; Yao and Byrne, 1998; Roche and Millero, 1998] methods are also used. The main differences between the single and multi-point methods are the time required to complete a titration and the data provided by the titration. Using a multi-point method is time consuming, requiring at least 20 minutes for sample preparation and the completion of ∼20 titration points. However, if the multi-point titration curve is fit by a non-
linear, least-squared regression [Dickson et al., 2007] or a Gran function [Millero et al., 1993a; Millero, 2007], a multiple-point titration can provide a measure of the TA, DIC, pH, and the standard electrode potential \(E^\circ\). When the \(E^\circ\) of an electrode is determined in a least-squares manner, it is not necessary to calibrate the electrode using a standard buffer to get accurate values of TA [Millero et al., 1993a]. However, the value of DIC is not as accurate as the more preferred coulometric titration for DIC, nor is the pH as precise as spectrophotometry [Dickson et al., 2007].

Single-point titrations are conceptually simpler and faster than multiple-point titrations. The TA is calculated from a solution titrated past the pH equivalence and purged of the evolved CO\(_2\) with a simple linear expression [Breland and Byrne, 1993]

\[
\text{TA} = \frac{N_a M_a - [H^+]_i (M_a + M_s)}{M_s}, \tag{2.6}
\]

where \(N_a\) is the acid molality (mol/kg), \(M_a\) is mass of acid (kg), \(M_s\) is the mass of the sample (kg), and \([H^+]_i\) is the hydrogen ion concentration on a given pH concentration scale (mol/kg). When the sample is titrated to pH \(\approx 4.0\), the error in the determination of TA is \(\sim \pm 0.5 \mu\text{mol kg}^{-1}\) if the precision of the measured pH is \(\pm 0.002\) or better [Breland and Byrne, 1993].

The main difficulty with the method is that titrations generally require calibration of the electrodes when the solution pH is monitored by potentiometry. However, by applying the methods for spectrophotometric pH to the single-point TA titration, the cumbersome calibration of glass electrodes is avoided. Spectrophotometric titrations for TA have demonstrated excellent precision (\(\pm 0.3 - 1.5 \mu\text{mol kg}^{-1}\)) using gravimetric methods to deliver the sample and acid [Breland and Byrne, 1993; Yao and Byrne, 1998].

The addition of an indicator solution can perturb the sample pH [Clayton and Byrne, 1993; Yao and Byrne, 1998], and in some cases it may be necessary to correct the solution pH for the indicator perturbation. For spectrophotometric TA, the indicator perturbation can be corrected
by adjusting the stock indicator pH until it matches the nominal pH of titration end point, or by calculating the change in the concentration of the protonated (HI) form of the indicator [Yao and Byrne, 1998]

\[
\Delta_{HI} = \frac{1}{1 + (R_{sample} - e_1)/(e_2 - R_{sample}e_3)} - \frac{1}{1 + (R_{stock} - e_1)/(e_2 - R_{stock}e_3)}.
\] (2.7)

When the indicator pH is not adjusted to match the pH of the titrated sample, it is necessary to add equation (2.7) to the concentration of measured proton in equation (2.6)

\[
TA = N_aM_a - ([H^+]_T + I_T\Delta_{HI})(M_a + M_s)
\]

(2.8)

2.1.3 Autonomous carbon measurements

Measurements of the carbon dioxide system based on the autonomous determination of spectrophotometric pH are capable of achieving a precision equivalent to manual spectrophotometric methods [Wang et al., 2007; Carter, 2011; Aßmann et al., 2011]. For spectrophotometric titrations of TA to be appropriate for ship-based measurements, or potentially even fully autonomous mooring-based measurements, a method not dependent on gravimetric measurements must be applied. Ideally, such a method would not significantly sacrifice the measurement precision. The instrument designed and described in this chapter makes significant progress towards the realization of TA titrations appropriate for semi-autonomous deployment.

2.2 Methods and Materials

2.2.1 System design

The instrument design is based on the concept of sequential injection analysis (SIA), which can be broken down into three essential steps: aspiration and rinse of a syringe pump with a wash/blank solution, sample and regent injection, and flow reversal of the sample/reagent mixture to a detector [Ruzicka and Marshall, 1990]. This basic concept has been applied to
semi-autonomous systems for the spectrophotometric determination of seawater pH with excellent reproducibility, ±0.001−0.0004 units [Hiscock, 2006; Carter, 2011]. In these systems, syringe pumps are used to aspirate sample and pH indicator to a flow-through spectrophotometer cell. For such a system to be appropriate for TA titrations, the volumetric precision of the pumps should be better than ±0.05%. Gravimetric measurements of repeat volumetric deliveries of 18 MΩ water indicate the syringe pumps (Kloehn, PN# 55023) tested in our lab are capable of a precision of ±0.01% for a full piston stroke delivery. Based on these results, SIA appears to be an excellent platform for the development of a simple, high precision system for the semi-autonomous, or underway determination of TA and pH.

A schematic of the system design is given in Figure 2.2. The main system components are: a diode array spectrophotometer (Agilent, 8453), a high precision syringe pump (Kloehn, PN# 55023) with a 25 mL zero-dead-space volume syringe (Kloehn, PN# 23734) and 8-way distribution valve (Kloehn, PN# 17877), a digital output control and RTD data logging unit (National Instruments, FP-1000/FP-DO-403/FP-RTD-122), a spectrophotometer cell (Starna Cell, PN# 585.3/Q/100/Z15), a custom aluminum cell holder capable of thermostating the spectrophotometer cell, a water bath (Thermo, Neslab RTE 7 Digital Plus), two solenoid valves (Cole-Parmer, PN# WU-01540-11), and a custom glass pipette. The tubing is 3/16” I.D. x 1/4” O.D. PTFE and all fluid connections are made using inert tube end fittings (Cole Parmer, PN# WU-06471-59 & WU-06471-57), with the exception of the glass pipette which is directly connected to the tubing with a 1/2 to 1/4 PFA reducing union (Swagelok, PN# PFA-820-6-4). The entire unit is housed in a custom HDPE housing, which elevated the rear of the spectrophotometer at 45°. The diode array spectrophotometer is run with both the deuterium (190 ∼ 300 nm) and halogen (350 ∼ 900 nm) lamps ignited. Instrument control is achieved using a program written in the LabVIEW.

2.2.2 Measurement Routine

A full measurement cycle combining the individual pH and TA measurements is completed in 13 − 14 minutes. A measurement begins by flushing the syringe and spectrophotometer
Figure 2.2: A schematic representation of the spectrophotometric TA-pH system. The system parts are as follows: A. Sample bottle, B. mCP, C. BCG, D. Acid bottle, E. Kloehn syringe pump, F. Glass pipette, G. 0.45\( \mu \)m air filter, H. Solenoid valves, I. Ascarite CO\(_2\) scrubber, J. Regulated compressed air line, K. Thermostated spectrophotometer cell holder and flow-through 10 cm cell, L. 100 MΩ Pt R.T.D., M. N.I. FieldPoint 1000 Relay controller and R.T.D. units. The green and purple lines are indicator tubing, red lines are acid tubing, light blue lines are compressed air tubing, and black lines are sample tubing. The Neslab RTE 7 is not included in the schematic, but is connected to K.
cell three times; the first two flushes rinse the residual acidified seawater from previous TA
titrations and the final rinse is used to record the absorbance of the seawater sample and spec-
trophotometer cell. While the sample is allowed to come to temperature (∼ 90 seconds), the
syringe pump aspirates ∼ 20% of the syringe volume with sample. Next, enough indicator is
added to bring the concentration of meta-cresol purple (mCP) in the final sample volume to
∼ 0.25 milliM. The total volume of the syringe is then filled with the seawater sample. Once
the blank absorbance is recorded, the spectrophotometer cell is rinsed with the mCP/sample
mixture. This solution is allowed ∼ 90 seconds to come temperature before 5 consecutive
absorbance measurements are taken and averaged to provide the spectra used for the pH de-
termination.

While the mCP/sample mixture is allowed to come to temperature in the spectrophotome-
ter cell, the syringe and glass mixing pipette are rinsed with an aliquot of sample. Once
the absorbance of mCP/sample has been measured and averaged, the mixing chamber sea-
water rinse is sent to the spectrophotometer cell, and the syringe, glass mixing pipette, and
spectrophotometer cell are rinsed with a second aliquot of sample. The seawater rinses are
necessary to remove any residual acidified sample from the mixing chamber and tubing. Af-
ter the seawater rinses, the syringe pump aspirates ∼ 20% of the syringe volume with the
sample, and then enough indicator to bring the final solution concentration of bromo-cresol
green (BCG) to ∼ 0.25 milliM. After the indicator aspiration, enough HCl in NaCl (the total
acid/salt ionic strength is ∼ 0.7 mol kg⁻¹) is added (∼5% of the syringe volume) to bring the
final solution pH to ∼ 3.2 − 4.5. After the acid addition, the total syringe volume is filled
with the seawater sample. This solution is dispensed to the glass mixing pipette to ensure
mixing of the acid/indicator/sample and then vigorously bubbled with CO₂-free compressed
air to remove the CO₂ evolved during the sample acidification. The air is scrubbed of CO₂
with an Ascarite trap. For a 25 mL sample volume, 60 seconds was found to be adequate to
remove the evolved CO₂, but not cause significant evaporation (monitored by conductivity)
of the sample. Ambient air is introduced using a compressed air stream at ∼ 6 psi; control is
achieved using the solenoid valves and D.O. controller. After the sample has been scrubbed of the evolved CO$_2$, the syringe pump moves the sample from the glass mixing pipette to the spectrophotometer cell. The second solenoid valve$^{iii}$ was used to release the pressure from the gas lines and prevent air bubbles from being introduced to the syringe pump.

Once the titrated sample is transferred to the spectrophotometer cell it is allowed to come to temperature, before five rapid measurements of the absorbance spectrum are measured and averaged. The averaged spectrum is then used to determine the pH of the acidified solution and the TA is determined using equation (2.8). As the pH is not monitored during the acid addition, the final pH of the single-point titration will not always be $\sim 4$ and it is necessary to correct the final pH for variations in the $\Delta_{HI}$ term. Densities of the sample and acid are used to convert from volumetric to gravimetric units.

### 2.2.3 Carbonate Ion Concentrations

In the initial laboratory tests, the mixing chamber seawater rinses were completed with acidified seawater. The absorbance spectra of these rinses were analyzed for a decrease in absorbance over the 220–230 nm range for CO$_3^{2-}$ ion detection [Martz et al., 2009]. As expected, a decrease in absorbance was observed, but the measured spectra were found to be influenced by residual traces of colorimetric indicator in the system. This could potentially have been overcome using additional rinses, but this was not examined further due to the errors in the TA from residual acid present in the system after rinsing. The acidified seawater was not fully cleared from the tubing or mixing chamber after then rinse, and the excess acid in the mixing chamber and tubing from these rinses caused errors in the TA determinations. The acidified rinses were replaced with seawater rinses and it was no longer possible to directly measure CO$_3^{2-}$ ion concentrations.

$^{iii}$The solenoid valve is a 3-way valve with the the common port sourced to the primary solenoid valve, the normally-closed port sourced to the glass mixing pipette, and the normally-open port open to the atmosphere.
2.3 Assessment and Results

2.3.1 Batch Test: Gulf Stream Seawater

The system was initially tested in the laboratory using Gulf Stream seawater (GSSW) collected off the coast of Miami. The seawater was collected, filtered with a 0.45 μm Nucleopore filter, and stored in a 50 L polypropylene carboy until use. The GSSW was not preserved with HgCl$_2$; preservation was not necessary to keep the TA constant and the pH changed as the volume of GSSW in the carboy decreased. Over a period of 3 days, the GSSW was sub-sampled and analyzed using 150 mL borosilicate glass bottles with ground glass stoppers. In order to make comparisons of the measured pH, 3 to 4 bottles were filled and sealed before the measurements were started. In total, 43 samples were analyzed for pH and TA. Deviations in TA from the average are shown in Figure 2.4. The average TA was 2333.73 ± 2.5 μmol kg$^{-1}$. The estimated precision was similar to previous studies using bromo-cresol green, but with much larger sample volumes: ±1.7−2.6 μmol kg$^{-1}$ [Roche and Millero, 1998] and ±1.8 μmol kg$^{-1}$ [Clayton et al., 1995]. Further laboratory assessment was conducted using Certified Reference Material for TA and TCO$_2$ (Batch # 112, S = 33.305, TA = 2223.26 ± 0.89 μmol kg$^{-1}$, TCO$_2$ = 2011.09 ± 0.47 μmol kg$^{-1}$, pH$_{sws}^{calc}$ = 7.9805 ± 0.003, t = 20°C) [Dickson et al., 2003]. The pH was determined to be 7.9765 ± 0.0005 and the TA is 2223.93 ± 1.9 μmol kg$^{-1}$ (n=3).

Comparison of replicate measurements of pH on GSSW were only made for each sub-sample batch. The average and range of each batch are shown in Figure 2.3, and the individual measurements are given in Table 2.1. The average standard deviation for all the batches was ±0.0006; this is in reasonable agreement with the reported precision (±0.0004) for spectrophotometric pH measurements [Clayton and Byrne, 1993].

2.3.2 Field Test: CLIVAR A22

After laboratory tests indicated the system was capable of attaining a precision in pH and TA that is comparable to established methods, field-based tests were conducted during the CLI-
Table 2.1: Individual and averaged bottle spectrophotometric pH for Gulf Stream Seawater. The average overall deviation is ±0.0006 units of pH.

<table>
<thead>
<tr>
<th></th>
<th>Batch 1</th>
<th>Batch 2</th>
<th>Batch 3</th>
<th>Batch 4</th>
<th>Batch 5</th>
<th>Batch 6</th>
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</thead>
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<td>7.9703</td>
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<tr>
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<td>7.9699</td>
<td>7.9702</td>
<td>7.9682</td>
<td>7.9676</td>
</tr>
<tr>
<td>Sample 4</td>
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<td>7.9691</td>
<td>7.9699</td>
<td>7.9682</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
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<td>7.9700</td>
<td>7.9697</td>
<td>7.9697</td>
<td>7.9681</td>
<td>7.9674</td>
</tr>
<tr>
<td>Std. Dev.</td>
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<td>0.0007</td>
<td>0.0006</td>
<td>0.0010</td>
<td>0.0001</td>
<td>0.0002</td>
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<table>
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<th>Batch 9</th>
<th>Batch 10</th>
<th>Batch 11</th>
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<td>7.9697</td>
<td>7.9718</td>
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<tr>
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<td>7.9668</td>
<td>7.9671</td>
<td>7.9710</td>
<td>7.9712</td>
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<td></td>
<td>7.9699</td>
<td>7.9708</td>
<td>7.9728</td>
</tr>
<tr>
<td>Mean</td>
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<td>7.9664</td>
<td>7.9672</td>
<td>7.9704</td>
<td>7.9702</td>
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</tr>
<tr>
<td>Std. Dev.</td>
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<td>0.0005</td>
<td>0.0006</td>
<td>0.0004</td>
<td>0.0010</td>
</tr>
</tbody>
</table>

VAR A22 cruise. The field test was conducted aboard the R.V. Atlantis and took place in the Northwestern Atlantic, beginning just north of the Sargasso Sea and ending in the Caribbean Sea; see Figure 2.5. Measurements of TA and pH from the spectrophotometric TA-pH system were compared to the same parameters measured using an open cell, potentiometric titration system and a spectrophotometric pH system, based on the design of Carter [2011]. These instruments are referred to as the open-cell potentiometric TA system and single-measurement pH system. Both systems were provided by Dr. Andrew Dickson.

2.3.2.1 The Open-Cell Potentiometric Titration System

The open cell potentiometric TA system was the primary instrument used to analyze TA on CLIVAR A22. The system was composed of two main subunits, one unit for volume delivery
Figure 2.3: The mean pH of Gulf Stream seawater. The symbols represent the average pH for each bottle (black) and batch (red), and the lines represent the standard deviations. The overall batch average and standard deviations are also numerically given.

Figure 2.4: TA of Gulf Stream seawater. The solid line is the average value and the dashed lines are ±2 times the standard deviation from the mean.
Figure 2.5: CLIVAR A22 cruise track. Departing Woods Hole, MA on March 24 and arriving Bridgetown, Barbados on April 17, 2012. For reference, the stations are plotted as solid markers.
and a second unit for the potentiometric titration; both units were controlled with a custom LabVIEW program. The volume delivery subunit was comprised of a 100 mL glass pipette, three solenoid pinch valves to control the flow of sample to and from the glass pipette, aquarium pumps to pressurize the sample bottle, a digital relay controller attached to a personal computer, and a thermistor to monitor the pipette temperature. The pipette temperature was used to calculate the sample density, which was used to convert the TA from volumetric to gravimetric units.

Titrations were conducted using the following procedure; after 100 mL of sample was delivered to a 200 mL water-jacketed beaker with volume subunit of the instrument, the beaker was attached to a water bath (Thermo, Neslab RTE 7 Digital Plus) and the sample temperature was monitored using a 100 Ω Pt R.T.D. connected to an Agilent 34970A data acquisition unit with a multiplexer unit (Agilent PN# 34901A). The sample was allowed to reach 20°C before an initial aliquot (~ 2.2 mL) of acid (~ 0.1 M HCl in ~ 0.6 M NaCl) was added to the sample with a Dosimat auto-titrator (Brinkmann-Metrohm, Dosimat 765). Aquarium pumps were then used to introduce ambient air and remove the evolved TCO$_2$ from the acidified sample before the final solution potential was determined using a double-junction combination glass electrode. The standard potential of the electrode was calibrated, in a least-squares fashion, by measuring the potential of 19 successive additions of 0.04 mL of acid past the titration end-point.

### 2.3.2.2 The Single-Measurement pH System

The single-measurement pH system [Carter, 2011] was the primary system for measuring pH on CLIVAR A22. The measurement routine of the system was similar to the procedure used in the spectrophotometric pH portion of a measurement completed with the TA-pH system, and to a previous pH system using a syringe pump [Hiscock, 2006]. A Kloehn syringe pump controlled the flow of sample and sample-indicator solution to a thermostated flow-through spectrophotometer cell and the absorbance was measured using an Agilent 8453 spectrophotometer. Both the single-measurement and TA-pH systems averaged 5 successive absorbance
spectrum per blank and sample, but the single-measurement spectrophotometer was run with only the tungsten (visible) light ignited. This is not expected to significantly impact comparison of the resulting pH values; Carter [2011] came to the same conclusion. However, a comparison of the pH values is expected to be limited by the use of different indicating dyes. The single-measurement system used purified meta-cresol purple [Liu et al., 2011] provided by Dr. Robert Byrne (University of South Florida), but the TA-pH system used a commercial indicator (Sigma Aldrich). The use of different stock solutions of mCP was intentionally designed to enable the calibration of the commercial indicator that was used on previous CLIVAR cruises by our lab. This was necessary as commercial indicators have been shown to have significant impurities, which can lead to errors in the measured pH, especially at higher pH [Yao et al., 2007; Liu et al., 2011]. This makes a direct comparison of the absolute pH between the two systems difficult.

2.3.2.3 TA-pH System Evaluations

The subsamples analyzed on the TA-pH system were collected directly from the Niskin bottles in 250 mL borosilicate glass bottles and thermostated at 25 ± 0.1°C until analysis. For consistency with the methods used for the single-measurement pH system, 0.2 mL of saturated mercuric chloride was added to each sample. During the cruise, 287 bottles were sampled and analyzed on the spectrophotometric TA-pH system. These same samples were also analyzed for TA using the open cell potentiometric titration system [Dickson et al., 2007] and the single-measurement spectrophotometric system for pH [Carter, 2011]. There were also 51 duplicates collected and analyzed on TA-pH system. The accuracy of the TA and pH was monitored using Certified Reference Materials (CRM) for seawater CO₂ analysis. By comparing these measurements, the field performance of the system was evaluated.

TA

Evaluation with CO₂ Reference Material — The CO₂ CRMs [Dickson et al., 2003] were used to monitor the accuracy and precision of the TA for both the potentiometric and spec-
Figure 2.6: The difference in the certified TA and spectrophotometric TA on CLIVAR A22. The solid line is the average offset and the dashed lines are ±2σ from the mean value.

Potentiometric TA systems. Based on replicate analysis (n = 127) of CRMs, the precision of the potentiometric TA was ±1 μmol kg⁻¹ (1σ) and was not significantly offset from the certified TA value (+0.1 μmol kg⁻¹). A similar analysis of the replicate CRM measurements analyzed on the spectrophotometric TA-pH system indicated the TA was offset from the certified value by 0.7 μmol kg⁻¹ and was precise to within ±4.5 μmol kg⁻¹ (n = 54); see Figure 2.6.

*Inter-system Evaluation* — Including duplicate measurements, 287 samples were analyzed on the combined spectrophotometric TA-pH system and were compared with the standard shipboard methods. A comparison of the measured TA between the spectrophotometric and potentiometric systems (Figure 2.7) indicates the two methods agree to within 1.1±5.6 μmol kg⁻¹.

**Intra-system Evaluation** — Duplicates were collected in different glass sample bottles from the same Niskin. Attempts to randomize the analysis of the duplicate measurements were made by analyzing some of the duplicates subsequent to one another and randomizing the order in which the other duplicates were analyzed. A total of 51 duplicates are analyzed for spectrophotometric TA.
Figure 2.7: The difference in the potentiometric and spectrophotometric TA. The mean difference between the procedures is $1.1 \pm 5.6 \, \mu \text{mol kg}^{-1}$. The solid line represents the mean offset and the dashed lines are $\pm 2$ standard deviations from the mean.

Figure 2.8: The difference in duplicate measurements of TA from the TA-pH system analyzed during CLIVAR A22. The solid line represents the mean offset and the dashed lines are $\pm 2$ standard deviations ($\sigma = 4.9$) from the mean.
Comparison of the TA duplicates (Figure 2.8) indicated the reproducibility of TA measured at sea with the TA-pH system was ±4.9 μmol kg⁻¹.

2.3.3 pH

Evaluation with CO₂ Reference Material — CRMs were also used to monitor the precision of the pH from the spectrophotometric single-measurement and TA-pH systems. Figure 2.9 shows the measured values of CRM Batch 112 determined with the TA-pH system. Based on the replicate analysis, the measured pH of CRM Batch 112 was $7.9175 \pm 0.0013$ units ($\text{pH}^\text{calc}_\text{SWS} = 7.9065 \pm 0.003$, $t = 25^\circ\text{C}$, $n = 51$). A similar analysis of the spectrophotometric pH for replicate measurements using the single-measurement system indicates the pH of CRM Batch 117 was $7.9318 \pm 0.0012$ units ($\text{pH}^\text{calc}_\text{SWS} = 7.9365 \pm 0.003$, $t = 25^\circ\text{C}$, $n = 23$).

Inter-system Evaluation — As expected, direct comparison of the pH measurements indicated there is an offset between the measured pH values from the two systems; see Fig-
ures 2.10 and 2.11. On average, the measured pH values with the impure indicator were \( \sim 0.008 \) units higher than the purified pH in the surface ocean, but only \( \sim 0.002 \) units higher in the deeper waters. At pH \( \approx 8.1 \), the observed differences in the spectrophotometric pH measurements were similar to those reported by Liu et al. [2011] for pure \( m \)CP and \( m \)CP manufactured by Sigma-Aldrich.

![Figure 2.10](image)

**Figure 2.10:** Purified pH versus the difference between the purified and un-purified pH. The regression analysis can be used to predict (1\( \sigma = 0.005 \)) the pH of seawater measured with the Sigma-Aldrich indicator without the effect of impurities in the indicator.

*Intra-system Evaluation* — Duplicates were collected in different glass sample bottles from the same Niskin. Attempts to randomize the analysis of the duplicate measurements were made by changing the order in which the duplicates were analyzed. A total of 51 duplicates were analyzed for pH. Duplicate analysis of pH from the spectrophotometric TA-pH system indicated the reproducibility of pH was \( \pm 0.0012 \) units.

2.4 Discussion

The estimated uncertainty of the TA-pH system is summarized and compared to other procedures in Table 2.2. Comparison of the uncertainty for the laboratory based pH shows the
Figure 2.11: pH profiles at CLIVAR A22 Station 66. The difference in the pure pH (squares) and the impure pH values is shown numerically for each bottle. The offset is larger at the surface where the pH is higher.

Figure 2.12: The difference in duplicate measurements of pH from the TA-pH system analyzed during CLIVAR A22. The solid line is the mean difference and the dashed lines are ±2 standard deviations from the mean value.
The TA-pH system has an associated uncertainty similar to previously established methods. The TA is also in relatively good agreement with other spectrophotometric methods based on volumetric sample delivery; precision for gravimetric methods is greater due to lower uncertainty associated with the initial sample mass.

The laboratory results indicate the TA and pH are precise to within $\pm 2.5 \text{ } \mu\text{mol kg}^{-1}$ and $\pm 0.0006$, respectively, but the sea trial was unable to reproduce this same level of performance for both TA and pH. The uncertainties for the measurements collected during the sea trial are about $\pm 0.0012$ for pH and $\pm 5 \text{ } \mu\text{mol kg}^{-1}$ for TA. These uncertainties are approximately twice as large as those observed in the laboratory. Despite both measurements being dependent on the spectrophotometric pH, due to differences in the analytical methodologies, it is believed the increased uncertainties of the two procedures are largely unrelated.

### 2.4.1 pH

The greater uncertainty for pH measurements made at sea with the TA-pH system is attributed to difficulties in maintaining the spectrophotometer cell and environmental temperatures. During the cruise, there were multiple instances where the air conditioning in the ship’s laboratory failed and the room temperature increased to as much as $\sim 30^\circ \text{C}$. This resulted in difficulties keeping a constant temperature in the thermostated spectrophotometer cell, and possibly instrumental error in the spectrophotometer. The bath temperature surrounding the spectrophotometer cell was monitored for both the single-measurement and TA-pH systems.

Over the duration of the cruise, the measured temperatures in both cells varied by as much as $0.12^\circ \text{C}$ during a given station analysis; see Figure 2.13. An uncertainty of $\pm 0.1^\circ \text{C}$ in the pH analysis temperature results in an uncertainty of about $\pm 0.0015$ units in pH. In seawater, lowering the temperature of a sample will increase the pH. As temperature of a solution affects the pH, the measurements are normalized to a common temperature. Millero [1979a,b] developed equations based on the acid dissociation constants of CO$_2$ in seawater, which can be used to correct for changes in pH$_{\text{sws}}$. The standard error of equation from Millero [1979b] is reported to be $\pm 0.003$, but deviations as high as 0.03 pH units have been observed at temper-
**Table 2.2:** A summary of the reported precision for TA and pH analyzed by different methods or systems.

<table>
<thead>
<tr>
<th>Source</th>
<th>Method</th>
<th>TA / $\mu$mol kg$^{-1}$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA-pH System Lab.</td>
<td>Duplicate</td>
<td>±2.5</td>
<td>±0.0006</td>
</tr>
<tr>
<td>TA-pH System Lab.</td>
<td>CRM</td>
<td>±1.9</td>
<td>±0.0005</td>
</tr>
<tr>
<td>TA-pH System At sea*</td>
<td>CRM</td>
<td>±4.5</td>
<td>±0.0013</td>
</tr>
<tr>
<td>TA-pH System At sea*</td>
<td>Comparison</td>
<td>±5.6</td>
<td>±0.001*</td>
</tr>
<tr>
<td>TA-pH System At sea*</td>
<td>Duplicate</td>
<td>±4.9</td>
<td>±0.0012</td>
</tr>
<tr>
<td>Potentiometric TA At sea*</td>
<td>Duplicate</td>
<td>±1</td>
<td>-</td>
</tr>
<tr>
<td>Potentiometric TA At sea*</td>
<td>CRM</td>
<td>±1</td>
<td>-</td>
</tr>
<tr>
<td>Spectrophotometric pH At sea*</td>
<td>Duplicate</td>
<td>-</td>
<td>±0.0009</td>
</tr>
<tr>
<td>Spectrophotometric pH At sea*</td>
<td>CRM</td>
<td>-</td>
<td>±0.0012</td>
</tr>
<tr>
<td>Martz et al. [2006] Lab.</td>
<td>Duplicate</td>
<td>±2.1$^{†}$</td>
<td>-</td>
</tr>
<tr>
<td>Yao and Byrne [1998] Lab.</td>
<td>Duplicate</td>
<td>±0.3 – 0.9$^{‡}$</td>
<td>-</td>
</tr>
<tr>
<td>Roche and Millero [1998] At sea</td>
<td>Comparison</td>
<td>±3.5</td>
<td>-</td>
</tr>
<tr>
<td>Roche and Millero [1998] Lab.</td>
<td>Duplicate</td>
<td>±2 – 3</td>
<td>-</td>
</tr>
<tr>
<td>Clayton et al. [1995] At sea</td>
<td>Duplicate</td>
<td>±1.8</td>
<td>-</td>
</tr>
<tr>
<td>Breland and Byrne [1993] Lab.</td>
<td>Duplicate</td>
<td>±1.5$^{‡}$</td>
<td>-</td>
</tr>
<tr>
<td>Granéli and Anfält [1977] Lab.</td>
<td>Duplicate</td>
<td>±2.3</td>
<td>-</td>
</tr>
<tr>
<td>Carter [2011] At sea</td>
<td>Duplicate</td>
<td>-</td>
<td>±0.0004</td>
</tr>
<tr>
<td>Carter [2011] At sea</td>
<td>CRM</td>
<td>-</td>
<td>±0.0009</td>
</tr>
<tr>
<td>Hiscock [2006] At sea</td>
<td>Duplicate</td>
<td>-</td>
<td>±0.002</td>
</tr>
<tr>
<td>Clayton and Byrne [1993] At sea</td>
<td>Duplicate</td>
<td>-</td>
<td>±0.0004</td>
</tr>
</tbody>
</table>

* Data from CLIVAR A22.
* Estimated from the standard deviation of the regression line between the difference in purified and un-purified pH.
$^{†}$ Requires an estimate of TCO$_2$.
$^{‡}$ Based on gravimetric methods.
$^{i}$ Based on volumetric methods.
atures below 20°C [Hunter, 1998]. A more accurate temperature conversion method has been outlined by Hunter [1998] using the measured pH combined with TA and the CO2SYS program [Lewis and Wallace, 1998; Pierrot et al., 2006; van Heuven et al., 2011]. Hunter [1998] estimated the TA from salinity and used this estimate with the measured pH to calculate the DIC. The pH at 25°C was then determined from the estimated TA and calculated DIC; the resulting error is given as ±0.0002 units [Hunter, 1998].

Temperature normalizations for the A22 pH data use a similar approach, but the calculation inputs are the measured TA, pH, and spectrophotometer cell temperature. With these values, the pH is calculated at an output temperature of 25°C using the CO2SYS program [van Heuven et al., 2011]. This calculation results in a reduction of the uncertainty in the pH measurements for both systems of ~ 0.0003 units and the temperature adjusted pH measurements are thought to be reliable to ±0.0009 units.

Figure 2.13: The mean pH spectrophotometer cell temperature and range for each station on CLIVAR A22.

Despite the temperature normalization, the uncertainty in pH is still higher than the uncertainty of pH measurements in the laboratory or during previous sea trials; the increased uncertainty is attributed to bubble formation observed during the cruise, or to errors in electrical
systems associated with rapidly changing temperature—e.g. thermal EMF within the internal
circuitry. The spectrophotometer cell used in the single-measurement pH system accumulated
bubbles in the optical path of the spectrophotometer. Bubbles entrained in the optical path of
a spectrophotometer cell can lead to increased noise in the measured absorbances, which will
decrease the precision of the spectrophotometric pH measurements. The accumulated bub-
bles could only be removed from the cell by flushing the system with an optical cell surfactant
prepared in 18 MΩ reagent grade water, or by removing the cell from the spectrophotometer
and manually dislodging the bubbles.

The TA-pH system also experienced difficulties due to bubble entrainment in the optical
cell. The bubbles were mostly an issue due to the narrow aperture (3 mm internal diameter)
of the optical windows. Due to the opaque nature of the cell it was not possible to observe the
bubbles except through the optical windows. This made it difficult to determine when bubbles
are present in the cell and which measurements are influenced by absorbance errors due to
bubbles. The bubbles at sea are thought to be due to outgassing as the sample is brought to
the analysis temperature and subjected to suction forces within the tubing and syringe.

2.4.2 TA

Due to the analytical nature of spectrophotometric TA measurements, an uncertainty of the
endpoint pH of \( \sim 0.001 \) is not expected to lead to a \( 5 \ \mu\text{mol kg}^{-1} \) overall uncertainty in the
measured TA. To determine the limiting factor in the precision of the TA measurements, the
uncertainties of the parameters in equation (2.8) are evaluated for their relative effect on the
overall TA uncertainty. Such an evaluation indicates:

- For an overall uncertainty of \( \pm 1 \ \mu\text{mol kg}^{-1} \) in TA, the associated uncertainty in pH is
  \( \pm 0.004 \) units, or \( \sim 0.1\% \) at \( \text{pH} = 4 \). This effectively rules out the observed deviations
  in the bath temperature as the source of increased error in TA.

- Based on the calibrations of the Kloehn syringe pump, the uncertainty in the initial
  volume delivery is believed to be less than 0.01\% and contribute \( \pm 0.3 \ \mu\text{mol kg}^{-3} \) to
the overall uncertainty in TA. In order for the initial volume delivery to account for the observed increase in the uncertainty of the measured TA, the Kloehn imprecision would need to increase to \( \sim 0.2\% \). While this could potentially occur, we do not feel this is the most probable explanation.

- An uncertainty of 0.01\% in the volume delivered by the syringe pump is associated with a full piston stroke from the unit. A full piston stroke nearly occurs (\( \sim 98\% \)) during the sample delivery, but not during the acid addition. Volumetric deliveries of the syringe pump for additions less than the total syringe volume were not independently calibrated. Based on the instrument performance in the laboratory, it appears the precision of the acid volume delivery is adequate for single point TA titrations, but this does not appear to hold true at sea. Differences in the supplied power on ships, or even increased vibrations could potentially lead to a decreased precision in the acid delivery.

There is no true supporting evidence for the claim that the system experienced a decrease in the precision of the volumetric acid delivery at sea. However, based on the analysis of the relative importance of the individual uncertainties in the measures required to determine TA, this is the most probable explanation. Therefore, an alternative delivery system for the acid should be developed for the spectrophotometric TA-pH system.

### 2.4.3 An Improved Spectrophotometric System for TA and pH

The at-sea reproducibility of the spectrophotometric TA measurements is believed to be impacted by a reduction in the precision in which the acid is delivered. This could potentially be due to differences in the power supplied in the lab versus at sea. An updated system, which is expected to maintain reproducibility of the acid delivery at sea, has been developed where the acid is delivered directly to the mixing chamber using a second Kloehn pump with a 250 \( \mu \)L syringe.

The redesigned system was tested in the laboratory on GSSW and initial results were promising. For this test, a Kynar gas sampling bag was filled with GSSW and subsamples
Figure 2.14: TA (2296.8 ± 1.9 μmol kg\(^{-1}\)) of Gulf Stream seawater analyzed on the redesigned TApH system. The solid line is the average value and the dashed lines are ±2 times the standard deviation (±3.8 μmol kg\(^{-1}\)) from the mean.

were analyzed directly from the sample bag. In the initial trial, 24 samples were analyzed; see Figures 2.14 and 2.15. The standard deviation for the TA was 2296.8 ± 1.9 μmol kg\(^{-1}\) (n = 23) and 7.8677 ± 0.0008 units for pH (n = 24). This evaluation excludes a single measurement collected for the TA due to a low measured absorption (maximum absorption < 0.003) in the absorbance spectra; this is attributed to a bubble in the indicator line. Attempts were made to gravimetrically analyze the volumetric precision of the acid delivered, but due to limitations of the analytical scale in the laboratory, this was not possible. The resolution of the scale was only 1 × 10\(^{-5}\) g and was unable to detect anything less than a 4% change in the volumetric delivery by the syringe. Instead the maximum imprecision associated with the volumetric acid delivery is estimated from the overall uncertainty in the measured TA. A change in the TA of ~ 2 μmol kg\(^{-1}\) correlated with a maximum relative error of ~ 0.08% in the volumetric delivery by the 250μL syringe.
Figure 2.15: pH (7.8677 ± 0.0008) of Gulf Stream seawater analyzed on the redesigned TApH system. The solid line is the average value and the dashed lines are ±2 times the standard deviation (±0.0016) from the mean.

2.5 Conclusions

Of the four carbon parameters, TA is likely to be the most difficult to measure with autonomous methods. Even though pH and pCO$_2$ are mathematically/thermodynamically poor choices for monitoring and constraining the carbon dioxide system, these parameters have the advantage of not requiring accurate volumetric or gravimetric measurements for underway sampling. While DIC measurements are dependent on an initial volumetric measurement, DIC systems have 2 major advantages over systems for TA. For DIC measurements, small amounts of residual acidified seawater in the titration/gas stripping chamber does not significantly affect the measurement, and the volumetric acid delivery for DIC measurements does not require high precision. For TA, a residual acidified seawater in the titration chamber will decrease the initial TA of a solution before the measurement can occur. In addition, the reproducibly of TA measurements is highly dependent on the volumetric delivery of the sample and acid.

The semi-autonomous system for the spectrophotometric determination of pH and TA outlined in this paper has an overall uncertainty in pH determinations, which are comparable with
previous methods. The spectrophotometric TA determined with the instrument has a greater reproducibility than previous methods by $\sim 3 \, \mu\text{mol kg}^{-1}$. It is believed the increase in the overall uncertainty for TA measurements is due to imprecise additions of acid during the titration, and an alternative method for acid delivery is suggested. A redesigned system has been tested and the initial results indicate the system is capable of achieving a precision comparable with that of previous gravimetric spectrophotometric TA titrations using bromocresol green.

2.6 Recommendations

PTFE Optical Cells — Due to the errors in duplicate pH measurements attributed to small bubbles forming in the optical cell path, a different type of optical cell is suggested for future use. Custom optical cells made of PTFE or some other chemically inert plastic have been used in other flow-through spectrophotometric applications with excellent results. Åßmann et al. [2011] suggest a cell design in which two optical fiber probes are inserted into a custom PET cell. The overall length of their cell is 50 mm, but the optical cell path is only 10 mm. The smaller path length is achieved by inserting the optical fibers so they are in the middle of the cell. Åßmann et al. [2011] suggest that any bubbles entrained within a cell of this design pass through the optical path length of the cell and do not interfere with the absorbance measurement. Such a design also allows for a temperature probe to be inserted directly into the cell without interfering with the absorbance measurements.

Reduction of the $\Delta_{\text{HI}}$ term — The system was tested with the indicator bromo-cresol green, and the titrations were conducted with a final pH $\approx 3.8$. The use of bromo-cresol purple is shown to increase the reproducibility of spectrophotometric TA measurements [Yao and Byrne, 1998]. It is suggested that this is a result of a decrease in the $\Delta_{\text{HI}}$ term in equation (2.8). The reduction in the $\Delta_{\text{HI}}$ term is due to the higher pH ($\approx 5$) at which a bromo-cresol purple titration can be terminated.

Sample and acid volumes — Increasing the volume of the sample and acid should result in a reduction in the uncertainty of the TA measurements. By increasing the sample and
acid volumes, the imprecision in the volumetric deliveries becomes less significant and the uncertainty in the TA measurement should decrease. Conversely, the sample volume could also be decreased for applications where available water volume is limited, but this would likely result in a decreased reproducibility in the TA measurements. An additional syringe pump could be added to reduce the volume of water lost in rinsing. The primary pump could be used to handle the seawater sample and indicators, while the added pump would be used to handle the flow of acidified seawater from the mixing pipette to the spectrophotometer cell.

In summary, these recommendations should result in a system capable of measuring both TA and pH with a precision that is at least comparable to most manual procedures, while requiring less user control.
Chapter 3.

The Free Proton Concentration Scale for Seawater pH

3.1 Background

The pH of most surface seawater is 8.1 ± 0.1 [Millero, 2007], and is thought to have been 0.1 pH units higher at the beginning of the Industrial Revolution [Raven et al., 2005]. The decline in ocean pH is referred to as ocean acidification [Doney et al., 2009], and is largely due to the absorption of CO$_2$ released through the combustion of fossil fuels by the ocean. Results from an ocean general-circulation model indicate the continued use of fossil fuels [in accordance with the IS92a scenario, Houghton et al., 2001] will further decrease the global average surface pH to 7.8 by the end of the century, and to 7.5 by the year 2250 [Caldeira and Wickett, 2003]. A decrease in ocean pH of this magnitude would lead to changes in both chemical and biological systems that have not been experienced in the last 20-300 million years [Feely et al., 2004; Caldeira and Wickett, 2003].

pH is described as a ‘master variable’ for many physical and biological processes in natural waters [Bates, 1982; Millero, 1986; Clayton et al., 1995], and the observed decrease in ocean pH has lead to an increased interest in understanding the effects further acidification will have on: the carbonate cycle [Feely et al., 2004; Millero, 2007], the kinetics and biological availability of trace metals [Millero et al., 2009a; Millero and DiTrolio, 2010; Pascal et al., 2010; Shi et al., 2010], and the ability of marine ecosystems and fisheries to adapt to a less alkaline environment [Guinotte and Fabry, 2009; Cooley and Doney, 2009]. Despite the current research interest in the pH of marine environments, a universally accepted definition of pH does not exist for ionic media.

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As a result, current research is significantly limited by a lack of comparability among experiments, which is partially due to the use of different or undocumented pH scales [Orr et al., 2009]. Despite the current research interest in the pH of marine environments, a universally accepted definition of pH does not exist for ionic media. As a result, current research is significantly limited by a lack of comparability among experiments, which is partially due to the use of different or undocumented pH scales ([Orr et al., 2009].

These same limitations, as described by Bates [1948], are largely overcome for dilute solutions by the adoption of a single pH scale [Covington et al., 1985; Buck et al., 2002]. As we will explain in the following section, pH in dilute solutions is not based on the concentration of proton\(^+\) in solution, but is instead a measure of the hydrogen ion activity [Bates, 1948; Covington et al., 1985; Buck et al., 2002]; where the activity of an ion is the effective ion concentration, and is essentially the concentration of an ion corrected for the non-ideal behavior of the ion in the presence of other charged particles. The activity of an ion, \(a_i\), can be calculated from

\[
a_i = \frac{\gamma_i m_i}{m^*},
\]

where \(\gamma_i\) is the single ion activity coefficient of \(i\) at the molal concentration of \(i\) (\(m_i\)), and \(m^*\) is the standard molality (1 mol kg\(^{-1}\)). The standard molality is required to keep activity a unit-less quantity.

The activity of a single ion cannot be measured directly, and a non-thermodynamic formula must be used to conventionally define the activity coefficient of a single ion [Bates, 1948]. The non-thermodynamic convention currently used to define the activity coefficient used to calculate pH is not valid for ionic media; making the use of a separate scale for pH in seawater necessary. Therefore, seawater pH scales are based the proton concentration, not the activity. This leads to difficulties in defining pH for seawater.

In the following sections we review the derivation of the activity pH scale, the concentra-

\(^{\text{v}}\)The term proton refers to the hydrogen ion, H\(^+\). The two terms will be used interchangeably, but refer to the same species.
tion scales used for seawater pH, and the associated difficulties in defining the proton concentration in seawater.

### 3.2 The Activity pH Scale

As stated in the previous section, the pH of a solution is defined as a function of the proton activity [Covington et al., 1985; Buck et al., 2002]

\[
\text{pH} = -\log(a_H) = -\log \left( \frac{m_H \gamma_H}{m^*} \right)
\]

(3.2)

where, as in equation (3.1), \(a_H\) is the activity, \(\gamma_H\) is the molal activity coefficient at the molal concentration of proton \((m_H)\) in solution, and \(m^*\) is the standard molality. The pH on this scale is traceable to the measured potential \((E)\) of HCl in buffer solutions, using the primary electrochemical cell

\[
\text{Ag(s)|AgCl(s)|Dilute Sol. + m_{\text{Cl}}|H_2(g,1\text{atm})|Pt(s)}.
\]

(I)

The \(E\) of cell (I) can be related to the mean activity of HCl

\[
a_{\text{HCl}}^\pm = m_H m_{\text{Cl}} \left\{ \frac{\gamma_{\text{HCl}}^\pm}{m^*} \right\}^2,
\]

(3.3)

using the Nernst equation

\[
E = E^* - \frac{RT}{F} \ln \left( \frac{m_H \gamma_H m_{\text{Cl}} \gamma_{\text{Cl}}}{m^*} \right)
\]

\[
= E^* - \frac{RT}{F} \ln \left( m_H m_{\text{Cl}} \left\{ \frac{\gamma_{\text{HCl}}^\pm}{m^*} \right\}^2 \right),
\]

(3.4)

where \(T\) is the absolute temperature, \(K\) is the gas constant, \(F\) is the Faraday constant, \(E^*\) is the standard potential of cell (I) [Bates and Bower, 1954], and \(\gamma_{\text{HCl}}^\pm\) is the mean activity coefficient of HCl. When the total solution concentration of the chloride ion is known, the
acidity function, $-\log(a_H\gamma_{Cl})$, is determined from measurements in cell (I) by rearrangement of equation (3.4).

As only the acidity function can be directly determined, activity pH scales must be based on a conventional definition for the activity coefficient of the chloride ion, $\gamma_{Cl}$ [Bates, 1973; Buck et al., 2002]. With a conventionally assigned value for $\gamma_{Cl}$, it is possible to determine $a_H$ and pH on the activity scale. Classically, $\gamma_{Cl}$ is defined using the Bates-Guggenheim convention [Bates and Guggenheim, 1960]

$$\log(\gamma_{Cl})^{tr} = \frac{-A(I/m^*)^{1/2}}{1 + Ba(I/m^*)^{1/2}}$$

(3.5)

where $\gamma_{Cl}^{tr}$ is the trace activity coefficient and is equal to $\gamma_{Cl}$ in the pure solvent (the limit of $m_{Cl} \to 0$), $I$ is the solution ionic strength (mol kg$^{-1}$), $A$ is the temperature dependent Debye-Hückel slope, $B$ is a constant, and $a$ is the ion size parameter. In the Bates-Guggenheim convention, the value of $Ba$ is fixed at 1.5. The activity pH is then determined by rearranging equations (3.4) and (3.5) and measuring $E$ in the limit of $m_{Cl} \to 0$

$$\text{pH} = \lim_{m_{Cl} \to 0} \left\{ \frac{E - E^\circ}{RTln10/F} + \log \left( \frac{m_{Cl}}{m^*} \right) \right\} + \log(\gamma_{Cl}^{tr}).$$

(3.6)

The operational pH determined from equation (3.6) is commonly referred to as either pH$_{NBS}$ or pH$_{IUPAC}$.

### 3.3 Seawater pH

Estimates of $\gamma_{Cl}^{tr}$ from the Bates-Guggenheim convention are only valid in low ionic strength media, and pH on the NBS scale is restricted to solutions where the ionic strength is $< 0.1$ mol kg$^{-1}$. Due to this limitation, in natural waters such as saline estuaries (defined here as having a salinity greater than 5) and seawater, an alternative scale is used [Dickson, 1984, 1993; Millero, 1986, 2007; Millero et al., 1993b]. For marine systems, pH is generally reported on a concentration scale [Khoo et al., 1977; Ramette et al., 1977; Dickson, 1984; Millero,
1986], and is no longer a measure of the proton activity, but is instead a measure of the proton concentration

$$\text{pH}_x = -\log \left( \frac{m_{H^+}}{m^*} \right), \quad (3.7)$$

where x represents the specific concentration scale in which the pH is reported. This leads to the question: How should the proton concentration scale be defined? Unfortunately, there is neither a single, nor simple answer.

In marine chemistry, three concentration scales are used: the free, total, and seawater scale. When the pH is based solely on the free proton concentration, the pH is defined on the free scale

$$\text{pH}_F = -\log \left( \frac{m_{H^+}}{m^*} \right). \quad (3.8)$$

If the pH is based on the concentrations of the free proton and the proton associated with $\text{SO}_4$, then pH is on the total scale

$$\text{pH}_T \approx -\log \left( \frac{m_{H^+} + m_{\text{HSO}_4}}{m^*} \right), \quad (3.9)$$

and when the pH is based on the concentrations of the free proton plus the proton associated with $\text{SO}_4$ and F, then pH is on the seawater scale

$$\text{pH}_{\text{SW}} \approx -\log \left( \frac{m_{H^+} + m_{\text{HSO}_4} + m_{\text{HF}}}{m^*} \right). \quad (3.10)$$

The relationships in equations (3.9 - 3.10) are only valid over seawater pH ranges, and exact definitions of the total and seawater concentration scales are more accurately given by

$$\text{pH}_T = \text{pH}_F - \log \left( \frac{1 + m_{\text{SO}_4}/K_{\text{HSO}_4}^*}{m^*} \right) \quad (3.11)$$

and

$$\text{pH}_{\text{SW}} = \text{pH}_F - \log \left( \frac{1 + m_{\text{SO}_4}/K_{\text{HSO}_4}^* + m_{F}/K_{\text{HF}}^*}{m^*} \right) \quad (3.12)$$
where $K_{\text{HSO}_4}^*$ and $K_{\text{HF}}^{\text{vi}}$ are the stoichiometric dissociation constants for the species $\text{HSO}_4^-$ and $\text{HF}^-$, and $m_{\text{SO}_4}$ and $m_{\text{F}}$ are the total molal concentrations of $\text{SO}_4^{2-}$ and $\text{F}^-$ in solution. Stoichiometric dissociation constants are determined from either the thermodynamic constant ($K_{HA}^\circ$), measured in a solution at infinite dilution, and the molal activity product ($\Gamma_{HA} = \gamma_H \gamma_A / \gamma_{HA}$)

$$K_{HA}^* = \frac{K_{HA}^\circ}{\Gamma_{HA}} = K_{HA}^\circ \gamma_{HA} / \gamma_H \gamma_A$$  

(3.13a)

When the activity product is not known, $K_{\text{HSO}_4}^*$ can be determined from the ion concentrations in the pure solvent

$$K_{HA}^* = \lim_{m_{\text{HCl}} \to 0} Q_{HA} = \lim_{m_{\text{HCl}} \to 0} \frac{m_H m_A}{m_{HA}},$$  

(3.13b)

where $Q_{\text{HSO}_4}$ is the molality product. The stoichiometric dissociation constant is recommended over the apparent dissociation constant

$$K_{HA}' = a_H \frac{m_A}{m_{HA}},$$  

(3.14)

as it can be defined using mass balance equations, and can have a higher degree of reproducibility [Dickson, 1981, 1984].

By examining equations (3.8 - 3.12), it is evident that differences between the pH concentration scales are small in solutions where $m_{\text{SO}_4}$ and $m_{\text{F}}$ are minor, but in seawater $m_{\text{SO}_4}$ is large enough to cause a significant difference between the pH scales. The use of different concentration scales can lead to: a maximum error of approximately 0.1 in pH (at $S=35$ and $25^\circ\text{C}$) if data is incorrectly treated on multiple pH scales [Marion et al., 2011]. If the pH and p$K_{HA}$ values are not on a common scale more error and confusion occurs when working with pH in natural waters [Dickson, 1984; Millero, 2010; Marion et al., 2011]. Further complication is added by the recommendation of different concentration scales. The pH$_F$ scale is recommended as it is conceptually more simple than the pH$_T$ or pH$_{\text{SWS}}$ scales [Dickson,

For dissociation constants (K) and activity coefficients (γ) the superscripts '*' and '∘' do not refer to a pH scale, but denote a stoichiometric or thermodynamic value.
1984], and also because only the free proton concentration affects the kinetic and equilibrium processes in solution [Millero et al., 2009a; Millero, 2010; Marion et al., 2011]. Conversely, the pH$_F$ scale is recommended as it is likely to be more accurate than the pH$_E$ scale [Dickson, 1990, 1993], and the pH$_{SWS}$ scale is frequently used because it is more representative of all the components of seawater that affect the interaction with H$^+$ and is more consistent with calculations from ionic interaction models [Millero, 2007].

### 3.3.1 Calibration of Seawater pH

The potential error associated with seawater pH measurements is not limited to the use of multiple pH scales, but is also related to the calibration of the measurement. In order for pH measurements in natural seawater to be relative to a standard scale, the measurements should be calibrated with a standard buffer in artificial seawater (ASW) that is traceable the cell

$$\text{Ag(s)|AgCl(s)|HCl in ASW|H}_2\text{(g,1atm)|Pt(s)}, \quad \text{(II)}$$

where the composition of artificial seawater is given in Table 3.4. Therefore, it is necessary to develop a set of buffers in artificial seawater calibrated with an electrochemical cell without a liquid junction (e.g. cell (II)). The development of such a standard buffer for seawater pH requires:


2. Calibration of the standard potential of cell (II) in artificial seawater. This calibration can be on either the free or total proton scale.

Dissociation constants and the pH of buffers in artificial seawater were first measured by Bates and co-workers [Ramette et al., 1977; Bates and Calais, 1981; Czerminski et al., 1982; Bates and Erickson, 1986] in the cell

$$\text{Ag(s)|AgCl(s)|BH}^+ \text{ and } B \text{ in ASW|H}_2\text{(g,1atm)|Pt(s)}, \quad \text{(III)}$$
where BH$^+$ and B represent the acidic and basic forms of the buffer. The original pH of the amine buffers was evaluated on the free scale, but a subsequent evaluation [Dickson, 1993] of these original buffer potentials and new measurements of tris in cell (III) [Millero et al., 1993b; DelValls and Dickson, 1998] determined the pH on the total scale.

The pH of a buffer, at a given molality (mol kg-H$_2$O$^{-1}$), is calculated from measurements in cell (III) from the equation [Dickson, 1993]

\[
pH' = -\log \left\{ \frac{m'_H}{m^*} \right\} = \frac{E - E'_m}{RT \ln(10)/F} + \log \left\{ \frac{m_{Cl}}{m^*} \right\} + 2 \log \left\{ \frac{\gamma_{HCl}^{\pm}}{\gamma_{HCl}^\pm} \right\}, \tag{3.15}
\]

where pH', $m'_H$ and $E'_m$ are on the free or total scale, and the activity coefficient ratio is assumed to be unity. Before the pH of a buffer can be measured, the standard potential ($E'_m$ in equation (3.15)) must be known. To date, there are three independent studies [Khoo et al., 1977; Dickson, 1990; Campbell et al., 1993] evaluating the standard potential of artificial seawater in cell (II) from 0 to 55°C and salinities of 5 − 45 (equivalent to an ionic strength range of approximately 0.1 to 0.94 mol kg$^{-1}$). Due to competition between Cl$^-$ and other halides in seawater, the Ag(s)|AgCl(s) half cell cannot be used in natural seawater. Due to the necessary presence of F$^-$ in solutions used to calibrate pH on the seawater scale, the seawater scale cannot be directly evaluated using cell (II), and it is necessary to convert the pH to the seawater scale from either the free or total scales. Further discussion of the standard potentials of cell (II) is therefore limited to the total and free pH scales.

In ionic media, it is convenient to define the standard potential for cell (II) at zero molality of added solutes [Khoo et al., 1977; Dickson, 1990]. By defining a new standard potential, the mean activity coefficients approach unity in the limit of zero molality of added solutes in the seawater media, and not in the limit of zero molality of added solutes in pure water [Khoo et al., 1977]. The new standard potential is defined on either the free pH scale ($E'_m$) [Khoo et al., 1977; Dickson, 1990]

\[
E'_m = E^* - \frac{2RT}{F} l\eta_{HCl}^{\pm}, \tag{3.16}
\]
or the total pH scale \( E^*_m \) [Dickson, 1990]

\[
E^*_m = E^* - \frac{2RT}{F}\ln(r^{HCl}_{\pm}) + \frac{RT}{F}\ln\left(1 + \frac{m_{SO_4}}{K^*_{HSO_4}}\right).
\] (3.17)

In the limit of \( m_{HCl} \to 0 \), the standard potentials can also be evaluated from the measured potentials of cell (II) using

\[
E^*_m = \lim_{m_{HCl} \to 0} \left\{ E + \frac{RT}{F}\ln\left(\frac{m_{HCl}m_{Cl}}{(m^*)^2}\right) \right\},
\] (3.18)

and

\[
E^*_m = \lim_{m_{HCl} \to 0} \left\{ E + \frac{RT}{F}\ln\left(\frac{m_{HCl}m_{Cl}}{(m^*)^2}\right) \right\}.
\] (3.19)

### 3.3.2 Derivation of the Free Proton Scale

The free scale is conceptually clearer than the total scale, but also more difficult to define. The variables required to determine \( E^*_m \) in equation (3.19) are known a priori, but in order to determine \( E^*_m \) from equation (3.18), the free proton concentration, \( m_H \), must first be calculated. In the presence of \( SO_4 \)

\[
m_H = m_{HCl} - m_{HSO_4},
\] (3.20)

where both \( m_H \) and \( m_{HSO_4} \) are unknown. To determine \( m_H \) from \( m_{HCl} \), equation (3.20) is combined with equation (3.13b) and rewritten as

\[
m_H = m_{HCl}/\left(1 + \frac{m_{SO_4}}{K^*_{HSO_4}}\right)
\] (3.21)

where \( K^*_{HSO_4} \) is determined from equation (3.13a) if both \( K^*_{HSO_4} \) and \( \Gamma_{HSO_4} \) are known. In the case where \( K^*_{HSO_4} \) is unknown, \( m_H \) must be estimated using an iterative, least-squares regression technique [Dickson, 1990; Campbell et al., 1993], or \( r^+_{HCl} \) must be estimated [Khoo et al., 1977; Bates and Erickson, 1986].
Values for $E_m^*$ and $K_{HSO_4}^*$ are previously determined from measurements in cell (II) using multiple approaches:

1. Khoo et al. [1977] determine $\gamma_{HCl}^{\pm}$ in artificial seawater, where SO$_4$ is replaced with Cl, and then assumed the activity coefficient in sulfate-free seawater is a reasonable estimate of $\gamma_{HCl}^{\pm}$ ($\pm0.002$) for seawater solutions with SO$_4$.

2. Using measured data from cell (II) [Khoo et al., 1977], Bates and Erickson [1986] re-evaluate $E_m^*$ and $K_{HSO_4}^*$ by estimating the Harned coefficient of HCl in seawater using a weighted analysis of $\gamma_{HCl}^{\pm}$ in individual solutions of the major sea salts.

3. Dickson [1990] uses new measurements in cell (II) and values of $\gamma_{HCl}^{\pm}$ and $\Gamma_{HSO_4}$, calculated with a Pitzer model valid at a 25°C [Harvie et al., 1984], to simultaneously evaluate $E_m^*$ and $K_{HSO_4}^*$ by a least-squares minimization of $\sum_i (E_i - E_{ci})^2$, where

$$E_{ci} = E_m^* - \frac{RT}{F} \ln \left( \frac{m_H m_{Cl}}{(m^*)^2} \right) - \frac{2RT}{F} \ln \left( \frac{\gamma_{HCl}^{\pm}}{\gamma_{HCl}^{\pm}} \right)$$

(3.22)

and

$$m_H = \frac{m_{HCl}}{1 + \left( \frac{m_{SO_4}}{K_{HSO_4} m^{*\gamma_{HSO_4}}} \right)}.$$  

(3.23)

At 25°C and S=35, the $E_m^*$ derived from these different approaches vary by as much as 1.6mV, representing a deviation an entire order of magnitude greater than the combined variation in $E_m^*$ from three independent evaluations of cell (II) [Khoo et al., 1977; Dickson, 1990; Campbell et al., 1993]. The questionable accuracy of $E_m^*$ has led to the recommended use of the total proton scale in seawater [Dickson, 1993]. However, the total proton scale is not representative of the proton concentration which effects biological systems and certain chemical processes, such as the speciation of trace metals [Millero et al., 2009a; Millero and DiTrolio, 2010].
Therefore, it is desirable to derive an accurate free proton concentration scale that can be universally applied to the marine sciences.

Here we derive an accurate free pH scale, or verify a previous derivation of the scale, by evaluating $E_m^*$ and $K_{HSO_4}^*$ with a Pitzer model valid from $0 \sim 45^\circ C$ in seawater solutions with salinities between $5 \sim 45$. In order to assess the relative accuracy of the Pitzer model, we compare the measured $E$ from cell (II) and $\gamma^\pm_{HCl}$ calculated with equation (3.4) to the modeled $E$ and $\gamma^\pm_{HCl}$ determined from the Pitzer equation. By validating the model against the measured values in cell (II), we should be able to resolve much of the associated uncertainty in the free seawater pH scale.

3.4 The Pitzer Ionic Interaction Model

Due to the limited ionic strength range over which the Bates-Guggenheim convention is valid, it becomes necessary to use an alternative model to conventionally define pH in media with ionic strengths greater than $\sim 0.1$ mol kg$^{-1}$. The ion-interaction model of Pitzer [Pitzer, 1991] is suggested as a potential alternative [Buck et al., 2002]. The Pitzer equation extends the ionic strength range of the Bates-Guggenheim convention by incorporating both long and short range interactions of ions in solution. In this equation, the long range interactions are given by a Debye-Hückel term and the short range interactions can be divided into interactions between dissimilar ions of like and opposite charges [Pitzer, 1991]. The activity coefficient of a single ion in solution can be determined from

$$
\ln(\gamma_M) = Z_M^2 f\gamma + \sum_c \sum_a m_c m_a B_{ca}^t + \sum_c \sum_{c'} m_c m_{c'} \phi_{cc'}^t + \sum_a \sum_{a'} m_a m_{a'} \phi_{aa'}^t \\
+ \sum_a m_a (2 B_{Ma} + E C_{Ma}) + \sum_c m_c (2 \phi_{Mc} + \sum_a m_a \psi_{Mca}) \\
+ |Z_M| \sum_c \sum_a m_c m_a C_{ca} + \sum_a \sum_{a'} \psi_{Maa'},
$$

(3.24)
where \( Z_M \) is the ion charge and \( E \) is the equivalent molality \( (E = \sum_i |Z_i|m_i) \). The Debye-Hückel term \( (f') \) is given by

\[
f' = -A_\phi \left\{ \frac{I^{1/2}}{1 + 1.2I^{1/2}} + \frac{2}{1.2} \ln(1 + 1.2I^{1/2}) \right\},
\]

(3.25)

where \( A_\phi \) is the Debye-Hückel slope [Pitzer, 1991]. The second \( (B_{Ma}) \) and third \( (C_{Ma}) \) virial terms for the interaction between ions of dissimilar charge are given by

\[
B_{Ma} = \beta_{Ma}^{(0)} + \beta_{Ma}^{(1)}g(\alpha_{1Ma} I^{1/2}) + \beta_{Ma}^{(2)}g(\alpha_{2Ma} I^{1/2}),
\]

(3.26a)

and

\[
C_{Ma} = \frac{C_{Ma}^\phi}{2|Z_M Z_d|^{1/2}},
\]

(3.26b)

where

\[
g(x) = \frac{2[1 - (1 + x) \exp(-x)]}{x^2},
\]

(3.27)

and \( \alpha_{Ma} \) is either a constant or temperature dependent coefficient for the electrolyte. In equation (A.1.4), the term \( \beta_{Ma}^{(2)} \) is for 2-2 electrolytes and not needed for electrolytes with lower charges [Pitzer, 1991].

Equation (A.1.1) is the original form of the ion-interaction model [Pitzer, 1991, and references therein], but several extensions of the model have since come into use. The most basic extension of the Pitzer model is the expansion of the third virial coefficient as a function of ionic strength [Archer, 1992a,b; Clegg et al., 1994]

\[
C_{Ma}^T = C_{Ma}^{(0)} + 4C_{Ma}^{(1)} h(\omega_{Ma} I^{1/2}),
\]

(3.28)

where \( C_{Ma}^\phi \) in equation (A.1.1) is replaced with \( C_{Ma}^T \). The expression for \( h \) in equation (A.1.9) is given elsewhere [Clegg et al., 1994] and \( \omega_{Ma} \) is a constant or a temperature dependent function for the electrolyte. Further extensions of the Pitzer model, with additional virial
coefficients, are also proposed [Pitzer et al., 1999]. These extended models have allowed for very accurate representations of osmotic and activity coefficients over the full solubility range of many electrolytes [Archer, 1991, 1992a; Rard and Clegg, 1997; Pitzer et al., 1999], but sources for extended parameters are limited [Rard and Wijesinghe, 2003].

Higher order terms for the short range ion interactions in equation (A.1.1) are defined for both binary \( \phi_{Mc} \) and triplet \( \psi_{Mca} \) interactions. In a solution of mixed electrolytes, the binary mixing parameter is equal to the sum of the interaction parameters between two ions of like charge \( \theta_{Mc} \) and the electrostatic mixing effects of the two ions in solution \( \theta_{Mc}^E \). The electrostatic mixing terms \( \theta_{Mc}^E, \psi_{Mc}^E \) account for interactions from mixing unsymmetrical ions of the same charge polarity; equations for these terms are given by Pitzer [1991]. The triplet interaction parameter, \( \psi_{Mca} \), represents the interactions between two ions of similar charge with a single ion of opposite charge. For the binary and triplet interaction parameters, the subscript \( M \) refers to the cation for which the activity coefficient is determined, and \( a \) and \( c \) refer to the remaining anions and cations in solution. Equation (A.1.1) can be rearranged to find the activity coefficient of an anion, denoted as \( X \), and is given elsewhere [Pitzer, 1991; Campbell et al., 1993; Millero and Pierrot, 1998].

Activity coefficients calculated with the Pitzer model are for free ion concentrations, and in seawater solutions it is necessary to correct these coefficients for the formation of an ion complex [Whitfield, 1975; Millero and Pierrot, 1998]. This correction is made using

\[
\gamma^*_H = \alpha_H \gamma_H, \tag{3.29}
\]

where \( \gamma^*_H \) is the stoichiometric or total activity coefficient, \( \gamma_H \) is the free activity coefficient of H, and \( \alpha_H \) is the free fraction of H. In seawater, \( \alpha_H \) is defined as

\[
\alpha_H = 1 \left/ \left(1 + \frac{[SO_4^{2-}]}{K_{HSO_4}^{*}} + \frac{[F^-]}{K_{HF}^{*}} \right) \right. \right. \tag{3.30}
\]
3.4.1 Ionic Interaction Models

Here we present a Pitzer model for use with the seawater solutions from cell (II). The Pitzer equation has been used to calculate acid dissociation constants, osmotic coefficients, and activity coefficients which are in good agreement with the measured parameters in seawater [Millero, 1983; Millero and Roy, 1997; Millero and Pierrot, 1998; Millero et al., 2001; Clegg and Whitfield, 1995]. We have found two other Pitzer model computer codes written specifically for use in seawater solutions, the MIAMI Ionic Interaction Model [Campbell et al., 1993; Millero and Roy, 1997; Millero and Pierrot, 1998], and the model of Clegg and Whitfield [1995]. These models are reported to be valid within the respective ranges of 0 to 50°C, and 0 to 40°C and up to an ionic strength of ~0.9 mol kg\(^{-1}\) (S \(\approx\) 45). The model presented in this paper is a modified version of the MIAMI model [Campbell et al., 1993; Millero and Roy, 1997; Millero and Pierrot, 1998], but has been updated with newer parameters for some electrolytes; see Section 3.4.2. We find good agreement between our model and that of Clegg et al. [1994]; this is discussed further in Section 3.4.3.

There are also Pitzer models not written predominantly for use in seawater solutions: FREZCHEM [Marion, 2002; Marion et al., 2008, 2011], PHREEQC [Parkhurst and Appelo, 1999] and the Harvie et al. [1984] (HMW) model. Good agreement between the FREZCHEM and the MIAMI models is achieved if the Pitzer parameters (\(B^0\) & \(C^0\)) are optimized for natural temperature and concentration ranges, and F\(^-\) and CO\(_3^{2-}\) are corrected for ion pairing [Marion et al., 2011].

3.4.2 Model Parameterization

The virial interaction parameters for the model used in this study are given in Table 3.1. Nearly all of the major seawater ion interaction parameters (Na, Mg, Cl, and SO\(_4^{2-}\)) are known as a function of temperature over the entire range of the model, with the exception of the coefficients for MgCl\(_2\), MgSO\(_4\), and CaCl\(_2\). Coefficients for the interaction of these ions are only determined at temperatures of 25°C and above; see Table 3.1. However, when calculating \(\gamma_{HCl}^\pm\)
Table 3.1: Sources and temperature ranges (°C) of the virial parameters used. The dashes indicate no parameters are available.

<table>
<thead>
<tr>
<th></th>
<th>Cl</th>
<th>SO$_4$</th>
<th>HSO$_4$</th>
<th>OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0-250$^{\text{a,b}}$</td>
<td>0-250$^\text{c}$</td>
<td>25$^{\text{d,*}}$</td>
<td>0-350$^\text{e}$</td>
</tr>
<tr>
<td>Mg</td>
<td>25-200$^\text{f}$</td>
<td>25-200$^\text{g}$</td>
<td>25$^\text{h}$</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>25-250$^\text{b}$</td>
<td>25$^{\text{i,*}}$</td>
<td>25$^{\text{i,*}}$</td>
<td>25$^\text{i}$</td>
</tr>
<tr>
<td>K</td>
<td>0-250$^\text{b}$</td>
<td>0-250$^\text{c}$</td>
<td>25$^\text{i}$</td>
<td>25$^\text{i}$</td>
</tr>
<tr>
<td>H</td>
<td>0-100$^\text{j}$</td>
<td>0-55$^\text{k}$</td>
<td>0-55$^\text{k}$</td>
<td>-</td>
</tr>
<tr>
<td>MgOH</td>
<td>25$^\text{i}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^\text{a}$ Möller [1988]  
$^\text{b}$ Greenberg and Möller [1989]  
$^\text{c}$ Holmes and Mesmer [1986a]  
$^\text{d}$ Hovey and Hepler [1990]  
$^\text{e}$ Pabalan and Pitzer [1987]  
$^\text{f}$ de Lima and Pitzer [1983]  
$^\text{g}$ Phutela and Pitzer [1986]  
$^\text{h}$ Rard and Clegg [1999]  
$^\text{i}$ Harvie et al. [1984]  
$^\text{j}$ Campbell et al. [1993]  
$^\text{k}$ Clegg et al. [1994]  

Data extrapolated to temperatures other than 25°C using calorimetric data from Pitzer [1991].
**Table 3.2:** Sources and temperature ranges (°C) for the cation-cation mixing parameters used. The dashes indicate no parameters are available.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$i'$</th>
<th>$\theta_{ii'}$</th>
<th>$\psi_{ii'/\text{Cl}}$</th>
<th>$\psi_{ii'/\text{SO}_4}$</th>
<th>$\psi_{ii'/\text{HSO}_4}$</th>
<th>$\psi_{ii'/\text{OH}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>Mg</td>
<td>25$^d$</td>
<td>25$^d$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>Ca</td>
<td>25$^d$</td>
<td>25$^d$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>K</td>
<td>25$^d$</td>
<td>25$^d$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>H</td>
<td>0-50$^a$</td>
<td>25$^d$</td>
<td></td>
<td>25$^d$</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>Ca</td>
<td>25$^d$</td>
<td>25$^d$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>K</td>
<td>25$^d$</td>
<td>25$^d$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>H</td>
<td>0-50$^b$</td>
<td>25$^d$</td>
<td></td>
<td>25$^d$</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>K</td>
<td>25$^d$</td>
<td>25$^d$</td>
<td></td>
<td></td>
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<tr>
<td>Ca</td>
<td>H</td>
<td>0-50$^c$</td>
<td>25$^d$</td>
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<tr>
<td>K</td>
<td>H</td>
<td>0-50$^a$</td>
<td>25$^d$</td>
<td></td>
<td>25$^d$</td>
<td>25$^d$</td>
</tr>
</tbody>
</table>

$^a$ *Campbell et al. [1993]*  
$^b$ *Roy et al. [1980]*  
$^c$ *Roy et al. [1982]*  
$^d$ *Harvie et al. [1984]*  
$^e$ *Rard and Clegg [1999]*

In seawater solutions it is suitable to extrapolate these coefficients to temperatures between 0 and 25°C [Campbell et al., 1993; Clegg and Whitfield, 1995; Millero and Roy, 1997; Millero and Pierrot, 1998]. Many of the ion interactions of minor ions with major and other minor ions are also only defined at 25°C. It is possible to determine the temperature dependence for some of these parameters using calorimetric temperature derivatives of the electrolytes [Pitzer, 1991], but for most of the minor species we do not find this necessary. Using the 25°C model parameters for the minor species does have a large effect on the model output at other temperatures, with the notable exception of HSO$_4^\text{−}$. The activity coefficient of this species is needed for the calculation of $K_{\text{HSO}_4^\text{−}}^*$, and using these parameters at other temperatures could result in inaccurate estimates the dissociation constant.
Table 3.3: Anion-anion mixing parameters used in the activity coefficient model. The dashes indicate there are no parameters available, or assumed to be zero.

<table>
<thead>
<tr>
<th>$i - i'$</th>
<th>$\theta_{ii'}$</th>
<th>$\psi_{ii'\text{Na}}$</th>
<th>$\psi_{ii'\text{Mg}}$</th>
<th>$\psi_{ii'\text{Ca}}$</th>
<th>$\psi_{ii'\text{K}}$</th>
<th>$\psi_{ii'\text{H}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl–SO$_4$</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>-</td>
</tr>
<tr>
<td>Cl–HSO$_4$</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>-</td>
<td>25$^b$</td>
<td>-</td>
<td>25$^a$</td>
</tr>
<tr>
<td>Cl–OH</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SO$_4$–HSO$_4$</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>-</td>
</tr>
<tr>
<td>SO$_4$–OH</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>25$^a$</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Harvie et al. [1984] $^b$ Rard and Clegg [1999]

The mixing parameters used in the activity coefficient model, Tables 3.2 and 3.3, are also mostly limited to 25°C, but the limited temperature range should not significantly affect the calculated activity coefficients [Millero and Schreiber, 1982; Clegg and Whitfield, 1995]. For seawater solutions, excluding different combinations of the H–Na, H–Mg, and H–Cl, mixing parameters can cause a difference of 1-3% in $\gamma_H$ [Clegg and Whitfield, 1995]; therefore, we expect the maximum error from using these mixing parameters at temperatures other than 25°C is less than 3%.

Because it is important to use a consistent set of ion interaction parameters and acid dissociation constants [Pitzer, 1991, Chapter 3], the thermodynamic HSO$_4^-$ dissociation constant derived with the ion interaction parameters for H$_2$SO$_4$ [Clegg et al., 1994] is used in the model.

In a critical evaluation of $K'_{\text{HSO}_4^-}$, the Clegg et al. [1994] dissociation constant is found to be in good agreement with other evaluations [Dickson et al., 1990; Matsushima and Okuwaki, 1988; Hovey and Hepler, 1990] from 0 to 50°C; whereas, the original results of Pitzer et al. [1977] appear to be in error below 25°C [Sippola, 2012].
3.4.3 Model Reliability

To assess the model reliability, the output $\gamma_{\text{HCl}}^\pm$ and $E$ were compared to experimentally measured reference values taken from the literature.

3.4.3.1 Dilute Media

The model output is found to be in exceptional agreement, $9.1 \times 10^{-5} \pm 2.3 \times 10^{-6}$, with published values of $K_{\text{HSO}_4}^+$ [Clegg et al., 1994], from $0 - 50^\circ C$. The measured $E$ in 0.01 mol kg$^{-1}$ HCl [Bates and Bower, 1954] is also evaluated against the model output, and found to be in good agreement, $0.006 \pm 0.02$ mV, from 0 to 50$^\circ$C.

3.4.3.2 Seawater Solutions

The model performance is also evaluated against $E_m^*$ and $\gamma_{\text{HCl}}^\pm$ in two solutions with compositions similar to seawater. Three independent studies have evaluated the $E$ in solutions that accurately approximate the ionic composition of the major species in seawater [Khoo et al., 1977; Dickson, 1990; Campbell et al., 1993], and a single study has evaluated $E$ in an artificial seawater solution where SO$_4$ is replaced with Cl [Khoo et al., 1977]. Compositions of the artificial seawater solutions are given in Table 3.4.

The model is first compared to measured values of $E$ [Khoo et al., 1977, Table 1] in sulfate-free artificial seawater. The pH of these solutions is inherently on the free proton scale, and equation (3.4) is used to calculate $\gamma_{\text{HCl}}^\pm$. The measured results are in excellent agreement with the model output; the average deviation in $\gamma_{\text{HCl}}^\pm$ is $4 \times 10^{-4} \pm 0.001$, or $-0.01 \pm 0.1$ mV in $E$. Our results in sulfate-free seawater, Figures 3.1-3.3, agree with the results of Clegg and Whitfield [1995]; see their Figure 1.

For acidified seawater solutions including sulfate, the application of a Pitzer model is difficult due to:

1. The limited temperature range for many of the HSO$_4$ parameters.

---

vii Measured values of $E$ are adjusted so the $E^o$ reported by Khoo et al. [1977] is equal to the standard value from Bates and Bower [1954].
Table 3.4: Artificial seawater composition at S=35

<table>
<thead>
<tr>
<th></th>
<th>ASW&lt;sup&gt;a,c&lt;/sup&gt;</th>
<th>ASW&lt;sup&gt;b,d&lt;/sup&gt;</th>
<th>SO&lt;sub&gt;4&lt;/sub&gt;-free ASW&lt;sup&gt;b,e&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( m ) (mol kg-H&lt;sub&gt;2&lt;/sub&gt;O&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>( m ) (mol kg-H&lt;sub&gt;2&lt;/sub&gt;O&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>( m ) (mol kg-H&lt;sub&gt;2&lt;/sub&gt;O&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.42764</td>
<td>0.42664</td>
<td>0.46444</td>
</tr>
<tr>
<td>MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.05474</td>
<td>0.05518</td>
<td>0.05518</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.02927</td>
<td>0.02926</td>
<td>0</td>
</tr>
<tr>
<td>CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.01075</td>
<td>0.01077</td>
<td>0.01077</td>
</tr>
<tr>
<td>KCl</td>
<td>0.01058</td>
<td>0.01058</td>
<td>0.01058</td>
</tr>
<tr>
<td>Ionic Strength</td>
<td>0.7225</td>
<td>0.7229</td>
<td>0.7227</td>
</tr>
</tbody>
</table>

<sup>a</sup> The composition of solutions with \( S \) other than 35 are calculated from

\[
m(S) = m(S=35) \frac{0.7225}{I(S)},
\]

where

\[
I(S) = \frac{19.919S}{1000 - 1.00198S}.
\]

<sup>b</sup> The composition of solutions with \( S \) other than 35 are calculated from

\[
m(S) = m(S=35) \frac{27.570S}{1000 - 1.0016S},
\]

where \( I(S) \) can be calculated from equation (3.33) by substituting \( m(S=35) \) with \( I(S=35) \).

<sup>c</sup> The artificial seawater composition used by Dickson [1990]; Campbell et al. [1993].

<sup>d</sup> The artificial seawater composition used by Khoo et al. [1977].

<sup>e</sup> The SO<sub>4</sub>-free artificial seawater composition used by Khoo et al. [1977].
2. Significant discrepancies between the HSO$_4$ parameters in the literature; depending on the selected HSO$_4$ Pitzer parameterizations the calculated $E_m^*$ of cell (II) can differ from measured values by as much as 0.6mV [Campbell et al., 1993].

3. Previous comparisons of Pitzer models with measurements in artificial seawater with sulfate report a systematic offset in $E_m^*$ of 0.3 to 0.24mV, and attribute the offset to inaccurate Pitzer parameters for HSO$_4$ [Campbell et al., 1993; Clegg and Whitfield, 1995]. Using measured values of $E_m^*$, we calculate an offset of 0.3mV will lead to an error of less than 1% in pH; Clegg and Whitfield [1995] come to a similar conclusion.

Because of these difficulties, we also evaluate the model against the measurements in artificial seawater [Khoo et al., 1977; Dickson, 1990; Campbell et al., 1993]. Each study uses slightly different concentrations of HCl, and the model comparisons are made using $E_m^*$ and $^{tr}\gamma_{\text{HCl}}^\pm$ as the parameters are normalized to $m_{\text{HCl}} = 0$. Using the Pitzer model, $\gamma_{\text{HCl}}^\pm$ is calculated and compared to each of the data points in Table 4 of Khoo et al. [1977], Table 2 of Dickson [1990], and Appendix 1 of Campbell et al. [1993]. $E_{\text{calc}}$ is determined with equation (3.4).
Figure 3.2: Comparison of the measured and calculated $E$ (mV) from $5 - 40^\circ$C in artificial seawater without sulfate; measured values are from Table 1 in Khoo et al. [1977] and calculated values are from the activity coefficient model. The solid lines represent the mean deviation, and dashed lines are the mean $\pm 2$ times the standard deviation.

Figure 3.3: Comparison of the measured and calculated $E$ (mV) in artificial seawater without sulfate; measured values are from Table 1 in Khoo et al. [1977] and calculated values are from the activity coefficient model. The solid lines represent the mean deviation, and dashed lines are the mean $\pm 2$ times the standard deviation.
and the calculated $\gamma_{\text{HCl}}^{\pm}$. $E_{\text{calc}}$ and $\gamma_{\text{HCl}}^{\pm}$ are then used to determine $E_{\text{m,calc}}^*$ and $\gamma_{\text{HCl}}^{\pm}$ from the intercept ($\beta_0$) of a quadratic equation of the form [Dickson, 1990]

$$\beta_0 + \beta_1[HCl] + \beta_2[HCl]^2,$$

where the parameters $\beta_0$, $\beta_1$, and $\beta_2$ are determined from a least-squares fit of $E_{\text{calc}}$, or $\gamma_{\text{HCl}}^{\pm}$ at a given temperature and salinity.

Deviations between $E_{\text{m}}^*$ and $E_{\text{m,calc}}^*$ are shown in Figures 3.4 - 3.7. Table 3.5 gives the modeled values for $E_{\text{m,calc}}^*$ from $S = 5 - 45$ and $t = 0 - 45^\circ$C. Above 45°C, deviations are found to be unsuitably large [Campbell et al., 1993] and the data is not used in the analysis. The mean deviation for $E_{\text{m,calc}}^*$ between Dickson [1990] and Campbell et al. [1993] is $\pm 0.06$ mV, and $\pm 0.1$ mV between Khoo et al. [1977] and Dickson [1990]. The calculated deviations are in excellent agreement with the deviations in the measured data sets: $\pm 0.04$ mV between Dickson [1990] and Campbell et al. [1993], and $\pm 0.1$ mV between Dickson [1990] and Khoo et al. [1977]. The agreement of $E_{\text{m}}^*$ and $E_{\text{m,calc}}^*$ for the combined data sets is $\pm 0.1$ mV, or $\pm 0.001$ in $\gamma_{\text{HCl}}^{\pm}$. The mean offset in $E_{\text{m}}^*$ for the combined data set is $0.18 \pm 0.1$ mV, a 25-40% decrease over previous models; see Figure 6 of Campbell et al. [1993], and Figures 3 and 4 of Clegg and Whitfield [1995]. The model is brought into better agreement with measurements of $E_{\text{m}}^*$ by using newer, more reliable virial and mixing parameters for MgHSO$_4$ [Rard and Clegg, 1999].

3.5 The Free Proton Scale

Using the composition of artificial seawater with sulfate from Table 3.4, the free scale standard potential and stoichiometric dissociation constants of HSO$_4$ and H$_2$CO$_3$ are evaluated from the model output. The pH of buffer solutions in artificial seawater are also evaluated on the free proton scale using the modeled standard potential.
Figure 3.4: Mean difference and range for the deviations in $E^*$ (mV) for artificial seawater with sulfate: (filled circles) Campbell et al. [1993], (shaded diamonds) Dickson [1990], (shaded boxes) Khoo et al. [1977]. The solid lines represent the mean deviation, and the dashed lines are the mean $\pm 2$ times the standard deviation of the combined data set.

Figure 3.5: Mean difference and range for the deviations in $E^*$ (mV) for artificial seawater with sulfate: (filled circles) Campbell et al. [1993], (shaded diamonds) Dickson [1990], (shaded boxes) Khoo et al. [1977]. The solid lines represent the mean deviation, and the dashed lines are the mean $\pm 2$ times the standard deviation of the combined data set.
Figure 3.6: Mean difference and range for the deviations in $E^\circ$ (mV) for artificial seawater with sulfate: (filled circles) Campbell et al. [1993], (shaded diamonds) Dickson [1990], (shaded boxes) Khoo et al. [1977]. The solid lines represent the mean deviation, and the dashed lines are the mean $\pm 2$ times the standard deviation of the combined data set.

Figure 3.7: Mean difference and range for the deviations in the mean HCl activity coefficient for artificial seawater with sulfate: (filled circles) Campbell et al. [1993], (shaded diamonds) Dickson [1990], (shaded squares) Khoo et al. [1977]. The solid lines represent the mean deviation, and the dashed lines are the mean $\pm 2$ times the standard deviation of the combined data set.
3.5.1 The Free Scale Standard Potential

Despite the small systematic offset in solutions containing SO$_4$, the model is shown to predict $\gamma_{\text{HCl}}^*$ with an error of less than 1%. Therefore, it is reasonable to use the modeled $\gamma_{\text{HCl}}^*$ to derive $E_m^*$ with equation (3.16). The obtained values of $E_m^*$ (V) are fit to the equation

\[
E_m^* - E^* = \{d_1 + d_2 T + d_3 T \ln(T) + d_4 T^2\} S^{1/2} \\
+ \{d_5 + d_6 T + d_7 T \ln(T)\} S \\
+ \{d_8 + d_9 T\} S^{3/2} + d_{10} S^2,
\]

where $E_m^*$ (V) is given by

\[
E^* = b_1 + b_2 T + b_3 T \ln(T) + b_4 T^2,
\]

and is taken from Dickson [1990]. The coefficients and goodness of fit for $E^*$ and $E_m^*$ are given in Table 3.6.

Based on the offset between the modeled and measured $E_m^*$, the error in $E_m^*$ is assumed to be a constant 0.2mV at all temperatures; the effect of this systematic error on the derived stoichiometric dissociation constants and buffer pH values is assessed in Section 3.6.

3.5.2 The Bisulfate Stoichiometric Dissociation Constant

Equation (3.13a) can be used to derive $K_{\text{HSO}_4}^*$ from the modeled activity coefficient product and the measured values of $K_{\text{HSO}_4}^*$. However, the modeled values of $\gamma_{\text{SO}_4}$ and $\gamma_{\text{HSO}_4}$ should be validated against the experimental measurements. As modeled values of $\gamma_{\text{HSO}_4}$ are limited to 25°C, it is not possible to verify these values over the full temperature range of $E_m^*$. To ensure the calculated values of $K_{\text{HSO}_4}^*$ are consistent with the measurements in cell (II), equations (3.16) and (3.17) are combined

\[
K_{\text{HSO}_4}^* = m_{\text{SO}_4} \left( \exp \left( \frac{E_m^* - E_m^*}{RT/F} \right) - 1 \right),
\]
Table 3.5: Values for $E^*_{m_{calc}}$ in artificial seawater with sulfate. The values are calculated according to the composition in Table 3.4 using the Pitzer model described in Section 3.4.

<table>
<thead>
<tr>
<th>t (°C)</th>
<th>5</th>
<th>15</th>
<th>25</th>
<th>35</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.24884</td>
<td>0.25305</td>
<td>0.25445</td>
<td>0.25487</td>
<td>0.25481</td>
</tr>
<tr>
<td>5</td>
<td>0.24681</td>
<td>0.25123</td>
<td>0.25274</td>
<td>0.25323</td>
<td>0.25323</td>
</tr>
<tr>
<td>10</td>
<td>0.24465</td>
<td>0.24933</td>
<td>0.25098</td>
<td>0.25156</td>
<td>0.25163</td>
</tr>
<tr>
<td>15</td>
<td>0.24239</td>
<td>0.24737</td>
<td>0.24917</td>
<td>0.24986</td>
<td>0.25003</td>
</tr>
<tr>
<td>20</td>
<td>0.24003</td>
<td>0.24535</td>
<td>0.24734</td>
<td>0.24815</td>
<td>0.24843</td>
</tr>
<tr>
<td>25</td>
<td>0.23759</td>
<td>0.24329</td>
<td>0.24548</td>
<td>0.24644</td>
<td>0.24684</td>
</tr>
<tr>
<td>30</td>
<td>0.23509</td>
<td>0.24120</td>
<td>0.24362</td>
<td>0.24474</td>
<td>0.24527</td>
</tr>
<tr>
<td>35</td>
<td>0.23253</td>
<td>0.23910</td>
<td>0.24176</td>
<td>0.24306</td>
<td>0.24373</td>
</tr>
<tr>
<td>40</td>
<td>0.22994</td>
<td>0.23701</td>
<td>0.23994</td>
<td>0.24142</td>
<td>0.24224</td>
</tr>
<tr>
<td>45</td>
<td>0.22732</td>
<td>0.23494</td>
<td>0.23815</td>
<td>0.23982</td>
<td>0.24079</td>
</tr>
</tbody>
</table>
and $K_{\text{HSO}_4}^*$ is determined from the measured $E_m^*$ and modeled $E_m^{*}$. Values of $K_{\text{HSO}_4}^*$ from equation (3.37) agree with values calculated from equation (3.13b) to within $\pm 0.005$. The resulting $K_{\text{HSO}_4}^*$ is fit to the equation

$$
\log(\frac{K_{\text{HSO}_4}^*}{K_{\text{HSO}_4}^*}) = (c_1 + c_2 T + c_3 T \ln(T) + c_4 T^2) S^{1/2} \\
+ (c_5 + c_6 T + c_7 T \ln(T)) S \\
+ (c_8 + c_9 T) S^{3/2} + c_{10} S^2,
$$

where $K_{\text{HSO}_4}^*$ is given by [Clegg et al., 1994]

$$
\log(K_{\text{HSO}_4}^*) = a_1 + a_2 \ln(T) + a_3 T^2 + a_4 T + a_5/T.
$$

(3.38)

The coefficients and goodness of fit for $K_{\text{HSO}_4}^*$ and $K_{\text{HSO}_4}^*$ are given in Table 3.6.

As the values of $K_{\text{HSO}_4}^*$ from equation (3.37) are traceable to the measured data and validated model data, we compare these values to previous studies [Khoo et al., 1977; Bates and Erickson, 1986; Dickson, 1990]. The resulting analysis shows the values for $K_{\text{HSO}_4}^*$ from Khoo et al. [1977] and Dickson [1990] are in good agreement with equation (3.37) from 25 to 45°C, but significant deviations occur at temperatures below 25°C and high salinity; see Figures 3.8 and 3.9. At a salinity of 35 or above and a temperature below 25°C, the values of $K_{\text{HSO}_4}^*$ from Khoo et al. [1977] and Bates and Erickson [1986] are systematically lower than the $K_{\text{HSO}_4}^*$ determined with equation (3.37). Whereas, over the same temperature and salinity range, $K_{\text{HSO}_4}^*$ from Dickson [1990] is greater than the values of $K_{\text{HSO}_4}^*$ from equation (3.37). The results at 25°C and $S = 35$ can also be compared to the formation constants of HSO$_4$ ($1/K_{\text{HSO}_4} = 11.21$) determined from equation (3.37). Culberson et al. [1970] determined the value of 12.08; [Dyrssen and Hansson, 1973] a value of 11.33, Khoo et al. [1977] a value of 11.92; Bates and Erickson [1986] and Dickson [1990] a value of 27.52. The Dickson [1990] value is much higher than the other estimates and we suspect this is due to the use of the HMW Pitzer model used by Dickson [1990]. New measurements of pH in seawater with and without sulfate are needed to provide more reliable values of $K_{\text{HSO}_4}^*$ in seawater.
Figure 3.8: Deviations in $K^*_{HSO_4}$ between equation (3.37) and previous evaluations [Khoo et al., 1977; Bates and Erickson, 1986; Dickson, 1990] as a function of temperature and salinity.

Figure 3.9: Deviations in $K^*_{HSO_4}$ between equation (3.37) and previous evaluations [Khoo et al., 1977; Bates and Erickson, 1986; Dickson, 1990] as a function of temperature and salinity.
Values of $K^\ast_{\text{HSO}_4}$ from Dickson [1990] are dependent on the HMW Pitzer model to estimate $\Gamma_{\text{HSO}_4}$. While the HMW Pitzer model has been shown to give reasonable predictions of the measured solubilities of various minerals, the model has not been fully validated against measured values of $\gamma_{\pm\text{HCl}}$. Campbell et al. [1993] have compared the calculated $E^*_m$ from various Pitzer models to the measurements from cell (II), and find the HMW Pitzer model is in error by 0.6 – 0.7 mV at 25°C and salinities greater than 25. We attribute this offset to error in $K^\ast_{\text{HSO}_4}$ [Pitzer et al., 1977] used in the Harvie et al. [1984] Pitzer model. The error in $K^\ast_{\text{HSO}_4}$ is only apparent at temperatures below 25°C [Sippola, 2012], and the observed error in $K^\ast_{\text{HSO}_4}$ increases with salinity due to differences in activity coefficients between dilute and ionic solutions. To verify the difference in $K^\ast_{\text{HSO}_4}$ can be attributed to the error in $K^\ast_{\text{HSO}_4}$, we calculate the difference in $K^\ast_{\text{HSO}_4}$ using different values of $K^\ast_{\text{HSO}_4}$ [Pitzer et al., 1977; Clegg et al., 1994] with the modeled $\Gamma_{\text{HSO}_4}$ at salinities of 5 and 45; see Figure 3.10. Based on this analysis, the apparent error of $K^\ast_{\text{HSO}_4}$ used in the HMW model [Pitzer et al., 1977] is more than adequate to explain the discrepancies between the $K^\ast_{\text{HSO}_4}$ calculated with equation (3.37) and that of Dickson [1990].

Khoo et al. [1977] and Bates and Erickson [1986] do not use a chemical model to derive values of $E^*_m$ or $K^\ast_{\text{HCl}}$, but instead use estimates of $\gamma_{\pm\text{HCl}}$ in solution. Khoo et al. [1977] calculate $\gamma_{\pm\text{HCl}}$ in a sulfate-free seawater solution, and use the $\gamma_{\pm\text{HCl}}$ as an estimate of $\gamma_{\pm\text{HCl}}$ in seawater solutions with sulfate. Our model suggests the differences in calculated $\gamma_{\pm\text{HCl}}$ between artificial seawater solutions with and without sulfate are negligible at low salinities, but become significant as the salinity increases; see Figure 3.11. However, the model does not predict an offset of the observed magnitude at low temperature and high salinity.

Bates and Erickson [1986] estimate $\gamma_{\pm\text{HCl}}$ by determining the Harned slopes of HCl in seawater from the Harned coefficients of the individual salts weighted according to their relative abundance in seawater. We have not yet arrived at an exact explanation for the observed differences between $K^\ast_{\text{HSO}_4}$ calculated from equation (3.37) and that of Bates and Erickson [1986],
Figure 3.10: The difference in $K^*_{\text{HSO}_4}$ calculated between $K^*_{\text{HSO}_4}$ from Pitzer et al. [1977] and Clegg et al. [1994] using the modeled $\Gamma$ and equation (3.13a). The error in $K^*_{\text{HSO}_4}$ becomes more apparent at high salinity due to differences between activity coefficients in dilute and ionic solutions.

Figure 3.11: The modeled $\gamma^+_{\text{HCl}}$ relative to artificial seawater (ASW) at 25°C.
but attribute the differences to deviations between $\gamma_{\text{HCl}}^{\pm}$ determined from the estimated seawater Harned coefficients and $\gamma_{\text{HCl}}^{\pm}$ from the Pitzer model.

Due to the exceptional agreement with the model and the measured $E^*_m$ in cell (II), we feel the values of $K_{\text{HSO}_4}^*$ and $E^*_m$ given in equations (3.37) and (3.35) are currently the most accurate available. It is now necessary to re-evaluate the free scale stoichiometric dissociation constants of carbonic acid and free scale pH values for buffer solutions in artificial seawater, so they are consistent with the new values of $K_{\text{HSO}_4}^*$ and $E^*_m$ fit to equations (3.35) and (3.38).

### 3.5.3 The Carbonic Acid Stoichiometric Dissociation Constants

Many of the experimentally measured first and second stoichiometric dissociation constants of $\text{H}_2\text{CO}_3$,

$$K_1^* = \frac{[\text{H}][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

and

$$K_2^* = \frac{[\text{H}][\text{CO}_3^-]}{[\text{HCO}_3^-]}$$

are made in natural seawater on the seawater pH scale [e.g. Dickson and Millero, 1987; Mojica Prieto and Millero, 2002; Millero et al., 2006]. As most seawater pH buffers are given on the total [Dickson, 1993; Millero et al., 1993b; DelValls and Dickson, 1998] or free pH scale [Ramette et al., 1977; Bates and Calais, 1981; Czerminski et al., 1982; Bates and Erickson, 1986], it is necessary to convert the stoichiometric seawater scale dissociation constants to a common pH scale; see equations (3.11 - 3.12). Recently, Millero [2010] compiled measurements of $K_1^*$ and $K_2^*$ in natural seawater from Mehrbach et al. [1973]; Mojica Prieto and Millero [2002]; and Millero et al. [2006], and converted the constants to the total and free pH scales using $K_{\text{HSO}_4}^*$ from Dickson [1990] and $K_F^*$ given by Perez and Fraga [1987]. Using equation (3.11) and the measured results previously compiled and converted to the total scale by Millero [2010], we convert $K_1^*$ and $K_2^*$ to the free scale with $K_{\text{HSO}_4}^*$ from equation (3.37);
Table 3.6: Coefficients for dissociation constants and the standard potential

\[ \log(K_{\text{HSO}_4}^\circ) \text{ - Equation (3.39)}^{(a)} \]

\[
\begin{align*}
  a_1 &= 562.69486 \\
  a_2 &= -102.5154 \\
  a_3 &= -1.117033 \times 10^{-4} \\
  a_4 &= 0.2477538 \\
  a_5 &= -13273.75
\end{align*}
\]

\[ E^\ast \text{ - Equation (3.36)}^{(b)} \]

\[
\begin{align*}
  b_1 &= -3.718950 \times 10^{-1} \\
  b_2 &= 2.108275 \times 10^{-2} \\
  b_3 &= -3.501816 \times 10^{-3} \\
  b_4 &= 2.892747 \times 10^{-6}
\end{align*}
\]

\[ \log(K_{\text{HSO}_4}/K_{\text{HSO}_4}^\ast) \text{ - Equation (3.38)} \]

\[
\begin{align*}
  c_1 &= 4.24666 \\
  c_2 &= -1.52671 \times 10^{-1} \\
  c_3 &= 2.67059 \times 10^{-2} \\
  c_4 &= -4.03724 \times 10^{-5}
\end{align*}
\]

\[ E_m - E^\ast \text{ - Equation (3.35)} \]

\[
\begin{align*}
  d_1 &= 3.01828 \times 10^{-2} \\
  d_2 &= -9.63992 \times 10^{-4} \\
  d_3 &= 1.65434 \times 10^{-4} \\
  d_4 &= -1.74735 \times 10^{-7}
\end{align*}
\]

\[ \text{pK}_1^\ast - \text{pK}_1^\circ \text{ - Equation (3.41)}^{(c)} \]

\[
\begin{align*}
  e_1 &= -2.86189 \times 10^{-2} \\
  e_2 &= 1.03972 \\
  e_3 &= -6.37046 \times 10^{-5} \\
  e_4 &= 22.0233
\end{align*}
\]

\[ \text{pK}_2^\ast - \text{pK}_2^\circ \text{ - Equation (3.41)}^{(c)} \]

\[
\begin{align*}
  e_1 &= 8.13868 \\
  e_2 &= 1.12907 \\
  e_3 &= -3.82925 \times 10^{-4} \\
  e_4 &= -245.174
\end{align*}
\]

\[ \text{K}_1^\ast \text{ - Equation (3.42)}^{(d)} \]

\[
\begin{align*}
  f_1 &= -126.34048 \\
  f_2 &= 6320.813 \\
  f_3 &= 19.568224
\end{align*}
\]

\[ \text{K}_2^\ast \text{ - Equation (3.42)}^{(d)} \]

\[
\begin{align*}
  f_1 &= -90.18333 \\
  f_2 &= 5143.692 \\
  f_3 &= 14.613358
\end{align*}
\]

Values at \( S_p = 35 \) and \( T = 298.15 \text{K} \):

\[
\begin{align*}
  E'(\text{V})^{(a)} &= 0.22240 \\
  E_m'(\text{V}) &= 0.24006 \\
  \text{pK}_{\text{HSO}_4}^\ast^{(b)} &= 1.9788 \\
  \text{pK}_{\text{HSO}_4}^\circ &= 0.9785 \\
  \text{pK}_{1}^\ast^{(c)} &= 6.3515 \\
  \text{pK}_{2}^\ast^{(c)} &= 10.3297 \\
  \text{pK}_{1}^\ast^{(d)} &= 5.9486 \\
  \text{pK}_{2}^\ast^{(d)} &= 9.0767
\end{align*}
\]

(a) Clegg et al. [1994]  (b) Dickson [1990]
(c) Millero et al. [2006] (d) adapted from Millero [2010] & equation (3.37)
the resulting values (mol kg-soln$^{-1}$) are fit to the equation [Millero, 2010]

$$pK_i^* - pK_i = e_1 S^{1/2} + e_2 S + e_3 S^2 + (e_4 S^{1/2} + e_5 S)/T + (e_6 S^{1/2} + e_7 S) \ln(T),$$  \tag{3.41}

where the values of $pK_i^*$ are [Harned and Scholes, 1941; Harned and Bonner, 1945; Millero et al., 2006]

$$pK_i^* = f_1 + f_2/T + f_3 \ln(T).$$  \tag{3.42}

Coefficients for $K_1^*$ and $K_2^*$ fit to equation (3.41) and $K_1^*$ and $K_2^*$ fit to equation (3.42) are provided in Table 3.6 and are valid for $S = 0 - 45$ and $t = 0 - 45^\circ C$.

### 3.5.4 Free-Scale pH Buffers

The pH of the buffers 2-amino-2-hydroxymethyl-1,3-propanediol (tris) [Ramette et al., 1977; DelValls and Dickson, 1998], 2-amino-2-methyl-1, 3-propanediol (bis) [Bates and Calais, 1981], tetrahydro-1,4-isoxazine (morpholine) [Czerminski et al., 1982], and 2-aminopyridine [Bates and Erickson, 1986] have been previously calibrated in artificial seawater, but are not consistent with the newly derived free scale equilibrium constants. With the modeled $E_m^*$ and the measured potentials of buffers in artificial seawater [DelValls and Dickson, 1998; Bates and Calais, 1981; Czerminski et al., 1982; Bates and Erickson, 1986], the free scale pH of the seawater buffer solutions is re-evaluated using equation (3.15). To extend the salinity range of these buffers to more dilute solutions ($S < 20$), the measured $E$ of tris [Bates and Hetzer, 1961] and morpholine [Hetzer et al., 1966] in the cell

$$\text{Ag(s)}|\text{AgCl(s)}|\text{BH}^+ \text{and B|H}_2(g,1\text{atm})|\text{Pt(s)}$$  \tag{VI}

are combined with the measured $E$ of tris [DelValls and Dickson, 1998] and morpholine$^\text{viii}$ [Czerminski et al., 1982] in cell (III); the decision to limit the pH of equi-molal tris solutions to the measurements of DelValls and Dickson [1998] is discussed below. For each of the amine

$^\text{viii}$It is necessary to extrapolate the reported $E$ to $m_{HB} = m_B = 0.04\text{mol kg}^{-1}$.
buffer solutions, the pH is then fit to the general equation (the pH from these equations is on the molality scale, mol kg-H$_2$O$^{-1}$)

$$\text{pH} = a_1 + a_2/T + a_3T + (b_1 + b_2/T + b_3T)S + c_1S^2,$$

where $T$ is the absolute temperature. For each buffer, the form of equation (3.43) is adjusted until all statistically non-significant coefficients are removed. Coefficients for the pH of each buffer, fit to equation (3.43), are given in Table 3.7, and the residuals are plotted in Figures 3.12 - 3.15.

There is an offset in the measured potentials of 0.04 m tris/tris-HCl in artificial seawater at $S = 35$ and $t = 25$ of 0.0047 units in pH. Due to the systematic nature of this offset, DelValls and Dickson [1998] suggest the measurements of Ramette et al. [1977] are in error; however, an international comparison among national metrological institutes indicates the range of uncertainty in a primary pH buffer is $\sim 0.005$ pH units [Spitzer, 2000, 2001]. Considering these results, an offset of 0.0047 pH units represents a reasonable inter-laboratory agreement. Despite the evidence indicating the measurements of Ramette et al. [1977] may not be in error, the data is excluded from the fit to equation (3.43) as the measurements of DelValls and Dickson [1998] are: (1) in excellent agreement with 3 other independent solutions of 0.04 mol kg$^{-1}$ tris/tris-HCl made over a 5 year period in Dr. Andrew Dickson’s lab, (2) made using tris traceable to the National Institute of Standards and Technology acidimetric Standard Reference Material (SRM 723b), and (3) made over a greater range of salinities. Further independent studies of pH buffers in cells (III) and (VI), over a wide range of temperature and salinities, are needed for improved confidence in the accuracy of the buffer solutions for seawater pH measurements.

### 3.6 Sources of Uncertainty

The uncertainty in seawater pH measurements on the free proton scale is largely controlled by: potential differences in $\gamma^+_\text{HCl}$ between artificial seawater and natural seawater solutions,
Figure 3.12: The residual pH of m=0.04 mol kg-H$_2$O$^{-1}$ buffers fit to equation (3.43) as a function of temperature: (○) 0°C, (▿) 5°C, (×) 10°C, (☆) 15°C, (△) 20°C, (□) 25°C, (+) 30°C, (◁) 35°C, (○) 40°C, (▷) 45°C.

Figure 3.13: The residual pH of m=0.04 mol kg-H$_2$O$^{-1}$ buffers fit to equation (3.43) as a function of temperature: (○) 0°C, (▿) 5°C, (×) 10°C, (☆) 15°C, (△) 20°C, (□) 25°C, (+) 30°C, (◁) 35°C, (○) 40°C, (▷) 45°C.
Figure 3.14: The residual pH of \( m=0.04 \) mol kg\(^{-1}\) \( \text{H}_2\text{O} \) buffers fit to equation (3.43) as a function of temperature: (○) 0°C, (▿) 5°C, (×) 10°C, (☆) 15°C, (△) 20°C, (□) 25°C, (+) 30°C, (◁) 35°C, (●) 40°C, (▷) 45°C.

Figure 3.15: The residual pH of \( m=0.04 \) mol kg\(^{-1}\) \( \text{H}_2\text{O} \) buffers fit to equation (3.43) as a function of temperature: (○) 0°C, (▿) 5°C, (×) 10°C, (☆) 15°C, (△) 20°C, (□) 25°C, (+) 30°C, (◁) 35°C, (●) 40°C, (▷) 45°C.
the experimental uncertainty in the measured potentials from cells (I - VI), and error in the
modeled values of $\gamma_{HCl}^\pm$ used to evaluate $E_m^\ast$. In order to arrive at an overall uncertainty in
the measured pH on the free proton scale and in the stoichiometric dissociation constants of
HSO$_4^-$ and H$_2$CO$_3$, it is necessary to evaluate the individual error contribution from each of
the sources.

3.6.1 Extrapolation from Artificial Seawater

The artificial seawater composition in Table 3.4 is representative of 99.7% of the total ionic
composition of seawater [Dickson et al., 2007], and the minor discrepancy with natural sea-
water is not expected to significantly impact pH measurements. Seawater is considered a
‘constant’ ionic media, and if the ionic strength is held constant, a small change in composi-
tion does not lead to a significant change in the activity coefficients. This concept is evident in
Figure 3.11, where the calculated $\gamma_{HCl}^\pm$ in NaCl approaches $\gamma_{HCl}^\pm$ in artificial seawater with the
continual addition of the major seawater ions. Figure 3.11 also shows the mean offset in $\gamma_{HCl}^\pm$
between artificial seawater with K$^+$ (representing $\sim$ 0.9% of the total ionic composition) and
seawater without K$^+$ is $-0.0003$ and is held nearly constant over all salinities. We therefore
expect that minor differences in the background ionic composition, including natural vari-
ability in the composition of seawater, will not significantly bias the measured pH of natural
solutions.

3.6.2 Measurement Uncertainty

The experimental uncertainty is dependent on measurements of the potential of HCl and amine
buffers in artificial seawater, but it appears the measured potentials of the buffer material are
the greater source of error. At 25°C and $S = 35$, the pH of 0.04 equi-molal tris/tris-HCl buffer
from DelValls and Dickson [1998] differs from the measured pH of Ramette et al. [1977]
by 0.0047 units. It is difficult to determine which of these studies provides a more accurate
evaluation of the pH for tris buffer in seawater solutions, as both studies can be shown to be in
agreement ($\pm 0.1 - 0.2$ mV) with measured values of $E_m^\ast$ from cell (II) [see Millero et al., 1993b;
DelValls and Dickson, 1998]. An offset in pH of 0.005 units correlates to an uncertainty in the measured $E$ of approximately 0.3mV. This is larger than the maximum variability (0.2mV) in the measured $E$ of artificial seawater extrapolated to 0.01mol kg$^{-1}$ HCl [Table 2, Campbell et al., 1993]; as both of the tris/tris-HCl buffer data sets are traceable to measurements in cell (II), the limiting factor for the accuracy of a seawater pH buffer appears to be potentially related the characterization of the solid buffer material.

3.6.3 The Pitzer Ion Interaction Model

Even though the measured uncertainty for a primary pH buffer in a dilute solution is about ±0.005 units, the overall uncertainty is ±0.01 units [Buck et al., 2002]. The increase in the overall uncertainty is associated with the error in the determination of $\gamma_{\text{Cl}}$ from the Bates-Guggenheim convention, and is estimated by varying the ion size parameter in the Debye-Hückel equation. Estimating the uncertainty associated with the Pitzer model is not as simple, and generally requires measurements of activity coefficients to determine the uncertainty from the mean difference and standard deviation between the modeled and measured results. While the comparison of the modeled and measured results does not give any indication to the accuracy of the individual Pitzer coefficients, it does indicate the parameterizations of the individual salts can be combined to give a suitable estimate, $0.2 \pm 0.2$ mV at the 95% confidence interval, of $E^*_m$ in artificial seawater.

3.6.4 Overall Uncertainty

The overall uncertainty in seawater pH measurements appears to be independent of the pH scale on which the buffer is defined, and possibly related to the characterization of the exact composition of the buffer material used. However, if it can be assumed, as suggested by DelValls and Dickson [1998], that the pH of tris/tris-HCl in artificial seawater is know to better than 0.002 units in pH, differences in the uncertainties between the free and total proton scales become apparent. The Pitzer model used to calibrate the free proton scale is expected to contribute a bias of 0.003 units to the pH of amine buffers calibrated on the free proton scale,
Table 3.7: Coefficients for 0.04 mol kg-H$_2$O$^{-1}$ buffer dissociation constants on the free scale for equation (3.43). The dashes represent coefficients that are not found to be statistically significant, and are excluded from the fit.

<table>
<thead>
<tr>
<th></th>
<th>2-Aminopyridine (amp)</th>
<th>2-Amino-2-hydroxymethyl-1,3-propanediol (tris)</th>
<th>Tetrahydro-1,4-isoxazine (morpholine)</th>
<th>2-Amino-2-methyl-1,3-propanediol (bis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5696</td>
<td>-3.9482</td>
<td>4.2725</td>
<td>-1.5114</td>
</tr>
<tr>
<td>1/T</td>
<td>1835</td>
<td>3038.5</td>
<td>1651.2</td>
<td>2845.3</td>
</tr>
<tr>
<td>T</td>
<td>$4.4425 \times 10^{-4}$</td>
<td>$6.203 \times 10^{-3}$</td>
<td>$-4.386 \times 10^{-3}$</td>
<td>$2.6369 \times 10^{-3}$</td>
</tr>
<tr>
<td>S</td>
<td>$-1.1777 \times 10^{-2}$</td>
<td>$3.53 \times 10^{-2}$</td>
<td>$-1.738 \times 10^{-3}$</td>
<td>$-1.2934 \times 10^{-3}$</td>
</tr>
<tr>
<td>S/T</td>
<td>2.831</td>
<td>-4.346</td>
<td>2.23</td>
<td>1.261</td>
</tr>
<tr>
<td>S T</td>
<td>—</td>
<td>$-6.194 \times 10^{-5}$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>S$^2$</td>
<td>$7.97 \times 10^{-5}$</td>
<td>$4.18 \times 10^{-6}$</td>
<td>$-1.96 \times 10^{-5}$</td>
<td>$-3.18 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\sigma$ - Fit</td>
<td>0.003</td>
<td>0.0008</td>
<td>0.0008</td>
<td>0.0003</td>
</tr>
<tr>
<td>S range</td>
<td>30 – 40</td>
<td>0 – 45</td>
<td>0 – 40</td>
<td>20 – 45</td>
</tr>
<tr>
<td>t range</td>
<td>5 – 40°C</td>
<td>0 – 45°C</td>
<td>5 – 40°C</td>
<td>5 – 40°C</td>
</tr>
<tr>
<td>pK$_{\text{HB}}^*$</td>
<td>6.8744</td>
<td>8.1765</td>
<td>8.6799</td>
<td>8.9168</td>
</tr>
</tbody>
</table>

$^a$ At S = 35 & T = 298.15 K

and lead to an uncertainty in pH of 0.003 units. This can be compared to calibrations of the pH of buffer solutions on the total proton scale which do not appear to be significantly biased [Khoo et al., 1977; Dickson, 1990; Campbell et al., 1993], and contributes an uncertainty of less than 0.002 units in pH.

The corresponding uncertainty in the estimate of K$_{\text{HSO}}^*$ determined from equation (3.37) and the errors in $E_m^*$ and $E_m$ is about ±0.03. This uncertainty is estimated by assuming the total uncertainty in K$_m^*$ can be attributed to the error in the estimates of $E_m^*$ and $E_m^*$. 
3.7 Conclusions

The Pitzer model used in this study agrees with the measured $E$ in 0.01 mol kg$^{-1}$ HCl [Bates and Bower, 1954] and $E^*_m$ in artificial seawater [Khoo et al., 1977; Dickson, 1990; Campbell et al., 1993] to within $\pm 0.04$ mV and $\pm 0.2$ mV, respectively. In solutions containing sulfate, there is a systematic offset of 0.2 mV between the measured and modeled results, corresponding to an error of about 0.003 in $\gamma^\pm_{\text{HCl}}$. Previous application of the Pitzer model to natural waters with sulfate find a slightly larger (0.24 – 0.3 mV), but similar offset. While the decrease in the magnitude of this offset approaches significance, it does not represent a major step forward in the application of chemical solution models to natural waters. We find it is important to use parameterizations of the Pitzer coefficients and thermodynamic dissociation constants which have been critically evaluated and compared with high quality datasets. These evaluations are limited in the literature, and when present are often limited to single temperature. New measurements and further critical evaluations of older datasets are essential to the advancement of modeling ion activities in solution.

Using the modeled $t\gamma^\pm_{\text{HCl}}$, we have obtained new values for $E^*_m$ in seawater solutions. $K^*_{\text{HSO}_4}$ has also been re-evaluated from measurements of $E^*_m$ in cell (II) [Khoo et al., 1977; Dickson, 1990; Campbell et al., 1993] and the validated model values of $E^*_m$. Values for both $E^*_m$ and $K^*_{\text{HSO}_4}$ are in good agreement with previous estimates for temperatures above 25°C, but not when the solution temperature is below 25°C and the salinity is greater than 35. Due to the agreement between the measured and modeled values of $\gamma^\pm_{\text{HCl}}$ and the use of a critically evaluated formalism of $K^*_{\text{HSO}_4}$ used in the model, the values of $E^*_m$ and $K^*_{\text{HSO}_4}$ from this study are presently believed to be the most accurate available. Based on the agreement between the measured and modeled $E^*_m$, values of $E^*_m$ are estimated to be precise to $\pm 0.2$ mV (at the 95% confidence interval), but are biased by 0.2 mV. Future improvements in solution modeling might lead to new values of $E^*_m$ that disagree with the values from equation (3.35) by as much as 0.2 mV. This bias results in an error of about 0.003 units in the calculated pH$_F$ of seawater buffers fit to equation (3.43).
Equations for the stoichiometric dissociation constants of $\text{HSO}_4^-$, $\text{H}_2\text{CO}_3$, and $\text{HCO}_3^-$ from $S = 0 - 45$ and $t = 0 - 45^\circ\text{C}$ and the pH of 0.04 mol kg$^{-1}$ amine buffers from $S = 2 - 45$ and $t = 0 - 45^\circ\text{C}$ are derived on the free proton scale. By incorporating the measured results used to derive the thermodynamic dissociation constants of tris [Bates and Hetzer, 1961] and morpholine [Hetzer et al., 1966], we have extended the lower limit of the salinity range for the pH equations to $S \sim 2$.

As the free proton concentration scale is biogeochemically relevant for all systems, it is recommended that this concentration scale be universally adopted for defining pH in seawater solutions. This is an essential step in decreasing the confusion and errors currently associated with use of multiple scales for pH measurements in marine and estuarine environments. However, more work is necessary to assess the accuracy of seawater pH buffers using the cells (III) and (VI) and to resolve the discrepancies between the measured and modeled activity coefficient data in solutions with sulfate. Campbell et al. [1993] suggested this offset should be attributed to inaccurate values for the Mg–$\text{HSO}_4^-$ interaction parameters. Here we have used critically evaluated constants for the Mg–$\text{HSO}_4^-$ Pitzer interaction parameters [Rard and Clegg, 1999], but still find an offset between the measured and modeled activity coefficients in solutions with sulfate. We suggest that offset between the measured and modeled activity coefficients can instead be attributed to the Ca–$\text{HSO}_4^-$ or Ca–$\text{SO}_4^-$ interaction parameters.

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Chapter 4.
Comparison of Spectrophotometric pH Indicators over Oceanic Environmental Ranges

4.1 Background

The calibration of experimental pH measurements in laboratory and field environments require buffers with a pH established against the standard hydrogen electrode and the silver, silver chloride half cell [Bates, 1961]. In seawater, pH measurements are commonly accomplished by potentiometry using a glass electrode with a liquid junction, or by spectroscopy with a pH sensitive colorimetric indicator. Both potentiometric and spectrophotometric methods require an initial calibration with a standard seawater pH buffer; generally, equi-molal tris/tris-HCl (2-amino-2-hydroxymethyl-1,3-propanediol) in an artificial seawater media [Hansson, 1973; Ramette et al., 1977; Dickson, 1993; DelValls and Dickson, 1998; Nemzer and Dickson, 2005], NaCl [Foti et al., 1999; Millero et al., 2009b], or Na-K-Mg-Ca-Cl-SO₄ brines [Millero et al., 1987].

When using potentiometric methods, frequent re-calibrations utilizing either standard buffers [Millero et al., 1993b; Dickson, 1993] or a titration coupled with a least squares analysis [Millero et al., 1993a; Dickson et al., 2007] are necessary for an accurate determination of pH. Conversely, colorimetric pH indicators are considered a “calibration-free” chemical sensor and are shown to have no drift over periods of multiple months [DeGrandpre et al., 1999]. This stability is largely due to spectrophotometric pH measurements being established on principle chemical properties of the indicator: the acid dissociation constants and molar absorptivities [Liu et al., 2011].

4.1.1 pH Calibration in Seawater

Independent calibrations of 0.040 equi-molal tris/tris-HCl seawater buffers are in agreement to better than ±0.005 units of pH [Ramette et al., 1977; DelValls and Dickson, 1998; Nemzer and Dickson, 2005]. However, replicate analyses of multiple batches of 0.040 equi-molal tris/tris-
HCl buffer indicates the results of Ramette et al. [1977] are potentially in error, and a more representative uncertainty in the standard pH of equi-molal tris/tris-HCl buffers is ±0.002 units [DelValls and Dickson, 1998; Nemzer and Dickson, 2005]. Despite the low uncertainty in the recent evaluations of seawater pH buffers, uncertainties for pH measurements conducted in real seawater are expected to be higher. This increased uncertainty is at least partially due to a lack of easily available seawater pH buffers that span the natural ranges of salinity, and a complete lack of buffers calibrated over the range of pH values observed in the ocean. For a better understanding of the associated uncertainties in real seawater pH measurements, it is necessary to discuss the potential impacts the limited calibrations can have on potentiometric and spectrophotometric pH measurements.

Potentiometric pH Calibration — The accuracy of seawater pH measured with glass electrodes is largely limited by differences in the ionic background between the buffer and sample, and the standard use of a single point pH calibration. When available, calibrated tris/tris-HCl buffers are generally in an artificial seawater media with a salinity of 35 [Riebesell et al., 2010]. For pH measurements with glass electrodes, Easley and Byrne [2012] demonstrate that a 10 unit change from the calibration salinity results in inconsistencies of 0.028 units of pH, and that even a 2 unit change in salinity can lead to an offset of ~ 0.005 units of pH. This uncertainty is associated with variations in the liquid junction potentials caused by changes in the salinity; as the junction potential variability is not equal for all electrodes, it is necessary that this variability be independently evaluated for each electrode. Therefore, for measurements made over a range of salinities and requiring accuracies of approximately 0.005 units of pH, it is necessary that individual electrodes be calibrated with a number of different buffers made over a range of salinities nominally separated by ~ 2 units. Another significant source of uncertainty in seawater pH measurements made by potentiometry is the standard use of a single-point pH calibration, as tris/tris-HCl seawater buffers are currently only evaluated at a single pH. In dilute media, it is suggested that the associated uncertainty in pH measured with an electrode calibrated at a single pH is ±0.3 units over a 3 unit change in pH [Buck et al., 2002]. This un-
certainty is partially due to the assumption that the slope of the electrode potential versus the change in pH is equivalent to the theoretical Nernstian slope (59.16 mV at 25°C), or to a value given by the manufacturer. As the pH of oceanic waters generally does not vary by more than ±1 unit, the uncertainty in using a single point pH calibration is likely less than ±0.3 units, but is potentially the largest source of uncertainty for potentiometric pH measurements.

Spectrophotometric pH Calibration — The most significant control on the accuracy of pH determined by spectrophotometry is associated with the indicator purity [Yao et al., 2007; Liu et al., 2011]. Due to impurities present in some indicators, there is a potential for significant differences in the absorption spectra of indicators, which can lead to inaccuracies upwards of 0.02 units of pH [Liu et al., 2011]. The magnitude of the error associated with the impurities for a given indicator are known to be affected by differences in the pH, but comparisons of the relative error have not been determined at different salinities. The colorimetric indicator meta-cresol purple (mCP) is commonly used in oceanography [Dickson et al., 2007], and is calibrated using equi-molal tris/tris-HCl buffers over a range of salinities and temperatures [Clayton and Byrne, 1993; Liu et al., 2011]. The pH measured using mCP is shown to be precise to ±0.001 – 0.0004 units [Clayton and Byrne, 1993; Hiscock, 2006]. However, unless the composition of the indicator is well characterized, these measurements can be inaccurate by as much as 0.02 units of pH [Liu et al., 2011]. When the impurities are removed from mCP, the accuracy of pH measured using the purified mCP is reported to be ±0.001 units of pH [Liu et al., 2011]. The accuracy of purified mCP pH values is supported by measurements that are in excellent agreement (±0.0002 units) with the measured spectrophotometric pH using thymol blue [Liu et al., 2011]. Thymol blue is a colorimetric pH indicator with a pH appropriate for surface water pH, and analysis of thymol blue indicates certain batches are free of indicator impurities that interfere with the pH absorption spectra [Liu et al., 2011]. Independent comparisons of thymol blue from two different manufactures (Kodak-Eastman [Zhang and Byrne, 1996], and BDH Chemicals [Mosley et al., 2004]) suggests the error in pH is less than ±0.001 at 25°C and S_p = 30 – 40 [Mosley et al., 2004].
Comparison of the measured pH using different colorimetric indicators has only been conducted on a single sample of seawater [Liu et al., 2011], and a more comprehensive analysis should compare the spectrophotometric pH measured with different indicators over a range of salinities and pH values. In order to assess the relative accuracy of spectrophotometric pH using impure colorimetric indicators over a wider range of environmental conditions, buffers in artificial seawater spanning salinities of $30 - 40$ and with a nominal pH range of $7.85 - 8.10$ were measured using 3 different batches of $m$CP and 3 batches of thymol blue at $25^\circ C$.

4.2 Methods

4.2.1 Seawater pH Buffers

There are four buffers calibrated for pH in seawater: 2-aminopyridine [Bates and Erickson, 1986], tetrahydro-1,4-isohexane (morpholinium) [Czerminski et al., 1982], 2-amino-2-methyl-1,3-propanediol (bis) [Bates and Calais, 1981], and tris [Ramette et al., 1977; DelValls and Dickson, 1998; Nemzer and Dickson, 2005]. At a salinity of 35 and a temperature of $25^\circ C$, the respective pH values for the 0.04 equi-molal buffers are 6.770, 8.573, 8.810, and 8.094 (mol kg$^{-1}$H$_2$O$^{-1}$) on the total proton scale (pH$_T$) [Dickson, 1993; DelValls and Dickson, 1998]. The nominal pH$_T$ of most seawater is $\approx 8.2 - 7.4$ units, making tris/tris-HCl the only calibrated seawater buffer within the pH range of natural seawater; therefore, tris/tris-HCl buffers are recommended for use in calibrating pH measurements made in seawater [Dickson et al., 2007]. Even though the remaining pH buffers are not within the natural ranges of seawater pH, these buffers are potentially useful in a multi-point calibration of glass electrodes. However, there is no buffer appropriate for calibration of pH indicators at low pH; 2-aminopyridine is the only seawater buffer with a pH of less than 8 units, but is well below the pH range for the colorimetric indicators used to measure seawater pH ($m$CP $\approx 8.0 \pm 1$ and thymol blue $\approx 8.5 \pm 1$). This effectively limits the calibrations of spectrophotometric indicators to the upper range of seawater pH values.

In order to extend the pH range over which seawater pH calibrations are effective, it is suggested that buffers at different pH values be adapted from the 0.04 equi-molal tris/tris-HCl
buffers by varying the molal ratio of tris/tris-HCl from 1:1 [Pratt, 2011]. The pH of the non-equimolal tris/tris-HCl buffers can be estimated from the Henderson-Hasselbalch equation

\[
pH = pK^*_i + \log_{10} \left( \frac{[A]}{[HA]} \right),
\]

(4.1)

where \(pK^*_i\) is the stoichiometric dissociation constant of 0.04 equi-molal tris/tris-HCl at a given temperature and salinity [Ramette et al., 1977; DelValls and Dickson, 1998], \([A]\) is the molal concentration of Tris, and \([HA]\) is the molal concentration of Tris-HCl. By varying the molal ratio of tris/tris-HCl, it is possible to evaluate the relative pH with a nominal range of 7.85 – 8.10 in artificial seawater buffers. An absolute comparison of the pH would require calibration of the non-equimolal buffers using a primary electrochemical cell.

4.2.1.1 Preparation of Seawater pH Buffers

The salts for tris/tris-HCl buffers were all high purity salts and used without purification. Sodium chloride, sodium sulfate (Baker Analyzed, Lot # G34475), potassium chloride (Mallinkrodt, Lot # G20638), Tris (Mallinkrodt, Lot # J39593), and Tris Hydrochloride (J.T. Baker, Lot # G41470) were dried in a vacuum over \(P_2O_5\) until use. Magnesium chloride and calcium chloride were added from solutions of MgCl\(_2\) \cdot 6H\(_2\)O (Baker Analyzed, Lot # G47477), and CaCl\(_2\) \cdot 2H\(_2\)O (Baker Analyzed, Lot # 443101), and the stock solution concentrations were calibrated from the densities determined using a vibrating tube densitometer. The hydrochloric acid was added using Tris Hydrochloride, where the \(m_{\text{Tris}}\) was corrected for the addition of \(m_{\text{Tris-HCl}}\) (e.g. for an equi-molal tris/tris-HCl buffer, \(m_{\text{Tris}} = 0.040 \text{ mol kg-H}_2\text{O}^{-1}\) and \(m_{\text{Tris-HCl}} = 0.040 \text{ mol kg-H}_2\text{O}^{-1}\)).

The tris/tris-HCl buffer was made with 18 MΩ regent grade water in a 500 mL borosilicate glass bottle with a ground glass stopper. The ground glass seal between the bottle and cap was sealed with Apezion Type-L grease and the glass cap was held securely in place with a rubber band and bottle neck clip. The individual buffer solutions were prepared over a 2 day period and were made with a salinity of 30, 35, or 40 and a tris/tris-HCl ratio of 0.035:0.045,
0.040:0.040, or 0.030:0.050. The buffer solutions were prepared according to the recommend procedure outlined by Dickson et al. [2007], with the exception that the HCl and a portion of the tris were replaced by tris-HCl. The relative compositions of the equi-molal buffer solutions at a salinity of 35 are given in Table 4.1. The prepared and sealed buffer solutions were stored in a dark closet, kept at room temperature, for approximately 6 weeks before analysis.

**Table 4.1:** The composition of 0.04 equi-molar tris/tris-HCl buffer in an artificial seawater solution of salinity 35.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Nominal Weight(^a)</th>
<th>Concentration</th>
<th>Nominal Weight(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m / \text{mol kg}^{-1}_\text{H}_2\text{O})</td>
<td>grams</td>
<td>(b / \text{mol kg}^{-1}_\text{soln})</td>
<td>grams</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.38762(^b)</td>
<td>22.6446</td>
<td>0.37087(^b)</td>
</tr>
<tr>
<td>(\text{Na}_2\text{SO}_4)</td>
<td>0.02927</td>
<td>4.1563</td>
<td>0.02801</td>
</tr>
<tr>
<td>KCl</td>
<td>0.01058</td>
<td>0.7884</td>
<td>0.01012</td>
</tr>
<tr>
<td>MgCl(_2)</td>
<td>0.05474</td>
<td>(-)^(c)</td>
<td>0.05238</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>0.01075</td>
<td>(-)^(c)</td>
<td>0.01029</td>
</tr>
<tr>
<td>Tris</td>
<td>0.08000</td>
<td>9.6837</td>
<td>0.07654</td>
</tr>
<tr>
<td>HCl</td>
<td>0.04000</td>
<td>(-)^(c)</td>
<td>0.03827</td>
</tr>
</tbody>
</table>

\(^a\) These are nominal weights; the actual weight should be evaluated from the mass corrected for the buoyant forces of air. See Section A.2 and Dickson et al. [2007].

\(^b\) The reported value is valid only equi-molal/equi-molinity buffers where \(m_{\text{HCl}} = 0.04000 \ \text{mol kg}^{-1}\_\text{H}_2\text{O}\) and \(b_{\text{HCl}} = 0.03827 \ \text{mol kg}^{-1}\_\text{soln}\).

\(^c\) These components are added as liquids and the weight of the added liquid is dependent on the concentration of the stock solution.

### 4.2.2 Spectrophotometric pH Indicators

The indicator solutions (thymol blue and meta-cresol purple) were prepared from sodium salts of the colorimetric indicator and were sourced from different manufactures. The thymol blue used to analyze the tris/tris-HCl was Sigma Aldrich (Lot # 15H3613), Acros Organics (Lot # A0280568), and Alfa-Aesar (Lot # L12509); the mcp was Sigma Aldrich (Lot # 87H3629), Acros Organics (Lot # A0264321), and Alfa-Aesar (Lot # J04Q051).
The stock indicators were made to a concentration of $2 \times 10^{-3}$ mol L$^{-1}$ in 18 MΩ in reagent grade water. The initial pH of the reagent grade water and indicator solutions was $\sim 4.5$; to minimize the perturbation of the pH in the buffer solutions, the pH of the stock indicator solutions was adjusted by adding small amounts of 0.1 mol L$^{-1}$ NaOH. The indicator pH was adjusted until the absorbance ratios (R, see Section 4.2.2.1) of the stock solutions were 0.82 for thymol blue [Zhang and Byrne, 1996] and 0.33 for mCP [Clayton and Byrne, 1993].

### 4.2.2.1 Evaluation of pH from Spectral Absorbance Ratios

The spectrophotometric pH of the solutions was determined using an equation derived from equation (4.1) (the Henderson-Hasselbalch equation) and the Beer-Lambert Law

$$\lambda A = \sum (\lambda \epsilon_m[m])b, \quad (4.2)$$

where $\lambda A$ and $\lambda \epsilon_m$ are the measured absorbance the molal absorptivity at wavelength $\lambda$, $[m]$ is the molal concentration of the absorbing species, and $b$ is path length of the spectrophotometer. For colorimetric indicators in seawater, the total absorbance at a given wavelength is expressed as

$$\lambda A = (\lambda \epsilon_{\text{I}_2^-}[\text{I}_2^-] + \lambda \epsilon_{\text{HI}^-}[\text{HI}^-] + \lambda \epsilon_{\text{H}_2\text{I}^-}[\text{H}_2\text{I}^-])b. \quad (4.3)$$

Through algebraic manipulation with the equations for the stoichiometric acid association constants ($\beta^*_i$) for the colorimetric indicator

$$\beta^*_1 = \frac{[\text{H}_2\text{I}]}{[\text{H}^+][\text{HI}^-]}, \quad (4.4a)$$

$$\beta^*_2 = \frac{[\text{HI}^-]}{[\text{H}^+][\text{I}_2^-]}. \quad (4.4b)$$

equation (4.3) becomes

$$\frac{\lambda A}{b} = [\text{I}_2^-](\lambda \epsilon_{\text{I}_2^-} + \lambda \epsilon_{\text{HI}^-}\beta^*_1[\text{H}^+] + \lambda \epsilon_{\text{H}_2\text{I}^-}\beta^*_1\beta^*_2[\text{H}^+]^2). \quad (4.5)$$
In solution, the total indicator concentration is defined as

$$[I]_T = [I^{-2}](1 + \beta_{1}^*[H^+] + \beta_{1}^*\beta_{2}^*[H^+]^2), \quad (4.6)$$

where at seawater pH, $m_{H_2I}$ is not significant, and the $\beta_{1}^*$ terms in equation (4.5) and equation (4.6) can be disregarded [Clayton and Byrne, 1993]. Removing the $\beta_{1}^*$ term and dividing equation (4.5) by equation (4.6) results in

$$\frac{\lambda_A}{[I]_T} = \frac{\lambda_A e_{I^-} + \lambda_A e_{HI^-} \beta_{2}^*[H^+]}{1 + \beta_{2}^*[H^+]}. \quad (4.7)$$

**Clayton and Byrne** [1993] define $R$, the absorbance ratio of the peak absorbencies of [HI$^-$/[I$^{2-}$]

$$R = \frac{\lambda_{HI^-} A}{\lambda_{I^{2-}} A} = \frac{\lambda_{HI^-} e_{HI^-} + \lambda_{HI^-} e_{HI^-} \beta_{2}^*[H^+]}{\lambda_{I^{2-}} e_{I^{2-}} + \lambda_{I^{2-}} e_{I^{2-}} \beta_{2}^*[H^+]}. \quad (4.8)$$

where using equation (4.4b), $\beta_{2}^*[H^+]$ can be shown to be equal to [HI$^-$/[I$^{2-}$]. When $\beta_{2}^*[H^+]$ in equation (4.8) is replaced with [HI$^-$/[I$^{2-}$], the spectrophotometric pH can be determined from [Clayton and Byrne, 1993]

$$pH_T = pK_{i}^* + \log_{10} \left( \frac{R - e_1}{e_2 - e_3} \right), \quad (4.9)$$

where $pK_{i}^*$ is the total scale stoichiometric acid dissociation constant of the colorimetric indicator, and $e_i$ are molar absorptivity ratios for the indicator [Clayton and Byrne, 1993]

$$e_1 = \lambda_{HI^-} e_{HI^-} / \lambda_{I^{2-}} e_{HI^-}$$

$$e_2 = \lambda_{I^{2-}} e_{HI^-} / \lambda_{I^{2-}} e_{HI^-}$$

$$e_3 = \lambda_{I^{2-}} e_{I^{2-}} / \lambda_{I^{2-}} e_{HI^-}. \quad (4.10)$$

Examples of the representative spectra for thymol blue and mCP are shown in Figure 4.1.
Figure 4.1: Thymol blue (black line) and mCP (gray line) absorbance spectra (Measured in CRM Batch # 96, S = 33.081 & pH_T(calc) = 7.907). The vertical dashed lines are the peak absorbance wavelengths for the HI^+ (578 nm for mCP, 596 for thymol blue) and I^2− (434 nm for mCP, 435 for thymol blue) species. The offset in the absorbance at 434 nm for mCP is due to absorbance contribution from the I^2− species.

4.2.2.2 pK^*_i and e_i

The pK^*_i and e_i have been calibrated in seawater as a function of salinity and temperature, and values for equation (4.9) used in this study are taken from the literature and are described below.

**Thymol Blue** — The pK^*_TB and e_i are given by [Zhang and Byrne, 1996]

\[
pK^{*}_{\text{TB}} = 4.706 \times S / T + 26.3300 - 7.17218 \log_{10}(T) - 0.017316 \times S,
\]

\[
e_1 = -0.00132 + 1.600 \times 10^{-5} \times T,
\]

\[
e_2 = 7.2326 - 0.0299717 \times T + 4.600 \times 10^{-5} \times T^2,
\]

\[
e_3 = 0.0223 + 0.0003917 \times T,
\]

\[
(e.1)
\]
where \( S \) is the salinity and \( T \) is the absolute temperature. The \( pK^*_\text{TB} \) and \( e_i \) in equation (4.11) are valid for a salinity range of \( 30 - 40 \) and a temperature range of \( 5 - 35 \degree C \) and are reported in \( \text{mol kg}^{-\text{soln}} \). For thymol blue, the absorbance peak for the \( \text{HI}^- \) species is recorded at 596 nm and at 435 nm for the \( I^2^- \) species; each of these absorbance measurements should be corrected for baseline shifts by subtracting the absorbance at a non-absorbing wavelength (730 nm) [Clayton and Byrne, 1993].

**meta-Cresol Purple** — The pH of impure, or commercially available \( m\text{CP} \) is determined using the \( pK^*_i \) and \( e_i \) given by [Clayton and Byrne, 1993]

\[
pK^*_m\text{CP} = \frac{1245.69}{T} + 3.8275 + (2.11 \times 10^{-3}) \times (35 - S),
\]

\[
e_1 = 0.00691,
\]

\[
e_2 = 2.2220,
\]

\[
e_3 = 0.1331.
\]

For \( m\text{CP} \), the absorbance peak for the \( \text{HI}^- \) species is recorded at 578 nm and at 434 nm for the \( I^2^- \) species. The measured absorbencies are corrected for baseline shifts from the blank absorbance spectrum by subtracting the measured absorbance at 730 nm from the 578 and 434 nm absorbencies. The \( pK^*_m\text{CP} \) and \( e_i \) in equation (4.12) are calibrated over a salinity range of \( 30 - 37 \) and a temperature range of \( 20 - 30 \degree C \) on the \( \text{mol kg}^{-\text{soln}} \) scale.

### 4.2.3 Measurement Routine

The pH absorbance measurements were made using a diode array spectrophotometer (Agilent # 8453) with a flow through glass spectrophotometer cell (internal volume \( \approx 0.7 \text{ mL} \)). The spectrophotometer cell was thermostated at \( 25 \pm 0.04 \degree C \) using a custom aluminum cell holder attached to a water bath. The temperature of the aluminum cell holder was monitored using a digital platinum thermometer. The buffer solution was pre-equilibrated at 25°C by immersing the sample bottle in a thermostated glass beaker. The tris/tris-HCl buffer and indicator were introduced to the spectrophotometer cell using syringe pumps with 25 mL glass
syringes. After blanking the spectrophotometer with buffer containing no pH indicator, absorbance measurements for each of the indicators in the buffer solution were measured after rinsing the spectrophotometer cell twice with approximately 15 mL of solution containing the buffer and indicator. An additional 120 seconds was allowed for the sample to re-equilibrate at 25°C before the absorbance measurements were recorded.

4.3 Results and Discussion

4.3.1 Measurement Reproducibility

Prior to the analysis of the tris/tris-HCl buffers, the reproducibility of the pH measurements was assessed by replicate analysis (n = 6) of Certified Reference Material (CRM) [Dickson et al., 2003]. Based on the mean of the standard deviations for each indicator, the reproducibility of the measurements was about ±0.0006 units of pH for thymol blue and ±0.002 units of pH for mCP, see Table 4.2. Previous studies have used un-purified mCP with reported precisions of as good as ±0.0004 units of pH [Clayton and Byrne, 1993; Carter, 2011]. Therefore, the decreased reproducibility in the mCP measurements is attributed to impurities in the indicator. Instead, the reproducibility is thought to be influenced by atmospheric CO$_2$(g) exchange as the (CRM) bottle headspace volume increased.

4.3.2 Thymol Blue

The mean CRM pH$_T$ determined with thymol blue is 7.8973 ± 0.003 units of pH and is offset from the calculated pH$_T$ of the CRM (7.907) by about 0.01 units. The offset between the measured and calculated pH$_T$ is slightly higher than the expected uncertainty in the calculated pH (±0.006 units) [Millero, 2007]. When the calculated CRM pH is compared to the mean values for the individual batches of thymol blue, the measured pH using the Acros Organics thymol blue is within the anticipated uncertainty of the calculated pH value (+0.002), while the mean pH for thymol blue from Alfa Aesar and Sigma Aldrich is offset by 0.013 and 0.010 units of pH, respectively.
Table 4.3: Measured thymol blue spectrophotometric pH for tris/tris-HCl seawater buffers.

<table>
<thead>
<tr>
<th>$m_{\text{HCl}}$</th>
<th>S</th>
<th>A.A.</th>
<th>A.O.</th>
<th>S.A.</th>
<th>$\bar{x}$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.035</td>
<td>30</td>
<td>8.160</td>
<td>8.166</td>
<td>8.164</td>
<td>8.164</td>
<td>0.003</td>
</tr>
<tr>
<td>0.035</td>
<td>35</td>
<td>8.171</td>
<td>8.177</td>
<td>8.177</td>
<td>8.175</td>
<td>0.003</td>
</tr>
<tr>
<td>0.035</td>
<td>40</td>
<td>8.180</td>
<td>8.186</td>
<td>8.186</td>
<td>8.184</td>
<td>0.003</td>
</tr>
<tr>
<td>0.040</td>
<td>30</td>
<td>8.054</td>
<td>8.056</td>
<td>8.057</td>
<td>8.056</td>
<td>0.002</td>
</tr>
<tr>
<td>0.040</td>
<td>35</td>
<td>8.066</td>
<td>8.070</td>
<td>8.070</td>
<td>8.069</td>
<td>0.002</td>
</tr>
<tr>
<td>0.040</td>
<td>40</td>
<td>8.076</td>
<td>8.080</td>
<td>8.079</td>
<td>8.079</td>
<td>0.002</td>
</tr>
<tr>
<td>0.050</td>
<td>30</td>
<td>7.838</td>
<td>7.839</td>
<td>7.836</td>
<td>7.838</td>
<td>0.002</td>
</tr>
<tr>
<td>0.050</td>
<td>35</td>
<td>7.848</td>
<td>7.850</td>
<td>7.850</td>
<td>7.850</td>
<td>0.001</td>
</tr>
<tr>
<td>0.050</td>
<td>40</td>
<td>7.858</td>
<td>7.860</td>
<td>7.862</td>
<td>7.860</td>
<td>0.002</td>
</tr>
</tbody>
</table>

$a$ Alfa Aesar  
$b$ Acros Organics  
$c$ Sigma Aldrich

Figure 4.2: The difference in the measured and mean thymol blue spectrophotometric pH. The mean pH is calculated from the thymol blue indicators at a given salinity and $m_{\text{HCl}}$. 
Table 4.2: Measured spectroscopic pH for CRM Batch 96: S=33.081, TA=2212.40, TC=2005.36, calculated pH\_T = 7.907 at 25\^\circ C.

<table>
<thead>
<tr>
<th>CRM #</th>
<th>A.A.\textsuperscript{a}</th>
<th>A.O.\textsuperscript{b}</th>
<th>S.A.\textsuperscript{c}</th>
<th>A.A.\textsuperscript{a}</th>
<th>A.O.\textsuperscript{b}</th>
<th>S.A.\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.8941</td>
<td>7.9012</td>
<td>7.8978</td>
<td>7.8952</td>
<td>7.8710</td>
<td>7.9031</td>
</tr>
<tr>
<td>2</td>
<td>7.8931</td>
<td>7.8997</td>
<td>7.8962</td>
<td>7.8992</td>
<td>7.8686</td>
<td>7.9015</td>
</tr>
<tr>
<td>3</td>
<td>7.8946</td>
<td>7.9010</td>
<td>7.8970</td>
<td>7.8946</td>
<td>7.8693</td>
<td>7.9009</td>
</tr>
<tr>
<td>4</td>
<td>7.8943</td>
<td>7.9004</td>
<td>7.8966</td>
<td>7.8916</td>
<td>7.8728</td>
<td>7.9029</td>
</tr>
<tr>
<td>5</td>
<td>7.8948</td>
<td>7.9003</td>
<td>7.8975</td>
<td>7.8928</td>
<td>7.8718</td>
<td>7.9049</td>
</tr>
<tr>
<td>6</td>
<td>7.8949</td>
<td>7.9006</td>
<td>7.8977</td>
<td>7.8911</td>
<td>7.8709</td>
<td>7.9041</td>
</tr>
<tr>
<td>(\bar{x})</td>
<td>7.8943</td>
<td>7.9005</td>
<td>7.8971</td>
<td>7.8941</td>
<td>7.8707</td>
<td>7.9029</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>0.0006</td>
<td>0.0005</td>
<td>0.0006</td>
<td>0.0030</td>
<td>0.0016</td>
<td>0.0015</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Alfa Aesar \quad \textsuperscript{b} Acros Organics \quad \textsuperscript{c} Sigma Aldrich

The results for the measured pH of the tris/tris-HCl buffers are given in Table 4.3 and Figure 4.2. The spectrophotometric pH values determined using thymol blue from the three manufactures are all in good agreement; the mean deviation over all salinities and \(m_{\text{HCl}}\) is ±0.002 units of pH, with a maximum deviation of about −0.004 units of pH. Overall, the individual batch of thymol blue from Alfa Aesar underestimates the mean pH by −0.002 to −0.004 units, while the Acros Organics and Sigma Aldrich pH differences are positively offset from the mean by about 0.002 to 0.003 units. The mean deviation between the measured pH using thymol blue sourced from Acros Organics and Sigma Aldrich is ±0.0008 units, which is only 0.0002 units from the estimated measured uncertainty associated with the replicate measurements of CRM using thymol blue.

There are no significant relationships between salinity and the deviations in the spectrophotometric pH measured using the batches of thymol blue evaluated in this study. This is in agreement with independent evaluations indicating the pK\textsuperscript{*}\(T_B\) from 2 different manufac-
tures is in agreement to better than ±0.001 units from $S = 30 − 40$ [Mosley et al., 2004]. A significant trend in the observed deviations between the different batches of thymol blue with the nominal buffer pH is also not observed; the discrepancy (≈ 0.001 units of pH; see Table 4.3) between the mean deviation at high pH versus the mean discrepancies at lower pH is not significant.

4.3.3 meta-Cresol Purple

The replicate analysis of the CRM pH using the Alfa Aesar, Acros Organics and Sigma Aldrich $m$CP indicate the measured CRM pH is 7.889 ± 0.014 units. The measured pH$_T$ using Sigma Aldrich $m$CP is in good agreement (±0.004 units) with the calculated CRM pH, but the pH determined with the Alfa Aesar and Acros Organics $m$CP are offset from the calculated pH$_T$ by 0.013 and 0.036 units of pH, respectively.

The measured pH$_T$ of the tris/tris-HCl buffer are given in Table 4.3 and the deviations from the mean values are shown in Figure 4.4. The deviations in the measured buffer pH$_T$ using $m$CP are approximately an entire order of magnitude greater than the deviations in the pH$_T$ measured using thymol blue. The $m$CP pH$_T$ measured using the indicator from Acros Organics is significantly offset (±0.025 units of pH) from the mean $m$CP pH$_T$. The agreement between the pH$_T$ values measured with Alfa Aesar and Sigma Aldrich $m$CP are generally within ±0.01 − 0.001 units of the mean $m$CP pH$_T$. There is no observable trend in the mean $m$CP pH$_T$ deviations as a function of salinity; however, the mean deviations are strongly associated with the nominal solution pH$_T$. The observed pH dependence is in agreement with previous observations of the relative errors for un-purified $m$CP pH$_T$ measurements [Yao et al., 2007; Liu et al., 2011].

4.3.4 Comparison of pH: Thymol Blue and $m$-Cresol Purple

Measurements of the tris/tris-HCl buffer indicate the uncertainty in the pH$_T$ determined with thymol blue in this study is about ±0.003 units of pH. This overall uncertainty for all batches of the measured thymol blue pH$_T$ is similar to the uncertainty associated with primary cali-
Figure 4.3: Measured $m$CP spectrophotometric pH for tris/tris-HCl seawater buffers.

<table>
<thead>
<tr>
<th>$m_{\text{HCl}}$</th>
<th>S</th>
<th>A.A.$^a$</th>
<th>A.O.$^b$</th>
<th>S.A.$^c$</th>
<th>$\bar{x}$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.035</td>
<td>30</td>
<td>8.157</td>
<td>8.121</td>
<td>8.167</td>
<td>8.149</td>
<td>0.024</td>
</tr>
<tr>
<td>0.035</td>
<td>35</td>
<td>8.162</td>
<td>8.130</td>
<td>8.174</td>
<td>8.155</td>
<td>0.023</td>
</tr>
<tr>
<td>0.035</td>
<td>40</td>
<td>8.154</td>
<td>8.133</td>
<td>8.179</td>
<td>8.155</td>
<td>0.023</td>
</tr>
<tr>
<td>0.040</td>
<td>30</td>
<td>8.051</td>
<td>8.021</td>
<td>8.058</td>
<td>8.043</td>
<td>0.020</td>
</tr>
<tr>
<td>0.040</td>
<td>35</td>
<td>8.067</td>
<td>8.032</td>
<td>8.071</td>
<td>8.056</td>
<td>0.021</td>
</tr>
<tr>
<td>0.040</td>
<td>40</td>
<td>−</td>
<td>8.032</td>
<td>8.077</td>
<td>8.054</td>
<td>0.032</td>
</tr>
<tr>
<td>0.050</td>
<td>30</td>
<td>7.842</td>
<td>7.811</td>
<td>7.841</td>
<td>7.831</td>
<td>0.017</td>
</tr>
<tr>
<td>0.050</td>
<td>35</td>
<td>7.854</td>
<td>7.827</td>
<td>7.854</td>
<td>7.845</td>
<td>0.016</td>
</tr>
<tr>
<td>0.050</td>
<td>40</td>
<td>7.855</td>
<td>7.830</td>
<td>7.859</td>
<td>7.848</td>
<td>0.015</td>
</tr>
</tbody>
</table>

$^a$ Alfa Aesar $^b$ Acros Organics $^c$ Sigma Aldrich

Figure 4.4: The difference in the measured and mean $m$CP spectrophotometric pH. The mean pH is calculated from the $m$CP indicators at a given salinity and $m_{\text{HCl}}$. 
brations of the buffer materials (±0.002 – 0.005 units) [Ramette et al., 1977; DelValls and Dickson, 1998; Nemzer and Dickson, 2005]; therefore, the mean pH$_T$ measured with the 3 batches of thymol blue is believed to be an accurate evaluation of the pH$_T$ of the prepared tris/tris-HCl buffers. For each buffer $m_{HCl}$, the relationship between the mean thymol blue pH$_T$ and salinity is approximately linear from S = 30 – 40. The mean experimental slope, 0.002 ± 0.0002 units of pH per unit of salinity, is in excellent agreement with the estimated slope using equation (4.1). However, the mean pH$_T$ is offset from the estimated pH$_T$ by ~ 0.03 units of pH. This offset could be attributed to error in: 1) the measurements of the tris/tris-HCl for the buffer preparation, 2) differences in the purity of the tris between the tris and tris-HCl reagents, or 3) the assumption that the air buoyancy correction for tris-HCl is equivalent to tris in the mass to weight conversions; see Section A.2.

Comparison of the mCP pH$_T$ measurements with the mean thymol blue pH$_T$ indicates there is a relationship between the difference in the mCP pH$_T$ and thymol blue pH$_T$ ($\Delta$pH$_T$ ≡ pH$_T^{mCP}$ — pH$_T^{TB}$) with the nominal buffer pH$_T$; see Figure 4.5. A linear relationship is found between the mean thymol blue pH$_T$ and $\Delta$pH$_T$ for the buffers with $m_{HCl}$ = 0.035 molal, but the linearity of this relationship does not appear to hold as $m_{HCl}$ increases. For the $m_{HCl}$ = 0.040 molal buffer solutions, the offset between the measured $\Delta$pH$_T$ and the estimated linear $\Delta$pH$_T$ is within the experimental reproducibility of the pH$_T$ measurements and is not significant. The offset between the measured and estimated linear $\Delta$pH$_T$ values in the $m_{HCl}$ = 0.050 molal buffer solutions are larger than the experimental reproducibility for the pH measurements and are thought to be significant. As the buffer solution pH$_T$ decreases, the change in the pH$_T$/salinity relationship with $\Delta$pH$_T$ is attributed to: the influence of 1) the ionic composition of the solution on the molal absorptivities of the individual mCP species [Liu et al., 2011], 2) the ionic interactions with the I$^2$– indicator species [Millero et al., 2009a], or 3) some combination of the two effects.

If the relationship between pH$_T$/salinity and $\Delta$pH$_T$ is solely dependent on the ionic interactions of I$^2$– with the seawater ions, it is expected that a linear relationship would predominate
Figure 4.5: The difference in the measured $m$CP spectrophotometric $pH_T$ and the mean thymol blue $pH_T$. The horizontal lines represent the mean differences between the $m$CP batch (S.A. = -0.0005 units of pH, dotted line; A.A. = -0.007 units of pH, solid line; A.O. = -0.038 units of pH, dashed line) and the mean thymol blue $pH_T$.

over all $m_{HCl}$ buffer molalities. As a linear relationship is not observed in the buffers with $pH_T \approx 7.85$ units, the relationship between the $pH_T$/salinity and $\Delta pH_T$ at lower solution $pH$ is thought to be influenced by differences in the molal absorptivity ratios between thymol blue and $m$CP. Such differences could be influenced by 1) errors in the evaluation of $pK^*_m$CP, $pK^*_TB$, or $e_i$ for the indicators, or 2) the thymol blue spectrophotometric $pH$ could be less reliable as the difference in solution $pH$ and $pK^*_TB$ increases. Evaluations of the molal absorptivity constants of purified $m$CP show a larger error in the derived values of the molal absorptivity ratio $e_1$ at $pH_T = 7.8$ relative to $pH_T = 8.2$ [Liu et al., 2011], suggesting the observed relationship between $pH_T$/salinity and $\Delta pH_T$ may be due to differences in the molal absorptivity ratios. However, this study is unable to demonstrate with any certainty if the observed relationship between $pH_T$/salinity and $\Delta pH_T$ at lower $pH_T$ is due to differences in the molal absorptivity ratios or $pH_T$ measurements with thymol blue being less reliable at $pH_T \approx 7.85$. A future study utilizing the methods for this study, but also measuring the buffer $pH_T$ with purified $m$CP should provide the results necessary to understand the relationship between $pH_T$/salinity and $\Delta pH_T$ for the un-purified indicators with greater certainty.
4.4 Conclusions

For spectrophotometric pH measurements using three independent batches of thymol blue, an error in the relative measured $pH_T$ of about $\pm 0.003$ units of pH over $S = 30 - 40$ and a nominal $pH_T$ range of $7.85 - 8.2$ is found. These results are in agreement with a previous comparison of thymol blue from $S = 30 - 40$ at a single pH [Mosley et al., 2004] that found the $pK_a^*$ of thymol blue is in agreement to $\pm 0.001$. The spectrophotometric pH measured using the un-purified forms of $mCP$ are shown to have a relative error of as much as 0.05 units of pH at $pH_T \approx 8.2$ units. While the magnitude of this offset is larger than previously observed [Yao et al., 2007; Liu et al., 2011], the relationship between the buffer pH and the error in the measured impure $mCP$ spectrophotometric pH is consistent. This suggests the impurities in the un-purified indicator salts are not only different between given manufactures, but differences in the impurities also exist within the individual chemical lots from a given manufacturer. Once seawater pH buffers become available over a wider range of solution pH, it will be possible calibrate individual batches of a colorimetric indicator. However, the calibration procedures used to derive the $pK^*$ and $e_i$ for a single indicator is a significant undertaking and application of these same procedures to attempt to derive the $pK^*$ and $e_i$ for various batches of indicators with impurities would be a monumental task [Byrne, R. H., personal communication, 2011].

As spectrophotometric pH measurements do not require frequent re-calibrations using either seawater pH buffers or titration techniques, spectrophotometric methods are convenient for measuring the pH of natural waters. However, due to impurities present in certain batches of these indicators, the accuracy of spectrophotometric pH measurements can be in significant error. When the $pH_T$ is anticipated to be greater than $\sim 7.9$ units, it is suggested that un-purified thymol blue be used in place of un-purified $mCP$. 

5.1 Background

Atmospheric CO$_2$ concentrations are known to have increased over the previous two centuries from 280 ppm to greater than 380 ppm [Solomon et al., 2007]. Reconstructions of anthropogenic CO$_2$ production indicate that only about half of the total CO$_2$ emissions remain in the atmosphere [Prentice et al., 2001], and approximately 40% of the total emissions are accumulated in the ocean [Orr et al., 2001; Sabine et al., 2004].

There is a considerable research effort focused on quantifying oceanic anthropogenic CO$_2$ storage and uptake, including multiple global efforts to measure inorganic CO$_2$ in the ocean and to constrain the anthropogenic CO$_2$ signal from these measurements [Brewer, 1987; Chen and Millero, 1979; Wallace, 1995; Gruber et al., 1996; Goyet et al., 1999; McNeil et al., 2003; Hall et al., 2004; Waugh et al., 2004; Tanhua et al., 2007; Touratier et al., 2007]. Sabine et al. [2004] used the combined data set of World Ocean Circulation Experiment/Joint Global Ocean Flux Study (WOCE/JGOFS) to derive a global distribution of the total oceanic anthropogenic CO$_2$ uptake of 118 Pg C (+20%) from the 1800s to 1994. A more recent estimate, using the distributions of dissolved CFCs and the transit time distribution method, calculates a similar anthropogenic CO$_2$ uptake of 94-121 Pg C [Waugh et al., 2006]. This intrusion of anthropogenic CO$_2$ has caused a decrease in surface water pH of approximately 0.1 since the industrial revolution [Raven et al., 2005] and continued uptake is anticipated to cause a further decrease of 0.3 - 0.4 by the end of the century [Caldeira and Wickett, 2003; Orr et al., 2005]. This acidification will cause shoaling of the aragonite and calcite saturation horizons [Feely, 2002; Feely et al., 2004], and consequently decreases in the rates of the coral growth [Gat-

---

Planktonic calcification [Riebesell et al., 2000] and the inorganic and organic speciation of trace metals in the surface oceans [Millero et al., 2009a] will also be affected. Metals forming strong bonds with OH\(^-\) and CO\(_3^{2-}\) will have a higher fraction in the free form (e.g. Cu\(^{II}\)), and the solubility of certain metals (e.g. Fe\(^{III}\)) will increase as the oceans acidify.

The average rates of anthropogenic CO\(_2\) intrusion and acidification over the previous two centuries are relatively well constrained, but our ability to understand how ocean chemistry will change under further anthropogenic stress is limited. Model and geochemical estimates indicate the storage of anthropogenic CO\(_2\) in the ocean will decrease due to a decreased carbonate buffer capacity and climate change [Wetzel et al., 2005; Ebleston et al., 2010; Le Quéré et al., 2010]. However, others have suggested that the anthropogenic CO\(_2\) uptake and storage in the North Atlantic might be less limited by changes in the carbonate system, i.e. a decrease in buffer capacity, than previously thought [Tanhua et al., 2008]. The Climate Variability and Predictability (CLIVAR)/CO\(_2\) Repeat Hydrography Program was launched to investigate the response of the atmosphere-ocean interactions to anthropogenic forcing on decadal time scales by reoccupying sections of the WOCE/IGOFS Global CO\(_2\) Ocean Survey. This paper evaluates the changes in the anthropogenic carbon storage, as well as the decreases in oceanic pH, on two cruises in the South Pacific and compares the findings with similar studies in the region.

5.2 Methods

5.2.1 Data Quality

The changes in ocean carbon chemistry from the increase in anthropogenic CO\(_2\) are examined on WHP sections P18 (∼ 110° W) and P06 (∼ 32° S) (Figure 5.1).

Prior to the CLIVAR expedition in 2007/2008, P18 was last occupied during the WOCE expedition in 1994. The P06 line has been occupied by three separate hydrographic programs: WOCE (1992), Blue Earth Global Expedition (BEAGLE 2003) and the CLIVAR Repeat CO\(_2\)
Figure 5.1: P06 (Dashed red line, $\sim$ 32°S) and P18 (Solid blue line, $\sim$ 110 – 103°W) cruise tracks.

Hydrography program (2009/2010). All bottle data from these programs are available from the Carbon Dioxide Information Analysis Center (http://cdiac.esd.ornl.gov/oceans/). At least 2 carbon parameters were measured on all cruises, with TCO$_2$ measured by coulometric titration on every cruise [Dickson et al., 2007; Johnson et al., 1987]. Total alkalinity (TA) was measured by potentiometric titration [Millero et al., 1993a; Dickson et al., 2007], and pH by spectrophotometry using the methods outlined by Clayton and Byrne [1993] on all cruises except for WOCE P06. Fugacity of CO$_2$ ($f$CO$_2$) was measured on WOCE P18, P06 and CLIVAR P18. $f$CO$_2$ was measured by non-dispersive infrared analysis [Dickson et al., 2007;
Wanninkhof and Thoning, 1993] for WOCE and CLIVAR P18. On WOCE P06, fCO₂ was measured by gas chromatography [Neill et al., 1997].

The accuracy of the WOCE/JGOFS data, including P18 and P06, was evaluated by the Global Ocean Data Analysis Project (GLODAP) [Sabine et al., 2005]. The BEAGLE cruise was examined together with the original WOCE/JGOFS cruises as part of the CARINA data synthesis [Sabine et al., 2010]. The P18 and P06 CLIVAR cruises were also compared to the GLODAP and CARINA data sets using the same tools but were not released in time to be included in the publication. No adjustments were recommended for any of the cruises used here. The overall uncertainty in the TCO₂ and TA data is estimated to be ±3 μmol kg⁻¹ and ±5 μmol kg⁻¹, respectively [Lamb et al., 2001]. Murata et al. [2007] also evaluated the consistency of the WOCE and BEAGLE P06 TCO₂ on σ₃ = 41.4 and TA on σ₈ = 27.2, and found no significant variability between the cruises.

5.2.2 Data Analysis

To make direct comparisons of the difference in the anthropogenic carbon storage, it is necessary to remove any natural mesoscale variability between the cruises. The multiple linear regression (MLR) approach [Wallace, 1995] determines the short term increase in anthropogenic CO₂ between two measured cruises by fitting the TCO₂ as a function of multiple physical and biological parameters. This method has the advantage of being independent of many assumptions required for the back-calculation techniques [Sabine et al., 2008] and any differences between CFC and CO₂ solubility and transport inherent in the CFC proxy approaches [Álvarez and Gourcuff, 2010]. The MLR is an empirical method based on a comparison of partial correlations with physical and biological parameters to remove the natural variability in TCO₂ [Wallace, 1995]. The method is not dependent on a Redfield ratio to correct for changes in biological production/respiration and, assuming the correct parameters are applied in the regression, it inherently corrects for water mass mixing and changes in circulation. The independent variables used in MLR calculations are not universal and are selected based on data availability, quality and statistical assessment of the fit [Friis et al., 2005]. The
independent variables that provide the most robust fit do not appear to be equivalent for all regions of the oceans. In the North Atlantic, Friis et al. [2005] found apparent oxygen utilization (AOU) is not necessary in the determination of anthropogenic CO$_2$, whereas [Sabine et al., 2008] found AOU is a necessary parameter in the Pacific Ocean.

This method assumes the MLR completely accounts for the natural variation and any differences between the two fits are from anthropogenic forcing. The MLR method is highly dependent on the ability of the partial correlations to parameterize the natural system, and Friis et al. [2005] recommend a modified version of the MLR, an ‘extended’ multiple linear regression (eMLR), to reduce error propagation and variability. In the eMLR approach both cruises are independently fit with respect to physical and biological parameters, and the anthropogenic change is determined by taking the difference in the coefficients of the independent parameters. By applying the differences in the coefficients, any random variability and propagated error in an independent parameter is partially canceled [Wanninkhof et al., 2010].

There are three major sources of uncertainty associated with this method. First, there is the assumption that a multiple parameter regression can fully constrain the measured parameter. As the standard errors of the regressions are comparable to the overall measurement uncertainties, we assume this uncertainty is similar to that of the measurement. Second, any biases in the measured parameters between cruises will increase the overall uncertainty. This uncertainty is minimized by careful evaluation of data quality and is previously addressed. Lastly, the method is dependent on the assumption that the differences in the regression coefficients are only related to the change in the anthropogenic carbon storage. The fact that there are no anthropogenic CO$_2$ changes in the deep waters, where anthropogenic influences should be negligible, indicates this uncertainty is less than the uncertainty introduced by the regression. The regression is therefore the largest source of uncertainty and the detection limit is defined as the maximum standard error in the regressions.

In this study, the eMLR technique is applied to determine the increase in anthropogenic CO$_2$ below the seasonal mixed layer (150 m) on both cruise tracks. On P18 the increase in
anthropogenic CO$_2$ is examined between 1994 and 2008. The increase in anthropogenic CO$_2$ on P06 is examined from 1992 to 2010, 1992 to 2003, and 2003 to 2010. The lower limit of data used for the fits is 1500m as there is no significant increase in anthropogenic CO$_2$ (less than 5 $\mu$mol kg$^{-1}$) found below 1200m in the South Pacific. The measured TCO$_2$ is fit to a linear function of physical and biological hydrographic data, and the $f$-test was used to ensure the model is robust. A t-test is used to evaluate the significance of each parameter in the model. The validity of the model is further evaluated by randomly selecting half the measured data and fitting it to the regression model. The data, not used in evaluation of the regression, is then used to calculate the model residuals. In all cases, the full data fit standard error is within ±0.15 of the model verification standard error. To ensure the model is robust for all regions and water masses, the residuals are plotted as a function of longitude/latitude and depth (Figure 5.2). The residuals for the BEAGLE and WOCE P06, and CLIVAR and WOCE P18 lines are given in Appendix A.3.1.

After iterating this routine with different combinations of hydrographic data, the measured TCO$_2$ is found to be best fit to a linear function of salinity (S), potential temperature ($\theta$), potential density ($\sigma_\theta$), oxygen (O), silicate (Si) and phosphate (P). Where the eMLR$_{CO_2}$ is calculated using:

\[
eMLR_{CO_2} = (a_2 - a_1) + (b_2 - b_1)S_2 + (c_2 - c_1)\theta_2(d_2 - d_1)\sigma_\theta_2
\]
\[
+ (e_2 - e_1)O_2 + (f_2 - f_1)Si_2 + (g_2 - g_1)P_2
\]  

(5.1)

The subscript 2 indicates the data and coefficients are from the most recent occupation, and the 1 represents coefficients derived from a prior occupation. The coefficients and standard errors for the fits are given in Table 5.1.

The standard errors for all the regressions are below 5 $\mu$mol kg$^{-1}$, and only increases of anthropogenic CO$_2$ above this value are regarded as significant. With the exception of oxygen, these parameters are the same as those used by Sabine et al. [2008] on P16. Because of
Figure 5.2: CLIVAR P06 TCO$_2$ fit residuals ($\mu$mol kg$^{-1}$). The figure is representative of those used to evaluate the residuals for the MLR fits for the cruise data sets.
<table>
<thead>
<tr>
<th></th>
<th>Intercept</th>
<th>Salinity</th>
<th>Potential</th>
<th>Potential</th>
<th>Oxygen</th>
<th>Silicate</th>
<th>Phosphate</th>
<th>Root Square</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature</td>
<td>Density</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>yₙ</td>
<td>S</td>
<td>θ</td>
<td>σₘ</td>
<td>O</td>
<td>Si</td>
<td>P</td>
<td>RSE</td>
<td></td>
</tr>
<tr>
<td>P06 2010</td>
<td>-49459</td>
<td>-16.99</td>
<td>3.9</td>
<td>50.82</td>
<td>-0.37</td>
<td>0.68</td>
<td>33.75</td>
<td>3.72</td>
</tr>
<tr>
<td>P06 2003</td>
<td>-34467</td>
<td>-1.5</td>
<td>-2.06</td>
<td>35.79</td>
<td>-0.51</td>
<td>0.54</td>
<td>18.52</td>
<td>3.31</td>
</tr>
<tr>
<td>P06 1992</td>
<td>-24100</td>
<td>2.89</td>
<td>-4.16</td>
<td>25.57</td>
<td>-0.56</td>
<td>0.49</td>
<td>19.85</td>
<td>4.17</td>
</tr>
<tr>
<td>P18 2008</td>
<td>-8075</td>
<td>11.58</td>
<td>-2.68</td>
<td>-6.16</td>
<td>-0.28</td>
<td>0.68</td>
<td>44.92</td>
<td>4.84</td>
</tr>
<tr>
<td>P18 1994</td>
<td>-740</td>
<td>13.8</td>
<td>-2.5</td>
<td>2.34</td>
<td>-0.29</td>
<td>0.66</td>
<td>48.84</td>
<td>4.7</td>
</tr>
</tbody>
</table>

**Table 5.1:** Model coefficients for P18 and P06 eMLR regressions.
the substantial changes in North Pacific dissolved oxygen concentrations, *Sabine et al.* [2008] independently fit AOU with an eMLR to provide an estimate of the change in apparent decomposition rate for organic matter in the water column. Separating the AOU term out allowed them to independently evaluate the changes in carbon resulting from atmospheric uptake and from changes in circulation driven apparent decomposition rates. Since AOU changes were very small in the South Pacific, this separation was not necessary. *Sabine et al.* [2008] found that including AOU in the TCO$_2$ fit gave very similar results to fitting AOU separately then subtracting the AOU eMLR from the TCO$_2$ eMLR. To ensure that none of the variation in TCO$_2$ is due to the dissolution or precipitation of carbonate minerals, the salinity normalized TA is compared on isopycnal surfaces. There are no significant TA changes between cruises and no need to correct the TCO$_2$ for carbonate precipitation or dissolution. These results are consistent with observations of *Murata et al.* [2007].

Due to the differences in seasonal processes both physical and biological, the eMLR is not used to predict the carbon system above 150m. Applying the eMLR to the full water column results in highly scattered residuals in the mixed layer and increases the standard error of the regression. In order to avoid the complications of calculating anthropogenic CO$_2$ in the mixed layer, *Sabine et al.* [2008] estimated the anthropogenic CO$_2$ in the surface waters of line P16 using atmospheric pCO$_2$ with TCO$_2$ and TA measurements from the mixed layer. This method is based upon observations that indicate the pCO$_2$ of Pacific surface waters are increasing at rates approximately equal to the atmosphere [*Feely et al.*, 2006; *Takahashi et al.*, 2006], and the observed consistency of the TA data between cruises. This same approach is applied for the upper 150m of P06 and P18. Data are taken from the upper 50m from CLIVAR P18/P06 and the CO$_2$ fugacity ($f$CO$_2$) is calculated using the CO2SYS program [*van Heuven et al.*, 2011]. The calculated $f$CO$_2$ is then corrected for changes in atmospheric CO$_2$ between the cruises using the global atmospheric annual mean CO$_2$. The TCO$_2$ is then calculated using the TA and $f$CO$_2$ values, and the surface anthropogenic CO$_2$ is derived from the difference in TCO$_2$ between cruises.
When at least 2 of the carbon parameters are known, it is possible to calculate the remaining unknown parameter(s) using the CO$_2$ acid dissociation constants [Millero, 2007, and references therein]. The change in pH due to anthropogenic forcing is calculated using the CO2SYS program [van Heuven et al., 2011], with the carbonate dissociation constants of Millero et al. [2006]. The pH is calculated, at 25°C, using inputs of TCO$_2$, TA, salinity, silica, and phosphate. Where the nutrients are used to remove the minor effect they have on the TA. The anthropogenic CO$_2$ is then subtracted from the TCO$_2$, and the pH is recalculated providing an estimate of the pH without anthropogenic influences. Anthropogenic acidification is then assumed to be equal to the difference in the calculated pH values.

5.3 Results

The increase in anthropogenic CO$_2$ on P06 (2003 - 2009/10) is within $\sim 2 - 3 \mu$mol kg$^{-1}$ of the eMLR detection limit, and is restricted to the upper 400m. This low storage is consistent with the anticipated average annual increase in anthropogenic CO$_2$. Due to the minor increase in measurable anthropogenic CO$_2$ between these sections, further analysis was not carried out and the results are not presented. Slightly lower increases are evident in the upper 200m of P06 (1992-2010) between 120 and 90°W. The largest increase on P18 occurs between 15 and 40°S, the region where the subtropical gyre is found (Figure 5.5).

The maximum increase in anthropogenic CO$_2$ on P06 (1992 - 2003) and P06 (1992 - 2010) occurs west of 170°W in the upper 550m (Figures 5.3 and 5.4). On all lines, the deepest infiltration of anthropogenic CO$_2$ occurs at the maximum penetration ($\sim 1000$m) of Antarctic Intermediate Water (AAIW). On P18, equatorial upwelling, north of 5°S, suppresses the storage of anthropogenic CO$_2$ below 300m, and the shoaling of anthropogenic CO$_2$ on the eastern boundary of P06 is consistent with coastal upwelling. These trends are consistent with isopycnal surfaces. Table 5.2 gives an overview of the total and average annual anthropogenic CO$_2$ storage rates for the mode/central water masses and intermediate water masses.

The P06 and P18 lines cross at 32°S and 110°W, and the anthropogenic CO$_2$ profiles can be directly compared at this point. Figure 5.6 shows the P18 and P06 crossover profile for the
Figure 5.3: Increase in anthropogenic CO$_2$ ($\mu$mol kg$^{-1}$) between CLIVAR (2010) and WOCE (1992) P06. A greater increase in the anthropogenic CO$_2$ occurs in the western South Pacific due to the formation of subtropical mode water and upwelling in the western South Pacific, and upwelling repressing the anthropogenic signal in the eastern South Pacific.

Figure 5.4: Increase in anthropogenic CO$_2$ ($\mu$mol kg$^{-1}$) between BEAGLE (2003) and WOCE (1992) P06. The overall structure of increased anthropogenic CO$_2$ inventory is similar to CLIVAR-WOCE P06, but the overall increase is of a lower magnitude.
**Figure 5.5:** Increase in anthropogenic CO₂ (μmol kg⁻¹) between CLIVAR (2008) and WOCE (1994) P18. The formation of intermediate water and subtropical underwater in the South Pacific leads to a greater increase in anthropogenic CO₂ than in the northern subtropics, where upwelling also acts to suppress the storage of anthropogenic CO₂.

**Figure 5.6:** Profiles of the annual average increase in anthropogenic CO₂ (μmol kg⁻¹ yr⁻¹) at the crossover point between P06 and P18.
average annual increase in anthropogenic CO$_2$. The intrusion of anthropogenic CO$_2$ has led to an overall decrease in the pH in the surface and intermediate water on P06 and P18 (Figures 5.7 & 5.8). The annual average increases are plotted so the data is normalized to a consistent time scale and direct comparisons can be made. The discrepancies in the profiles are within the estimated standard error of the calculations.

For the upper 250m the annual average pH change is -0.0018 yr$^{-1}$ on P06 and -0.0014 on P18. This change in pH is directly calculated using the TCO$_2$ and anthropogenic CO$_2$ concentrations, and therefore has been corrected for any natural variations in physical and biological factors that would affect the pH. The decrease in pH is thus directly attributed to increases in anthropogenic CO$_2$. The maximum penetration of the calculated decrease in pH coincides with the maximum penetration of measurable increases in anthropogenic CO$_2$ in AAIW, and the maximum changes in pH correspond to the greatest increases of anthropogenic CO$_2$. As the pH change is calculated using the anthropogenic CO$_2$ signal, it is expected that the maximum changes coincide. Attempts are made to verify that the calculated change in pH reflects the differences in measured pH, which with the exception of WOCE P06 was directly determined on each cruise. However, it is difficult to derive the pH change, from anthropogenic forcing, through direct comparison of the measured data as the natural background variability is similar to the calculated pH change.

Table 5.2: Total (μmol kg$^{-1}$) and annual mean uptakes (μmol kg$^{-1}$ yr$^{-1}$) of anthropogenic CO$_2$ for the central and mode and intermediate water masses.

<table>
<thead>
<tr>
<th></th>
<th>Mode and Central Water</th>
<th>Intermediate Water</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Total Uptake</td>
<td>Annual Mean Uptake</td>
</tr>
<tr>
<td>P06 (1992-2010)</td>
<td>16.9 ± 3.2</td>
<td>0.94 ± 0.2</td>
</tr>
<tr>
<td>P06 (1992-2003)</td>
<td>10.2 ± 2.6</td>
<td>0.93 ± 0.2</td>
</tr>
<tr>
<td>P18 (1994-2008)</td>
<td>12.4 ± 4.1</td>
<td>0.89 ± 0.4</td>
</tr>
</tbody>
</table>
5.4 Discussion

Murata et al. [2007] presented anthropogenic CO$_2$ increases on P06, from 1994 to 2003, using the isopycnal technique [Peng et al., 1998]. Here we present a new evaluation of the 1992-2010 anthropogenic CO$_2$ and a comparison of the 1992-2003 anthropogenic CO$_2$ using the eMLR technique. The methods of this study differ from those of Murata et al. [2007] in both the calculation technique and the region over which we apply our calculation. Murata et al. [2007] applied the isopycnal calculation over the entire water column, whereas the eMLR is only applied over the region below the seasonal mixed layer and the mixed layer anthropogenic CO$_2$ is derived from atmospheric pCO$_2$. Due to large seasonal TCO$_2$ variations in the mixed layer, calculations of anthropogenic CO$_2$ in the mixed layer using the isopycnal technique are likely influenced by seasonal processes [Murata et al., 2007], where as the method applied here should not be as highly influenced by the seasonality of the mixed layer. Due to the discrepancies in the treatment of the mixed layer, a direct comparison of the column inventories is a poor evaluation of the consistency between the studies. Consistency is instead evaluated

![Figure 5.7: Average annual decrease in anthropogenic pH between CLIVAR (2010) and WOCE (1992) P06. The decrease in pH was only calculated and plotted over regions with significant (> 5 μmol kg$^{-1}$) increase in anthropogenic CO$_2$. Units are pH-units yr$^{-1}$.](image-url)
Figure 5.8: Average annual decrease in anthropogenic pH between CLIVAR (2008) and WOCE (1994) P18. The decrease in pH was only calculated and plotted over regions with significant (> 5 $\mu$mol kg$^{-1}$) increase in anthropogenic CO$_2$. Units are pH-units yr$^{-1}$.

by comparing the average annual anthropogenic CO$_2$ increase in the mode and central water masses (MW) and intermediate (IW) water masses between the studies. Between the studies there are significant discrepancies in the location of the anthropogenic CO$_2$ storage, but when the concentrations of anthropogenic CO$_2$ in the mode and intermediate water masses are averaged over the length of the P06 line and compared they are in good agreement (Table 5.3). Murata et al. [2007] observe higher concentrations of anthropogenic CO$_2$ in the MW east of 160°W, where as this study finds higher concentrations of MW anthropogenic CO$_2$ west of 160°W. The high concentrations of anthropogenic CO$_2$ observed by [Murata et al., 2007] west of 160°W are greater than the anticipated increases based on changes in atmospheric pCO$_2$ and are compensated by a decrease in AOU from 1992 to 2003. When the data are corrected for observed changes in AOU the observed increases in anthropogenic CO$_2$ are more consistent with the anticipated increase calculated from the increase in atmospheric CO$_2$ [Murata et al., 2007] and our results.
Table 5.3: Comparison of the mean anthropogenic CO$_2$ uptake ($\mu$mol kg$^{-1}$) surface and intermediate mode water masses on P06 (1992-2003).

<table>
<thead>
<tr>
<th></th>
<th>Mode and Central Water</th>
<th>Intermediate Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Murata et al. [2007]</td>
<td>10.3 ± 3.1</td>
<td>4.1 ± 2.0</td>
</tr>
<tr>
<td>This Study</td>
<td>10.2 ± 2.6</td>
<td>6.3 ± 1.9</td>
</tr>
</tbody>
</table>

There are no previous published studies of decadal changes on the P18 line, but Sabine et al. [2008] have conducted a decadal study on the P16 line (150°W). The structure and magnitude of the annual change in the anthropogenic CO$_2$ column inventory for the southern region of P16 is similar to that of P18. The maximum increase in anthropogenic CO$_2$ is found within the subtropical gyre on each of the lines and the concentrations of anthropogenic CO$_2$ decrease in the equatorial region and south of approximately 55°S. Spatial differences in the storage of anthropogenic CO$_2$ on P18 and P16 [Sabine et al., 2008] are due to differences in equatorial upwelling and variability in the locations of convergence zones.

A comparison of annual average anthropogenic CO$_2$ uptake rates for the South Pacific from this and other studies is shown in Table 5.4. There is a discrepancy in the average inventories for meridional cruises extending south of 50°S (P16 of Sabine et al. [2008]; P18 of this study) and cruises occurring north of 50°S (P14 & P15 of Peng et al. [2003]; P06 of Murata et al. [2007] P06 of this study). The low inventories of anthropogenic CO$_2$ poleward of 55°S on P16 and P18 appear to be diluting the average annual uptakes from $\sim$ 0.9 mol m$^{-2}$ yr$^{-1}$ to $\sim$ 0.4 mol m$^{-2}$ yr$^{-1}$. However, calculations indicate the low anthropogenic CO$_2$ inventories south of 50°S are not small enough to decrease the average uptake by the observed amount. The remaining difference in the uptake rates is instead attributed to the formation of mode water in the western South Pacific. Murata et al. [2007] noted higher anthropogenic CO$_2$ in the thermocline of the eastern South Pacific basin, and attribute it to differences in Sub-Antarctic Mode Water (SAMW). A SAMW salinity maximum occurs west of 160°W, and a salinity minimum occurs off the southern tip of South America [Piola and Georgi,
Table 5.4: Comparison of the annual average anthropogenic CO$_2$ uptake rates in the South Pacific.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>Nominal Track</th>
<th>Uptake Rate (mol m$^{-2}$ yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Murata et al.</em> [2007]</td>
<td>Isopycnal</td>
<td>32°S</td>
<td>1.0 ± 0.4</td>
</tr>
<tr>
<td><em>Peng et al.</em> [2003]</td>
<td>Isopycnal</td>
<td>170°E and 170°W</td>
<td>0.94 ± 0.4</td>
</tr>
<tr>
<td><em>Peng et al.</em> [2003]</td>
<td>MLR</td>
<td>170°E and 170°W</td>
<td>0.90 ± 0.3</td>
</tr>
<tr>
<td><em>Sabine et al.</em> [2008]</td>
<td>eMLR$^\dagger$</td>
<td>150°W</td>
<td>0.41</td>
</tr>
<tr>
<td>This Study</td>
<td>eMLR</td>
<td>110°W</td>
<td>0.46 ± 0.2</td>
</tr>
<tr>
<td>This Study</td>
<td>eMLR</td>
<td>32°S</td>
<td>0.72 ± 0.2</td>
</tr>
<tr>
<td>This Study</td>
<td>eMLR</td>
<td>32°S: East of 170°W</td>
<td>0.87 ± 0.1</td>
</tr>
<tr>
<td>This Study</td>
<td>eMLR</td>
<td>32°S: West of 170°W</td>
<td>0.66 ± 0.1</td>
</tr>
<tr>
<td>This Study</td>
<td>TTD</td>
<td>32°S</td>
<td>0.79 ± 0.2</td>
</tr>
<tr>
<td>This Study</td>
<td>TTD</td>
<td>32°S: East of 170°W</td>
<td>0.93 ± 0.2</td>
</tr>
<tr>
<td>This Study</td>
<td>TTD</td>
<td>32°S: West of 170°W</td>
<td>0.72 ± 0.1</td>
</tr>
</tbody>
</table>

$^\dagger$ *Sabine et al.* [2008] used the eMLR method to fit both TCO$_2$ and AOU. The eMLR$_{TCO_2}$ was corrected for changes in AOU using Redfield ratios to calculate a change in TCO$_2$ from the eMLR$_{AOU}$. The results from this approach are qualitatively similar to results from an approach using AOU as a regressor.
1982]. However, our results indicate there is no significant difference (greater than 5 μmol kg-1) in SAMW uptake of anthropogenic CO₂ for either the eastern or western region of the South Pacific, and the higher inventory of anthropogenic CO₂ in the western basin is due to the subduction of subtropical mode water (STMW) (Figure 5.9). STMW shows a greater increase in anthropogenic CO₂ because the Revelle factor of STMW is lower than that of the SAMW. The Revelle factor is a buffer factor related to the change in TCO₂ for a given change in pCO₂ and is inversely related to the anthropogenic CO₂ uptake capacity of a water mass [Sabine et al., 2004]. The large increase in anthropogenic CO₂ in the subtropical gyre, evident in P06 (1992-2010) and P18 (1994-2008), is due to subduction within the gyre leading to the formation of subtropical underwater (STUW).

We attempt to resolve the discrepancies between our results and those of Murata et al. [2007] by using the transit time distribution (TTD) method for anthropogenic CO₂. A TTD can be used to calculate the concentration of a passive tracer using the time-dependent surface history of the tracer, and has been used to give estimates of oceanic anthropogenic CO₂ that are largely independent of measured carbon [Hall et al., 2002; Waugh et al., 2004, 2006; Tanhua et al., 2008; Khatiwala et al., 2009]. See Appendix A.3 for additional details. The TTD is determined on CLIVAR P06, using the methods of Waugh et al. [2004], from in-situ measurements of CFC-12. The atmospheric history of CFC-12 [Bullister, 2011], a constant surface saturation [Waugh et al., 2004] of 95% for CFC-12 [Hartin et al., 2011], and the measured salinity and temperature are used to create the time-dependent CFC-12 surface history. In order to apply the calculated TTD to determine the total anthropogenic CO₂ it is necessary to derive the surface history of anthropogenic CO₂. The surface history of anthropogenic CO₂ is determined using similar methods to those outlined for the determination of anthropogenic CO₂ in the mixed layer of the eMLR, see section 5.2. The overall total anthropogenic CO₂ calculated from the TTD for BEAGLE and WOCE P06 show higher inventories in the western South Pacific, see Figures A.3.5 - A.3.6 in Appendix A.3.4. As the TTD determines the total anthropogenic CO₂ and not the temporal increase between cruises, the change in
Figure 5.9: Increase of anthropogenic CO$_2$ (µmol kg$^{-1}$) between CLIVAR (2010) andWOCE (1992) on P06. The formation of subtropical mode water in the western South Pacific leads to a greater storage of anthropogenic CO$_2$ in the western region of the basin.
anthropogenic CO₂ between BEAGLE and WOCE P06 is calculated by subtracting the total inventoried derived from the TTD method, see Figure A.3.7 in Appendix A.3.4. The average annual uptake calculated from the difference between the BEAGLE and WOCE TTD anthropogenic CO₂ inventories is $\sim 0.79 \text{ mol m}^{-2}\text{yr}^{-1}$. This value is consistent with the results of both this study and Murata et al. [2007].

The TTD results indicate the total anthropogenic CO₂ inventories in western South Pacific are larger (Figures A.3.5 and A.3.6), but anthropogenic CO₂ in the eastern South Pacific is increasing at a faster rate than the western South Pacific (Figure A.3.7). These results are not consistent with the isopycnal method [Murata et al., 2007], see Table 5.4, but are consistent with the results from the eMLR method (section 5.3). The average uptakes calculated with the eMLR for the western and eastern regions of the South Pacific are $\sim 0.72 \text{ mol m}^{-2}\text{yr}^{-1}$ and $\sim 0.93 \text{ mol m}^{-2}\text{yr}^{-1}$, respectively. The observed trend of higher increases in the eastern basin continues with the CLIVAR data, suggesting regions with higher initial concentrations of anthropogenic CO₂ are storing less anthropogenic CO₂ than regions with lower initial inventories, see Figures A.3.8 and A.3.9 in Appendix A.3.4.

The anthropogenic pH change on the P06 and P18 lines shows pH decreasing over all regions, with the smallest increases south of 55°S and in the coastal and equatorial upwelling regions. The average annual change on P06 (1992-2003 & 1992-2010) and P18 (1994-2008) is $-0.0016 \pm 0.0005 \text{ yr}^{-1}$, and is consistent with the expected rate of change of $-0.0018 \text{ yr}^{-1}$ found when calculating the change in pH as a function of increase in atmospheric pCO₂ for this period (1992-2010) using the CO2SYS program with a constant TA. This value is also consistent with the decreased pH reported in the mixed layer of the North Pacific [Byrne et al., 2010], and from time series annual averages in the surface waters off of Hawaii of $(-0.0019 \pm 0.0003 \text{ yr}^{-1})$ and the subtropical North Atlantic (-0.0015 yr⁻¹) [González-Dávila et al., 2007]. As it appears acidification rates are closely coupled with atmospheric pCO₂ growth rates over the Pacific, it is probable that acidification will become an even greater problem as atmospheric pCO₂ growth rates continue to rise.
The majority of our present understanding of the effects of ocean acidification come from laboratory and short-term field studies and it is difficult to evaluate all the possible impacts on decadal time scales. However, it is evident that carbonate mineral saturation states are decreasing in response to acidification and biogeochemical cycles are likely impacted \cite{Doney2009}. Many calcifying organisms, such as coral, are likely to be adversely affected by decreases in carbonate saturation \cite{Gattuso1998, Kleypas1999, Langdon2000, LangdonAtkinson2005}, and calcification in the Great Barrier Reef of Australia may have already been negatively impacted by ocean acidification \cite{Wei2009}. The speciation of trace metals and inorganic nutrients will also be affected \cite{Millero2009, Doney2009}. \cite{Pascal2010} have found increases in free Cu concentrations and antagonistic toxicity in coastal copepods when the pH of seawater is decreased. Increased free Cu could have dramatic impacts on Pacific fisheries by increasing toxicity in both low and high trophic level species. Even though many of the potential effects of ocean acidification are not well constrained, these results demonstrate the pH of surface waters in the South Pacific is declining and organisms within these systems are likely to be impacted.

5.5 Conclusions

The results presented are estimates of the minimum decadal changes in anthropogenic CO$_2$ and pH on P06 and P18 in the South Pacific. There are significant regional differences in the uptake of anthropogenic CO$_2$ related to water mass subduction and upwelling. Our results indicate the regions of STMW and STUW formation represent the greatest increase in anthropogenic CO$_2$, but SAMW and AAIW also show significant decadal increases. It appears the average annual increase in anthropogenic CO$_2$ in the western South Pacific is greater than in the eastern region due in part to the subduction of STMW. It is also evident the pH of surface waters are decreasing at rates equivalent to the increases in atmospheric CO$_2$, but many of the potential impacts this will have on marine organisms are not well constrained on decadal time scales. These results indicate the importance of the repeat hydrography programs in the understanding of the decadal and spatial variability in the anthropogenic carbon system.
5.6 Chapter Acknowledgements

The authors wish to acknowledge the support of the National Science Foundation Chemical Oceanography section and the National Oceanic and Atmospheric Administration Office of Climate Observations for supporting our CO$_2$ studies. We would also like to thank Samar Khatiwala for making the code available for calculation of the TTD and providing assistance with the calculations.
Chapter 6.

Closing Discussion

6.1 Summary of Results

The preceding chapters discuss the theoretical and analytical procedures used to define and measure pH in seawater. Seawater pH is of significant interest to researchers studying the effects of Ocean Acidification on marine environments. Ocean Acidification is a direct response to the increase in anthropogenically derived CO$_2$ in the global oceans; current estimates indicate the acidification has led to a decrease in the surface ocean of 0.1 units of pH since the Industrial Revolution. Despite the current research interest in the pH of marine environments, a universally accepted definition of pH does not exist for ionic media and research is significantly limited by a lack of comparability among experimental measurements. This is at least partially due to the use of different or undocumented pH scales [Orr et al., 2009].

Despite the recognized need for a single operational definition of pH, the selection of such a scale is difficult to universally apply [e.g. Bates, 1948, 1952] and has taken over 50 years to be realized for dilute solutions [Buck et al., 2002; Baucke, 2002]. The difficulty in defining a single scale is largely because the effective concentration of the hydrogen ion cannot be measured directly, and a non-thermodynamic formula is used to conventionally define pH from a thermodynamically measurable quantity. However, the convention used to define the activity pH scale for dilute media is only applicable to solutions with an ionic strength of less than 0.1 mol kg$^{-1}$ (salinity < 5) and a single scale is still not realized for seawater. A particular goal of this dissertation is to contribute towards the advancement of a single pH scale that is universally applicable for seawater. Overall, the work presented in this dissertation contributes to an increased understanding of the theoretical and analytical aspects of the measurement of pH in seawater.
6.1.1 Chapter 2

In Chapter 2, a semi-autonomous system for the spectrophotometric detection of pH and TA is described and tested. The rationale for this study is to develop a more efficient method for the simultaneous determination of TA and pH from discrete samples. Combining these measurements results in the reduction in measurement time, personnel needed at sea, and equipment volume. The outlined system was based on the concept of sequential injection analysis [Ruzicka and Marshall, 1990]. Initial laboratory tests indicated the reproducibility of the TA measurements was comparable to previous automated methods for the analysis of spectrophotometric TA and approached that of manual spectrophotometric TA measurements. Despite field trials of the instrument being unable to achieve the same reproducibility as land-based spectrophotometric measurements, it is expected that an updated version of the system will maintain a similar reproducibility in the TA measurements at sea. Such an instrument will be useful for studies focused on quantifying changes in calcification under different acidification scenarios, as pH and TA provide an accurate evaluation of the carbon dioxide system in seawater and the measurements are directly correlated to the processes controlling calcification.

6.1.2 Chapter 3

The rational for Chapter 3 is to re-evaluate the stoichiometric acid association constant for the formation of HSO$_4^-$ using the electrochemical measurements of HCl in artificial seawater and to develop equations for the standard potential and buffer pH on the free proton scale. The re-evaluated values can be used for studies pertaining to the impacts of Ocean Acidification has on chemical kinetics and biological processes in natural waters. As the free concentration of proton is relevant to kinetic processes and because it is most appropriate for biological systems [Riebesell et al., 2010], it is suggested that this scale should be universally adapted for seawater pH measurements.

The measured potentials in 0.01 mol kg$^{-1}$ HCl [Bates and Bower, 1954] and artificial seawater [Khoo et al., 1977; Dickson, 1990; Campbell et al., 1993] are within ±0.04mV and
±0.2 mV of the modeled values determined in this study, respectively. In solutions containing sulfate, a systematic offset of 0.2 mV between the measured and modeled data is observed and corresponds to an error of about 0.003 in $\gamma_{\text{HCl}}^\pm$. Previous applications of the Pitzer model to natural waters with sulfate find a slightly larger (0.24 – 0.3 mV), but similar offset. The re-determined values of $E_m^*$ and $K_{\text{HSO}_4}^*$ are in good agreement with previous estimates when the solution temperature is above 25°C, but not for solutions where the temperature is below 25°C and the salinity is greater than 35. The discrepancies with the previous estimates are shown to be due to inaccurate evaluations of thermodynamic acid dissociation constants or limitations of the assumptions made in the estimation of the mean HCl activity coefficients of the solution. Due to the agreement between the measured and modeled values of $\gamma_{\text{HCl}}^\pm$ and the use of a critically evaluated formalism of $K_{\text{HSO}_4}^*$ used in the model, the values of $E_m^*$ and $K_{\text{HSO}_4}^*$ in this study are presently believed to be the most accurate available. Additional measurements are necessary to assess the accuracy of seawater pH buffers and to resolve the discrepancies between the measured and modeled activity coefficient data in seawater solutions containing sulfate.

6.1.3 Chapter 4

In Chapter 4, comparisons of the impure colorimetric pH indicators meta-cresol purple and thymol blue from 3 different manufactures are made over a salinity range of 30 – 40 units and pH$_T$ range of $\sim$ 7.85 – 8.2 units. Analysis of the thymol blue indicators used in the study suggest the overall error in the pH$_T$ measured with indicators sourced from the different manufactures is ±0.003 units of pH. There are no observable trends in the measured thymol blue pH$_T$ as a function of salinity or pH. These results are in agreement with a previous comparison of thymol blue from S $= 30 – 40$ at a single pH [Mosley et al., 2004] that finds the pK$_a^*$ values of thymol blue are in agreement to ±0.001. The spectrophotometric pH measured using the un-purified forms of meta-cresol purple are shown to have a relative error of as much as 0.05 units of pH at pH$_T$ $\approx$ 8.2 units. Unlike the results for thymol blue, the relative error in the pH measured with meta-cresol purple has a strong dependence on the solution pH and
a smaller dependence on the solution salinity. Due to impurities present in meta-cresol purple, un-purified thymol blue should be used in place of un-purified meta-cresol purple, when possible.

**6.1.4 Chapter 5**

In Chapter 5, the extended multiple linear regression (eMLR) technique is used to quantify decadal changes in anthropogenic CO$_2$ on the WHP lines P18 and P06. The decrease in pH is also calculated from the changes in anthropogenic CO$_2$. Results indicate that on average anthropogenic CO$_2$ surface ocean concentrations are increasing by $\sim 1\mu$mol kg$^{-1}$ yr$^{-1}$, and pH is decreasing by 0.0018 units of pH yr$^{-1}$. These results are in good agreement with other studies in the Pacific [Byrne et al., 2010; Sabine et al., 2008]. However, the results do not agree with a previous determination of the average annual uptake of anthropogenic CO$_2$ between 1992 and 2003 on P06 [Murata et al., 2007]. The 1992-2003 findings determined using the isopycnal method [Peng et al., 1998] report higher anthropogenic CO$_2$ storage in the eastern South Pacific. However, the eMLR findings (1992-2009/10) indicate a greater uptake of anthropogenic CO$_2$ in the western South Pacific. The results of the eMLR are supported by independent estimates using the transient time distribution (TTD) [Hall et al., 2002; Haine and Hall, 2002; Waugh et al., 2004; Hall et al., 2004], and are more consistent with the formation of subtropical mode water. As subtropical mode water is expected to contain higher concentrations of anthropogenic CO$_2$ than either subantarctic mode water or Antarctic intermediate water due to a lower Revelle factor in the higher latitude water masses [Sabine et al., 2004], it is thought this study is a better reflection of the actual inventory of anthropogenic CO$_2$ in the South Pacific.

**6.2 Suggestions and Thoughts for Future Work**

Overall, the work conducted in this dissertation demonstrates pH measurements in seawater can be made with a reproducibility that is sufficient to resolve the rates of Ocean Acidification on decadal time scales. However, additional work on primary measurements—Harned cell
measurements using the standard hydrogen and silver, silver chloride electrodes—of pH in seawater media is required to ensure both accuracy and comparability of pH measurements in seawater.

6.2.1 Establishment of Standard Traceability for Seawater pH

Significant advancements in the inter-comparability of seawater pH measurements can be provided if a standardized reference program for seawater pH buffers is established. The final product of such a program would significantly contribute to the development of a standard comparability for seawater pH through the establishment of an accurate environmental record of ocean pH and a wide-spread comparability of experimental results dependent on accurate evaluations of seawater pH. Implementation of a single, traceable marine pH scale would significantly advance understanding of the fundamental effects Ocean Acidification could have on biogeochemical processes in the ocean.

6.2.2 Standard Traceability for Estuarine pH

Measurements of the potentials of buffer material in artificial seawater characterized by salinities between 5 and 20 should also be evaluated. Such measurements would enable the pH of estuarine regions to be characterized. There are no current buffers for natural waters with salinities between 5 and 20 that have been calibrated with the standard hydrogen electrode. As it was recently demonstrated that changes in salinity of 10 units can contribute an error in the pH of ∼ 0.03 units [Easley and Byrne, 2012], such measurements are essential for studies related to Ocean Acidification in coastal regions.

6.2.3 Advancement of Ionic Interaction Models

In Chapter 3, the need for accurate evaluations of both measured thermodynamic and modeled non-thermodynamic single ion activity coefficients is demonstrated. A re-evaluation of the measurements [Rard and Clegg, 1999] used to derive the model coefficients required to determine activity coefficients in seawater, leads to a decrease in the offset between the measured and modeled mean HCl activity coefficient in seawater solutions with sulfate. However,
the offset between the measured and modeled values is not completely resolved and results in a bias of approximately 0.003 pH units in the standard potential on the free proton concentration scale. This indicates the $\text{SO}_4$ and $\text{HSO}_4$ coefficients should be re-evaluated from the measured data, or that the measurements used to derived the coefficients are in error and new measurements are required.
A.1: Chapter 3

A.1.1 Equations

According to Pitzer [1991] the activity coefficient of cation $M$ can be determined from an expansion of the molal derivative of the Gibbs free energy according to the virial equation of state for a gas. The resulting virial expansion gives the equation

$$
\ln(\gamma_M) = Z_M^2 (f^\gamma + \sum_c \sum_a m_c m_a B'_{ca} + \sum_c \sum_{c'} m_c m_{c'} \phi'_{cc'} + \sum_a \sum_{a'} m_a m_{a'} \phi'_{aa'}) \\
+ \sum_a m_a (2B_{Ma} + EC_{Ma}) + \sum_c m_c (2\phi_{Mc} + \sum_a m_a \psi_{Mc_a})
$$

(A.1.1)

In equation (A.1.1), $Z_M$ is the charge of species $M$ and $E$ is the equivalent molality ($E = \sum_i |Z_i|m_i$). The remaining terms in equation (A.1.1) are given below.

$$
f^\gamma = -A_\phi \left\{ \frac{I^{1/2}}{1 + 1.2 I^{1/2}} + \frac{2}{1.2} \ln(1 + 1.2 I^{1/2}) \right\}
$$

(A.1.2)

where $A_\phi$ is determined from [Möller, 1988]

$$
A_\phi = 3.3690153 \times 10^{-1} - 6.3210043 \times 10^{-4} \times T + 9.14252359 / T \\
- 1.35143986 \times 10^{-2} \times \ln(T) + 2.26089488 \times 10^{-3} / (T - 263)
$$

(A.1.3)

$$
+ 1.921185973 \times 10^{-6} \times T^2 + 4.52586464 \times 10^1 / (680 - T)
$$

For the original derivation of the Pitzer equation

$$
B_{Ma} = \beta_{Ma}^{(0)} + \beta_{Ma}^{(1)} g(\alpha_{1Ma} I^{1/2}) \\
+ \beta_{Ma}^{(2)} g(\alpha_{2Ma} I^{1/2})
$$

(A.1.4)
\[ g(x) = \frac{2[1 - (1 + x)\exp(-x)]}{x^2} \]  

(A.1.5)

and the derivative of \( B_{Ma} \) is given by

\[ B'_{Ma} = \beta_{Ma}^{(1)} g'(\alpha_{1_{Ma}} I^{1/2}) + \beta_{Ma}^{(2)} g'(\alpha_{2_{Ma}} I^{1/2}) \]  

(A.1.6)

\[ g'(x) = -2[1 - (1 + x + x^2/2) \times \exp(-x)] \]  

(A.1.7)

In general, \( \alpha_{1_{Ma}} = 2 \) for 1-1 & 2-1 electrolytes, \( \alpha_{1_{Ma}} = 1.4 \) and \( \alpha_{2_{Ma}} = 12 \) for 2-2 electrolytes, but special cases exist where \( \alpha \) deviates from these values.

\[ C_{Ma} = \frac{C^{\phi}_{Ma}}{2|Z_M Z_a|^{1/2}} \]  

(A.1.8)

For the virial interaction parameters determined with additional higher order ionic strength terms \( C_{Ma} \) has been expanded, much like the \( B_{Ma} \) terms of the original Pitzer equation. Equations for \( C^T \) - type interactions with higher order terms used in this model are given by [Clegg et al., 1994]

\[ C^T_{Ma} = C^{(0)}_{Ma} + 4C^{(1)}_{Ma} h(\omega_{Ma} I^{1/2}) \]  

(A.1.9)

\[ h(x) = \frac{\{6 - [6 + x(6 + 3x + x^2)] \exp(-x)\}}{x^4} \]  

(A.1.10)
With the expansion of $C^T$ as a function of ionic strength, the $\sum_c \sum_a m_c m_a B'_{Ma}$ term in equation (A.1.1) becomes $\sum_c \sum_a m_c m_a (B'_{Ma} + E C^{T \prime}_{Ma})$ where

$$C^{T \prime}_{Ma} = 4C^{(1)}_{Ma} h'(\omega_{Ma} I^{1/2})$$  \hfill (A.1.11)

$$h'(x) = \exp(-x)/2 - 2h(x)$$  \hfill (A.1.12)

The mixing terms in equation (A.1.1) are defined for ‘like-like’ charge interactions

$$\phi_{Mc} = \theta_{Mc} + \theta^E_{Mc}$$  \hfill (A.1.13)

where the first derivative of $\phi_{Mc}$ is given by

$$\phi'_{Mc} = \theta^E_{Mc}$$  \hfill (A.1.14)

Equations for the electrostatic mixing terms ($\theta^E_{Mc}$ & $\theta^E_{Mc}$) are derived from cluster integrals, and we find the derivations impractical to reproduce here. The reader is referred to Pitzer [1991, Chapter 3, Appendix B] and/or Clegg et al. [1994, Appendix I] for the full derivations of these terms. Our model uses the derivation of Pitzer [1991].

### A.1.2 Coefficients

Tables reporting the equations, or values, for calculating the $B$, $C$, $C^T$, $\phi$ and $\psi$ terms used.
Table A.1.1: Pitzer equation parameters for Na salts.

<table>
<thead>
<tr>
<th>CF</th>
<th>$P$</th>
<th>$P_1$</th>
<th>$P_2$</th>
<th>$P_3$</th>
<th>$P_4$</th>
<th>$P_5$</th>
<th>$P_6$</th>
<th>$P_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Möller [1988] &amp; Greenberg and Möller [1989]</td>
<td>$\beta(0)$</td>
<td>1.43783204×10$^1$</td>
<td>5.60767406×10$^{-3}$</td>
<td>-4.22185236×10$^2$</td>
<td>-2.51226677</td>
<td>-2.6178135×10$^6$</td>
<td>4.43854508</td>
<td>-1.70502337</td>
</tr>
<tr>
<td></td>
<td>$\beta(1)$</td>
<td>-4.83060685×10$^{-1}$</td>
<td>1.40677479×10$^3$</td>
<td>1.19311989×10$^2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.23433299</td>
</tr>
<tr>
<td></td>
<td>$C$</td>
<td>-1.05188714×10$^{-1}$</td>
<td>-1.80529413×10$^{-5}$</td>
<td>8.61185543</td>
<td>1.2488095×10$^{-2}$</td>
<td>3.41172108×10$^{-8}$</td>
<td>6.3040995×10$^{-3}$</td>
<td>2.93922611×10$^{-1}$</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>$P$</td>
<td>$P_1$</td>
<td>$P_2$</td>
<td>$P_3$</td>
<td>$P_4$</td>
<td>$P_5$</td>
<td>$P_6$</td>
<td>$P_7$</td>
</tr>
<tr>
<td>Holmes and Mesmer [1986b]</td>
<td>$\rho(0)$</td>
<td>-1.727×10$^2$</td>
<td>1.7828×10$^3$</td>
<td>9.133×10$^{-6}$</td>
<td>-</td>
<td>-</td>
<td>-6.552</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\rho(1)$</td>
<td>7.534×10$^1$</td>
<td>5.61×10$^3$</td>
<td>-5.7513×10$^{-4}$</td>
<td>1.11068</td>
<td>-3.7882×10$^2$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$C$</td>
<td>1.1745×10$^{-2}$</td>
<td>-3.3038×10$^{-4}$</td>
<td>1.8579×10$^{-5}$</td>
<td>-3.92×10$^{-2}$</td>
<td>1.4213×10$^1$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HSO$_4$</td>
<td>$P$</td>
<td>$P_1$</td>
<td>$P_2$</td>
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* $P = p_1 + p_2 \times T + p_3 / (T + p_4 \times ln(T) + p_5 \times T^2 + p_6 / (680 - T) + p_7 / (T - 227)$

* $P = p_1 + p_2 \times (298.15 - 298.15^2 / T) + p_3 \times (T^2 + 298.15^2 / T - 3 \times 298.15^2 / T - 2 \times 298.15^2 + p_4 \times (T + 298.15^2 / T - 2 \times 298.15^2 + p_5 \times (ln(T / 298.15) + 298.15 / T - 1) + p_6 \times (1 / (T - 263)) + (263 \times T - 298.15)^2 / (T \times (298.15 - 263)^2)) + p_7 \times (1 / (680 - T) + (298.15^2 - 680 \times T) / (T \times (680 - 298.15)^2))$

* $P = p_1 + p_2 / T + p_3 \times ln(T) + p_4 \times T + p_5 \times T^2 + p_6 / (T - 227) + p_7 / (647 - T)$

* $a_{Na,SO_4} = 1.4$
Table A.1.2: Pitzer equation parameters for Mg salts.

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$P = p_1 - p_2 \times T + p_3 \times T^2$

$P = p_1 \times (T/2 + 298^2/2 \times T - 298) + p_2 \times (T^2/6 + 298^3/3 \times T - 298^2/2) + p_3 \times (T^3/12 + 298^4/4 \times T - 298^3/3) + p_4 \times (T^5/20 + 298^5/5 \times T - 298^4/4) + p_5 \times (298 - 298^2/T) + p_6$
Table A.1.3: Pitzer equation parameters for Ca salts.

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\(^a\) \( P = p_1 + p_2 \times T + p_3 / T + p_4 \times \ln(T) + p_5 / (T - 263) + p_6 \times T^2 + p_7 / (680 - T) \)

\(^b\) \( P = p_1 + p_2 \times (T - 298.15) \)
Table A.1.4: Pitzer equation parameters for K salts.

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$^a$ $P = p_1 + p_2 \times T + p_3 \times \ln(T) + p_4 \times T^2 + p_6 \times (T - 273)$

$^b$ $P = p_1 + p_2 \times (298.15 - 298.15^2 / T) + p_3 \times \ln(T) + p_4 \times (T + 298.15^2 / T - 2 \times 298.15) + p_5 \times (T - 298.15^2 / T - 298.15) + p_6 \times (T - 263)) + (263 \times T - 298.15)^2 / (T \times (298.15 - 263)^2))$

$^c$ $P = p_1 + p_2 \times (T - 298.15)$

$^* \varphi_{K,SO_{4}} = 1.4$
Table A.1.5: Pitzer equation parameters for H$^+$ interactions.

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$^a$ $P = p_1 + p_2 \times T + p_3 / T$

$^b$ $P = p_1 + (T-328.15) \times (p_2 / 1000 + (T-328.15) \times (p_3 / 2000 + (T-328.15) \times p_4 / 6000))$

$^c$ $a_{\text{HSO}_4} = 2 - 1842.843 \times (1 / T - 1 / 298.15)$
**Table A.1.6:** Pitzer equation parameters for MgOH$^+$ interactions.

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<tr>
<td></td>
<td>$\beta^{(1)}$</td>
<td>1.658</td>
</tr>
<tr>
<td></td>
<td>$C^\phi$</td>
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</tr>
</tbody>
</table>

$\text{Harvie et al. [1984]}$

**Table A.1.7:** Ion-ion ($\theta_{ij}$) interaction terms.

<table>
<thead>
<tr>
<th>i</th>
<th>j</th>
<th>$t / ^\circ \text{C}$</th>
<th>$p_1$</th>
<th>$p_2$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>Na</td>
<td>0 – 50</td>
<td>3.6×10$^{-2}$</td>
<td>-5.09×10$^{-4}$</td>
<td><em>Campbell et al. [1993]</em></td>
</tr>
<tr>
<td>Mg</td>
<td>0 – 50</td>
<td>5×10$^{-3}$</td>
<td>-2.275×10$^{-4}$</td>
<td><em>Roy et al. [1980]</em></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0 – 50</td>
<td>3.2×10$^{-2}$</td>
<td>3.275×10$^{-4}$</td>
<td><em>Roy et al. [1980]</em></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0 – 50</td>
<td>6.12×10$^{-2}$</td>
<td>3.275×10$^{-4}$</td>
<td><em>Campbell et al. [1993]</em></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>Mg</td>
<td>25</td>
<td>7×10$^{-2}$</td>
<td>–</td>
<td><em>Harvie et al. [1984]</em></td>
</tr>
<tr>
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<td>25</td>
<td>7×10$^{-2}$</td>
<td>–</td>
<td><em>Harvie et al. [1984]</em></td>
<td></td>
</tr>
<tr>
<td>K</td>
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<td>-1.2×10$^{-2}$</td>
<td>–</td>
<td><em>Harvie et al. [1984]</em></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>Ca</td>
<td>25</td>
<td>7×10$^{-3}$</td>
<td>–</td>
<td><em>Harvie et al. [1984]</em></td>
</tr>
<tr>
<td>K</td>
<td>25</td>
<td>0</td>
<td>–</td>
<td><em>Harvie et al. [1984]</em></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>K</td>
<td>25</td>
<td>3.2×10$^{-2}$</td>
<td>–</td>
<td><em>Harvie et al. [1984]</em></td>
</tr>
<tr>
<td>Cl</td>
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<td>25</td>
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<td>–</td>
<td><em>Harvie et al. [1984]</em></td>
</tr>
<tr>
<td>HSO$_4$</td>
<td>25</td>
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<td>–</td>
<td><em>Harvie et al. [1984]</em></td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>25</td>
<td>-5×10$^{-2}$</td>
<td>–</td>
<td><em>Harvie et al. [1984]</em></td>
<td></td>
</tr>
<tr>
<td>SO$_4$</td>
<td>HSO$_4$</td>
<td>25</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>OH</td>
<td>25</td>
<td>-1.3×10$^{-2}$</td>
<td>–</td>
<td><em>Harvie et al. [1984]</em></td>
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</tr>
</tbody>
</table>

$^a \theta_{ij} = p_1 + p_2 \times (T - 298.15)$
Table A.1.8: Triplet anion-anion-cation ($\phi_{ijk}$) interaction terms

<table>
<thead>
<tr>
<th>i</th>
<th>j</th>
<th>k</th>
<th>$t/°C$</th>
<th>$p_1$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
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<td>H</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Na</td>
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<tr>
<td>Mg</td>
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<td>Harvie et al. [1984]</td>
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<tr>
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<td>-1.8x10$^{-2}$</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>0</td>
<td>Harvie et al. [1984]</td>
</tr>
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<td>HSO$_4$</td>
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<td>1.3x10$^{-2}$</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
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<td>-6x10$^{-3}$</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
<td>Mg</td>
<td>25</td>
<td></td>
<td></td>
<td>0</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
<td>Ca</td>
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<td></td>
<td></td>
<td>0</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
<td>K</td>
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<td></td>
<td>0</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
<td>OH</td>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Na</td>
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<td>Harvie et al. [1984]</td>
</tr>
<tr>
<td>Mg</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</tr>
<tr>
<td>Ca</td>
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<td></td>
<td></td>
<td>0</td>
<td>Harvie et al. [1984]</td>
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<tr>
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<td>0</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>HSO$_4$</td>
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<td>–</td>
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<tr>
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<td>-7.8x10$^{-2}$</td>
<td>Rard and Clegg [1999]</td>
</tr>
<tr>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</tr>
<tr>
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<td></td>
<td>-6x10$^{-3}$</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
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<td>–</td>
<td>–</td>
<td>–</td>
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</tr>
<tr>
<td>K</td>
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<td></td>
<td></td>
<td>0</td>
<td>Harvie et al. [1984]</td>
</tr>
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Table A.1.9: Triplet cation-cation-anion ($\psi_{ijk}$) interaction terms.

<table>
<thead>
<tr>
<th>i</th>
<th>j</th>
<th>k</th>
<th>$t$ / °C</th>
<th>$p_1$</th>
<th>Ref.</th>
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<tr>
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<td>Harvie et al. [1984]</td>
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<td>Harvie et al. [1984]</td>
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<tr>
<td>K</td>
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<td>-1.1.10^{-2}</td>
<td>Harvie et al. [1984]</td>
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<td>1.97.10^{-1}</td>
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<td>Cl</td>
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<td>-1.5.10^{-2}</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
<td></td>
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<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>Cl</td>
<td>25</td>
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<td>-7.10^{-3}</td>
<td>Harvie et al. [1984]</td>
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<tr>
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<td>-5.5.10^{-2}</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
<td></td>
<td>HSO$_4$</td>
<td>25</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>Cl</td>
<td>25</td>
<td>25</td>
<td>-1.8.10^{-3}</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
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<td>25</td>
<td>-1.10^{-2}</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
<td></td>
<td>HSO$_4$</td>
<td>25</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mg</td>
<td>Ca</td>
<td>Cl</td>
<td>25</td>
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<td>Harvie et al. [1984]</td>
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<tr>
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<tr>
<td>K</td>
<td>Cl</td>
<td>25</td>
<td>25</td>
<td>-2.2.10^{-2}</td>
<td>Harvie et al. [1984]</td>
</tr>
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<td>25</td>
<td>-4.8.10^{-2}</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
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<td>25</td>
<td>-</td>
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</tr>
<tr>
<td>Ca</td>
<td>K</td>
<td>Cl</td>
<td>25</td>
<td>-2.5.10^{-2}</td>
<td>Harvie et al. [1984]</td>
</tr>
<tr>
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<td>25</td>
<td>-</td>
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<td></td>
<td>HSO$_4$</td>
<td>25</td>
<td>25</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>
A.2: Chapter 4

A.2.1 Determination of Mass from Apparent Mass in Air

Measurements of the gravitational mass of an object should be corrected for air buoyancy effects for the highest accuracy. This correction takes into account the differences in the air buoyancy effects between the material being weighed on an analytical balance to that of the built-in standard weights. Such corrections are essential for the production of buffer materials with accurate pH values.

Once corrected for the supporting buoyant force, the mass of the quantity being measured is related to the mass of the standard built-in weight by

\[ a = b \frac{1 - \rho_{\text{air}}/\rho_b}{1 - \rho_{\text{air}}/\rho_a}, \]  

(A.2.1)

where \( a \) is the gravitational mass of the quantity being measured, \( b \) is the mass of the standard, \( \rho_{\text{air}} \) is the air density at ambient atmospheric conditions, and \( \rho_i \) is the density of either \( a \) or \( b \) [Schoonover and Jones, 1981; Dickson et al., 2007]. When determining the true gravimetric mass, also referred to as the mass in a vacuum, equation (A.2.1) is more commonly given by [Dickson et al., 2007]

\[ m = w + w \rho_{\text{air}} \left( \frac{m}{w \rho_m} - \frac{1}{\rho_w} \right), \]  

(A.2.2)

where \( m \) is the true gravimetric mass, \( w \) is weight of the sample uncorrected for buoyancy effects, \( \rho_m \) is the density of the quantity being measured, and \( \rho_w \) is the density of the standard mass. The density of the standard weight is based on either brass standards, where \( \rho_b \) is adjusted to 8.4 g cm\(^{-3}\), or \( \rho_b \) is 8.0 g cm\(^{-3}\) for stainless steel standard weights. At sea level and normal room temperatures, the density of air (\( \rho_{\text{air}} \)) can be approximated as 0.0012 g cm\(^{-3}\) [Schoonover and Jones, 1981; Dickson et al., 2007]. When higher accuracy is required or the altitude is far removed
from sea level, $\rho_{\text{air}}$ can be determined from [Dickson et al., 2007]

$$\rho_{\text{air}} = \frac{3.4848(P - 0.0037960U \cdot e_s)}{T} \times 10^{-3}, \quad (A.2.3)$$

where $P$ is the air pressure (kPa), $U$ is the relative humidity, $T$ is absolute temperature, and $e_s$ is the saturation vapor pressure [Dickson et al., 2007]

$$e_s = 1.7526 \times 10^8 \cdot \exp\left(\frac{-5315.56}{T}\right). \quad (A.2.4)$$

Making the proper substitution at sea level and assuming $m \approx w$, equation (A.2.1) becomes

$$m = w + w \cdot 0.0012 \left(\frac{1}{\rho_m} - \frac{1}{8}\right), \quad (A.2.5)$$

where $w$ is weight of the substance in air, and $\rho_m$ is the density of the substance. The densities can be found in standard physical-chemical reference charts [e.g. Weast et al., 1989]; see Table A.2.1 for the values of $\rho_m$ used in this study.

**Table A.2.1**: Densities of solid salts and solutions used in the mass buoyancy corrections. The densities of the solutions were directly evaluated using a vibrating tube densitometer.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl (s)</td>
<td>2.165</td>
<td>[Dickson et al., 2007]</td>
</tr>
<tr>
<td>Na$_2$SO$_4$ (s)</td>
<td>2.68</td>
<td>[Dickson et al., 2007]</td>
</tr>
<tr>
<td>KCl (s)</td>
<td>1.984</td>
<td>[Dickson et al., 2007]</td>
</tr>
<tr>
<td>Tris (s)</td>
<td>1.35</td>
<td>[Dickson et al., 2007]</td>
</tr>
<tr>
<td>Tris-HCl (s)</td>
<td>1.35</td>
<td>Estimated from $\rho_{\text{Tris}}$</td>
</tr>
<tr>
<td>MgCl$_2$ (aq)</td>
<td>1.069</td>
<td>Measured</td>
</tr>
<tr>
<td>CaCl$_2$ (aq)</td>
<td>1.074</td>
<td>Measured</td>
</tr>
<tr>
<td>H$_2$O</td>
<td></td>
<td>Calculated</td>
</tr>
</tbody>
</table>
A.2.1.1 Program for the Apparent Mass of Salts in ASW

function make_trisrecipe

% Function description:
% The program is constructed using the steps recommended in
% the DOE CO2 Handbook; Dickson et al., 2007.
%
% Using the nominal recipe given for tris/tris-HCl buffer by
% DelValls & Dickson for weights of salts in air at sea
% level, calculate the buoyancy corrected masses of the
% salts necessary to make \( ? \) kg of the buffer in H2O at given
% molalities of Tris and HCl in an artificial seawater soln,
% of salinity \( S \).
%
% Note 1: Multiple salinities are supported, but
% only a single temperature, concentration of HCl, and/or
% concentration of Tris are supported. If more than 1
% salinity or buffer concentration are input, the program
% will return an error. **Multiple temps/buffer ratios may
% be functional, but have not been tested and are therefore
% disabled.**
%
% Note 2: Tris and HCl concentrations are generally given in
% mol/kg-H2O, but I have found it more convenient to create a
% buffer based on a total solution weight and not adding a
% given weight of H2O to be buffer. Therefore, I have
% organized this file to accept the input molalities of
% Tris and HCl based on the molality scale (mol/kg-H2O),
% but convert the output weights to the molinity scale
% (mol/kg-soln) for the buffer preparation. Weights for a
% H2O weight (total buffer mass is assumed) are also output.
%
% Note 3: The program can use either Tris(s) + HCl(aq), or
% Tris(s) + Tris-HCl(s). The program will prompt for the
% proper input.
%
% Programming notes.
% Last modified:
% To do:
% - Add routines to calculate the density of MgCl2/CaCl2
% solutions
% - Enable support for multiple mTris/mTris-HCl ratios

%% Prompts
clc
display('Calculate salts for tris/tris-HCl buffer in ASW from')
display('DelValls & Dickson 1998; in mol / kg-H20')
display('DelValls & Dickson 1998/SOP 6 Dickson et al., 2007')
display('Supply data in prompts below; if left blank,')
display('the input will default to values in ():')
display('density of MgCl2 stock (required or from molality),')
display('density of CaCl2 stock (required or from molality),')
display('molality of MgCl2 stock (required or from density),')
display('molality of CaCl2 stock (required or from density),')
display('density of HCl stock (required for HCl(aq)),')
display('molality of HCl stock (required for HCl(aq))')
'
display('Press ctrl+c to abort!')
'
\%
\%
\% Densities and concentrations of the current stock solutions of MgCl2, CaCl2, and HCl are commented out and added in the next section. It is also assumed the molality of Tris in each buffer solution before the addition of HCl is 0.08 mol/kg-H2O.
\%
t=input('Temperature (20oC): ');
relhumid= input('Relative Humidity (1): ');
atmpres= input('Local Atmospheric Pressure (101.325 kPa): ');
S=input('Salinity of ASW for buffer solution (35): ');
kgSoln= input('Total mass of water for buffer solution (1): ');
mTris= input('Total mol of Tris for buffer solution (0.080): ');
mHCl= input('Total mol of HCl for buffer solution (0.040): ');
which_acid= input('Use HCl(0) or Tris-HCl(1)? (no default): ');
if which_acid==0
    stock_dens.HCl= input('Density of stock HCl solution: ');
    stock_molal.HCl= input('Molality of stock HCl solution: ');
elseif which_acid==1
    else
        error('Incorrect input for HCl type')
end
\%
\% stock_dens.MgCl2= input('Density of stock MgCl2 solution: ');
\% stock_dens.CaCl2= input('Density of stock CaCl2 solution: ');
\% stock_molal.MgCl2= input('Molality of stock MgCl2 solution: ');
\% stock_molal.CaCl2= input('Molality of stock CaCl2 solution: ');
\%
\% For current chemical stocks
stock_molal.MgCl2 = 0.9896;
stock_molal.CaCl2 = 0.8934;
stock_dens.MgCl2 = 1.069;
stock_dens.CaCl2 = 1.074;
\%
\% Only allow a single temperature
if size(t,1) > 1 || size(t,2) > 1
    error('Only a single temperature is supported!')
end
\%
\% Only allow a single mHCl/mTris
if size(mHCl,1) > 1 || size(mHCl,2) > 1
    error('Only a single concentration of HCl is supported!')
end
if size(mTris,1) > 1 || size(mTris,2) > 1
    error('Only a single concentration of Tris is supported!')
end
\%
\% Look for blank inputs
if isempty(t)
    t=20;
end
if isempty(relhumid)
    relhumid=1;
end
if isempty(atmpres)
    atmpres=101.325;
end
if isempty(S)
    S=35;
end
if isempty(kgSoln)
    kgSoln=1;
end
if isempty(mTris)
    mTris=0.08;
end
if isempty(mHCl)
    mHCl=0.04;
end
if isempty(stock_dens.MgCl2)
    error('density of MgCl2 solution required!')
end
if isempty(stock_dens.CaCl2)
    error('density of CaCl2 solution required!')
end
if isempty(stock_molal.MgCl2)
    error('molality of MgCl2 solution required!')
end
if isempty(stock_molal.CaCl2)
    error('molality of CaCl2 solution required!')
end
if which_acid==0 && isempty(stock_molal.HCl)
    error('molality of HCl stock solution required!')
end
if which_acid==0 && isempty(stock_dens.HCl)
    error('density of HCl stock solution required!')
end

%% Constants
% Molar masses Dickson 2007, IUPAC
mw.Tris    = 1.0079 .* 11 + 15.999 .* 3 + 12.011 .* 4 + 14.007;
mw.NaCl    = 22.990 + 35.453;
mw.MgCl2   = 24.305 + 35.453 .* 2;
mw.CaCl2   = 40.078 + 35.453 .* 2;
mw.KCl     = 39.098 + 35.453;
mw.Na2SO4  = 22.990 .* 2 + 32.066 + 15.999 .* 4;
mw.HCl     = 1.0079 + 35.453;
mw.TrishCl = mw.Tris + mw.HCl;
% Temperature functions
T = t + 273.15;
es = 1.7526e8 .* exp(-5315.56 ./ T);
% Densities
% Calculated densities
dens.air   = ((3.4848 .* (atmpres-0.0037960 .* relhumid .* es)./...  
              T))./ 1000;
dens.H2O = (999.842594 + (6.793952e-2 + (-9.095290e-3 +...
  (1.001685e-4 + (-1.120083e-6 + 6.536332e-9.*...
  t).*t).*t).*t).*t)./1000;
dens.Soln = ((8.24493e-1 + (-4.0899e-3 + (7.6438e-5 +...
  (-8.2467e-7 + 5.3875e-9*t).*t).*t).*t).*S + ...t).* S.* sqrt(S) + 4.8314e-4 .* S .^ 2) ./ 1000 + dens.H2O;

% Densities of measured substances
dens_salt.Tris = 1.35;
dens_salt.TrisHCl= 1.35; % estimated
dens_salt.NaCl = 2.165;
dens_salt.KCl = 1.984;
dens_salt.Na2SO4 = 2.68;

%% Molalities
% % Start with the molalities given by D&D and determine the req
% molality at the input salinity
% % Note: I could not get equation (4) in SOP6 of Dickson et al.,
% 2007 to work properly at S = 35, but the DelValls & Dickson, 1998
% equation (Footnote a in Table 1) works.
% % Units: mol / kg - H2O
% istr35 = ((19.919 .* 35) ./ (1000 - 1.00198 .* 35)); % IonStr @ S=35
molal_salt.Tris = mTris;
molal_salt.HCl = mHCl;
if which_acid == 1
    molal_salt.Tris = molal_salt.Tris - molal_salt.HCl;
end
molal_salt.NaCl = (0.42762 .* ((19.919 .* S) ./ (1000 -...1.00198 .* S)))./ istr35;
if molal_salt.NaCl > 0
    molal_salt.NaCl = molal_salt.NaCl - molal_salt.HCl; % Subtract mHCl
end
molal_salt.MgCl2 = (0.05474 .* ((19.919 .* S) ./ (1000 -...1.00198 .* S)))./ istr35;
molal_salt.CaCl2 = (0.01075 .* ((19.919 .* S) ./ (1000 -...1.00198 .* S)))./ istr35;
molal_salt.KCl = (0.01058 .* ((19.919 .* S) ./ (1000 -...1.00198 .* S)))./ istr35;
molal_salt.Na2SO4 = (0.02927 .* ((19.919 .* S) ./ (1000 -...1.00198 .* S)))./ istr35;

%% Salt mass in solution
% % Sum of all the salts in solution. Required value for converting to
% molinity (grams / kg-soln) scale.
% % units: grams / kg-H2O
% mass_salt = molal_salt.Tris .* mw.Tris +...
molal_salt.NaCl .* mw.NaCl +...
molal_salt.Na2SO4 .* mw.Na2SO4 +...
molal_salt.KCl .* mw.KCl +...
molal_salt.CaCl2 .* mw.CaCl2 +... 
molal_salt.MgCl2 .* mw.MgCl2 +... 
molal_salt.HCl .* mw.HCl;
weight_H2O = (1000 ./ (1000 + mass_salt)) .* 1000;

%%% Convert Molality to Molinity
%%% To convert from molality to molinity it is necessary to multiply
%%% by the mass ratio: kg-H2O / kg-soln. The molinity at S=35 agrees
%%% with Table 1 in Nemzer & Dickson, 2005.
%%% units: mol / kg-soln
molin_salt.Tris = molal_salt.Tris .* 1000 ./ (1000 + mass_salt);
molin_salt.HCl = molal_salt.HCl .* 1000 ./ (1000 + mass_salt);
molin_salt.NaCl = molal_salt.NaCl .* 1000 ./ (1000 + mass_salt);
molin_salt.MgCl2 = molal_salt.MgCl2 .* 1000 ./ (1000 + mass_salt);
molin_salt.CaCl2 = molal_salt.CaCl2 .* 1000 ./ (1000 + mass_salt);
molin_salt.KCl = molal_salt.KCl .* 1000 ./ (1000 + mass_salt);
molin_salt.Na2SO4 = molal_salt.Na2SO4 .* 1000 ./ (1000 + mass_salt);

%%% Weights of salts and solutions from masses
%%% Convert mass to weight at the input environmental conditions
%%% For HCl (aq)
if which_acid == 0

% Grams for molinity buffer
% units - grams from mol / kg-soln
% Stock salts
gram_soln.Tris_salt = (molin_salt.Tris .* mw.Tris ./... 
(1+dens.air.*(1./dens_salt.Tris-1/8)) .* kgSoln .*... 
(1+dens.air.*(1./dens.Soln-1/8)));
(1+dens.air.*(1./dens_salt.NaCl-1/8)) .* kgSoln .*... 
(1+dens.air.*(1./dens.Soln-1/8)));
gram_soln.KCl_salt = (molin_salt.KCl .* mw.KCl ./... 
(1+dens.air.*(1./dens_salt.KCl-1/8)) .* kgSoln .*... 
(1+dens.air.*(1./dens.Soln-1/8)));
(1+dens.air.*(1./dens_salt.Na2SO4-1/8)) .* kgSoln .*... 
(1+dens.air.*(1./dens.Soln-1/8)));

% Stock solutions
gram_soln.HCl = ((kgSoln .*... 
(1+dens.air.*(1./dens.Soln-1/8))) .*... 
molin_salt.HCl ./ stock_molal.HCl) ./... 
(1+dens.air.*(1./stock_dens.HCl-1/8)).*1000;
gram_soln.MgCl2_stock = ((kgSoln .*... 
(1+dens.air.*(1./dens.Soln-1/8))) .*... 
molin_salt.MgCl2 ./ stock_molal.MgCl2) ./... 
(1+dens.air.*(1./stock_dens.MgCl2-1/8)).*1000;
gram_soln.CaCl2_stock = ((kgSoln .*... 
(1+dens.air.*(1./dens.Soln-1/8))) .*... 
molin_salt.CaCl2 ./ stock_molal.CaCl2) ./...
(1+dens.air.*(1./stock_dens.CaCl2-1/8)).*1000;

% H20
gram_soln.H20 = weight_H2O ./ (1+dens.air.*(1./dens.H2O-1/8)) .*...
               kgSoln .* (1+dens.air.*(1./dens.Soln-1/8));

% % Grams for molality buffer
% units - grams from mol / kg-H20
% %
% Stock salts
gram_H2O.Tris_salt = (molal_salt.Tris .* mw.Tris ./...
                      (1+dens.air.*(1./dens_salt.Tris-1/8)) .* kgSoln .*...
                      (1+dens.air.*(1./dens.H2O-1/8)));
gram_H2O.NaCl_salt = (molal_salt.NaCl .* mw.NaCl ./...
                      (1+dens.air.*(1./dens_salt.NaCl-1/8)) .* kgSoln .*...
                      (1+dens.air.*(1./dens.H2O-1/8)));
gram_H2O.KCl_salt = (molal_salt.KCl .* mw.KCl ./...
                      (1+dens.air.*(1./dens_salt.KCl-1/8)) .* kgSoln .*...
                      (1+dens.air.*(1./dens.H2O-1/8)));
gram_H2O.Na2SO4_salt = (molal_salt.Na2SO4 .* mw.Na2SO4 ./...
                      (1+dens.air.*(1./dens_salt.Na2SO4-1/8)) .* kgSoln .*...
                      (1+dens.air.*(1./dens.H2O-1/8)));

% Stock solutions
gram_H2O.HCl = ((kgSoln .*...
               (1+dens.air.*(1./arena.H2O-1/8))) .*...
               molal_salt.HCl ./ stock_molal.HCl) ./...
               (1+dens.air.*(1./stock_dens.HCl-1/8)).*1000;
gram_H2O.MgCl2_stock = ((kgSoln .*...
               (1+dens.air.*(1./arena.H2O-1/8))) .*...
               molal_salt.MgCl2 ./ stock_molal.MgCl2) ./...
               (1+dens.air.*(1./stock_dens.MgCl2-1/8)).*1000;
gram_H2O.CaCl2_stock = ((kgSoln .*...
               (1+dens.air.*(1./arena.H2O-1/8))) .*...
               molal_salt.CaCl2 ./ stock_molal.CaCl2) ./...
               (1+dens.air.*(1./stock_dens.CaCl2-1/8)).*1000;

% H2O
gram_H2O.H20 = kgSoln .* 1000 .*...
               (1+dens.air.*(1./dens.Soln-1/8));

% % For Tris-HCl (s)
% %
% elseif which_acid == 1
% %
% Grams for molality buffer
% units - grams from mol / kg-soln
% %
% Stock salts
gram_soln.Tris_salt = (molin_salt.Tris .* mw.Tris ./...
                      (1+dens.air.*(1./dens_salt.Tris-1/8)) .* kgSoln .*...
                      (1+dens.air.*(1./dens.Soln-1/8)));
(1+dens.air.*(1./dens.Soln-1/8));
(1+dens.air.*(1./dens_salt.Na2SO4-1/8)) .* kgSoln .**
(1+dens.air.*(1./dens.Soln-1/8)));
gram_soln.HCl = (molin_salt.HCl .* mw.TrisHCl ./
(1+dens.air.*(1./dens_salt.TrisHCl-1/8)) .* kgSoln .**
(1+dens.air.*(1./dens.H2O-1/8)));

% Stock solutions
gram_soln.MgCl2_stock = ((kgSoln .**
(1+dens.air.*(1./dens.Soln-1/8))) .**
molin_salt.MgCl2 ./ stock_molal.MgCl2) ./
(1+dens.air.*(1./stock_dens.MgCl2-1/8)).*1000;
gram_soln.CaCl2_stock = ((kgSoln .**
(1+dens.air.*(1./dens.Soln-1/8))) .**
molin_salt.CaCl2 ./ stock_molal.CaCl2) ./
(1+dens.air.*(1./stock_dens.CaCl2-1/8)).*1000;

% H2O
gram_soln.H2O = weight_H2O ./ (1+dens.air.*(1./dens.H2O-1/8)) .**
kgSoln .* (1+dens.air.*(1./dens.Soln-1/8));

% Grams for molality buffer
% units - grams from mol / kg-H2O
%
%
% Stock salts
gram_H2O.Tris_salt = (molal_salt.Tris .* mw.Tris ./
(1+dens.air.*(1./dens_salt.Tris-1/8)) .* kgSoln .**
(1+dens.air.*(1./dens.H2O-1/8)));
gram_H2O.NaCl_salt = (molal_salt.NaCl .* mw.NaCl ./
(1+dens.air.*(1./dens_salt.NaCl-1/8)) .* kgSoln .**
(1+dens.air.*(1./dens.H2O-1/8)));
gram_H2O.KCl_salt = (molal_salt.KCl .* mw.KCl ./
(1+dens.air.*(1./dens_salt.KCl-1/8)) .* kgSoln .**
(1+dens.air.*(1./dens.H2O-1/8)));
gram_H2O.Na2SO4_salt = (molal_salt.Na2SO4 .* mw.Na2SO4 ./
(1+dens.air.*(1./dens_salt.Na2SO4-1/8)) .* kgSoln .**
(1+dens.air.*(1./dens.H2O-1/8)));
gram_H2O.HCl = (molal_salt.HCl .* mw.TrisHCl ./
(1+dens.air.*(1./dens_salt.TrisHCl-1/8)) .* kgSoln .**
(1+dens.air.*(1./dens.H2O-1/8)));

% Stock solutions
gram_H2O.MgCl2_stock = ((kgSoln .**
(1+dens.air.*(1./dens.H2O-1/8))) .**
molin_salt.MgCl2 ./ stock_molal.MgCl2) ./
(1+dens.air.*(1./stock_dens.MgCl2-1/8)).*1000;
gram_H2O.CaCl2_stock = ((kgSoln .**
(1+dens.air.*(1./dens.H2O-1/8))) .**
molin_salt.CaCl2 ./ stock_molal.CaCl2) ./
(1+dens.air.*(1./stock_dens.CaCl2-1/8)).*1000;

% H2O
gram_H2O.H2O = kgSoln .* 1000 .**
(1+dens.air.*(1./dens.Soln-1/8));
else
end

%% Print Summary
clc % clean up command line
display('Summary')
display('')
display(['Tmp: ' num2str(t) ' (oC)'])
display(['Atm Prs: ' num2str(atmpres) ' (kPa)'])
display(['Salinity: ' num2str(S)])
display(['mTris: ' num2str(mTris) ' (mol / kg-H2O)'])
display(['mHCl: ' num2str(mHCl) ' (mol / kg-H2O)'])
display(['Mass of buffer soln: ' num2str(kgSoln*1000) ' (g)'])
display('Stock Molalities:')
display(stock_molal)
display('Mass of constituents (g / kg-soln): ')
display(gram_soln)
display('Mass of constituents (g / kg-H2O): ')
display(gram_H2O)
if size(gram_soln.Tris_salt,1)>1 || size(gram_soln.Tris_salt,2)>1
    display(['Input with multiple salinities. The total '...
        ' salt/stoich-soln'])
    display(['weights required for a total solution weight of '...
        num2str(kgSoln) ' kg are:'])
    display(['Tris salt: ' num2str(sum(gram_soln.Tris_salt)) ' (g)'])
    display(['NaCl salt: ' num2str(sum(gram_soln.NaCl_salt)) ' (g)'])
    display(['KCl salt: ' num2str(sum(gram_soln.KCl_salt)) ' (g)'])
    display(['Na2SO4 salt: ' num2str(sum(gram_soln.Na2SO4_salt)) ' (g)'])
    display(['MgCl2 stock: ' num2str(sum(gram_soln.MgCl2_stock)) ' (g)'])
    display(['CaCl2 stock: ' num2str(sum(gram_soln.CaCl2_stock)) ' (g)'])
    display(['HCl: ' num2str(sum(gram_soln.HCl)) ' (g)'])
else
end
end
A.3: Chapter 5

A.3.1 eMLR Residuals

Figure A.3.1: BEAGLE P06 TCO$_2$ fit residuals ($\mu$mol kg$^{-1}$).
Figure A.3.2: WOCE P06 TCO$_2$ fit residuals (µmol kg$^{-1}$).
Figure A.3.3: CLIVAR P18 TCO$_2$ fit residuals (µmol kg$^{-1}$).
Figure A.3.4: WOCE P18 TCO$_2$ fit residuals ($\mu$mol kg$^{-1}$).
A.3.2 Transit Time Distributions

Atmospheric gases, such as CO$_2$ and CFCs, are transported from regions where water masses are subducted below less dense surface waters. Understanding the transport of these water masses to the interior ocean is important for constraining ocean circulation and quantifying the ocean’s role in global climatic processes. A variety of methods are used to quantify interior ocean transport, including tracing changes in hydrographic tracers as water parcels are exported from the surface ocean [Alvarez-Borrego and Park, 1971], to the observation of transient tracers, such as CFCs, in the interior ocean [Fine et al., 2002; Fine, 2011]. It is often assumed these water parcels are simply exported to the interior ocean by purely advective processes, but this assumption does not always completely, or accurately explain interior transport [Robbins et al., 2000]. The ocean is complex and assuming water masses are transported to the interior free of influence from diffusive processes is not adequate to explain some interior observations. Purely advective transport is often assumed in observation-based calculations of anthropogenic CO$_2$ [Hall et al., 2002], and this assumption might, at least partially, be responsible for the observed differences in anthropogenic CO$_2$ from different data based methods [e.g. Wanninkhof et al., 1999]. The transit time distribution (TTD) technique tracks a passive tracer from an atmospheric source to the interior ocean [Haine and Hall, 2002], and can be used to determine an ocean anthropogenic CO$_2$ inventory incorporating both advective and diffusive transport [Waugh et al., 2004; Hall et al., 2004]. The concentration of a passive tracer ($c$) is calculated in the ocean interior at a given time ($t$) and location ($r$) from

$$c(r, t) = \int_{0}^{\infty} c_0(t - t')G(r, t') dt'$$

(A.3.1)

where $c_0(t - t')$ is the change in the atmospheric concentration between $t$ and the initial concentration of the tracer. $G(r, t')$ is the TTD at $r$, and is calculated by approximation using inverse

---

*x* ‘Diffusive’ refers all processes leading to errors in the assumption of pure advective transport. This includes, but is not limited to, diapycnal mixing and isopycnal mixing by eddy stirring.
Gaussian functions representing the mean transit time \( \Gamma = \int_0^\infty \xi G(\xi) d\xi \) and the TTD mean width \( \Delta^2 = \frac{1}{2} \int_0^\infty (\xi - \Gamma)^2 G(\xi) d\xi \) [Waugh et al., 2004, 2006]

\[
G(t) = \sqrt{\frac{\Gamma^3}{4\pi \Delta^2 t^3}} \exp \left( -\frac{\Gamma(t - \Gamma)^2}{4\Delta^2 t} \right).
\]

To calculate \( G(t) \), \( \Delta \) and \( \Gamma \) are first determined. This is achieved by determining the ratio between \( \Delta \) and \( \Gamma \); a ratio of 1 appears to be valid for the global ocean [Hall et al., 2004; Waugh et al., 2004, 2006; Tanhua et al., 2009]. With a value for \( \Delta/\Gamma \) established, the measured concentration of a transient tracer at location \( r \) and the atmospheric concentration history of the transient tracer are used to derived either \( \Delta \) or \( \Gamma \) from a matrix convolution [Haine and Hall, 2002; Waugh et al., 2004; Hall et al., 2004; Waugh et al., 2006; Tanhua et al., 2009]. With \( \Delta \) and \( \Gamma \) established, \( G(t) \) can be determined at \( r \) from equation A.3.2. The anthropogenic \( \text{CO}_2 \), \( c(r, t) \), can be determined from equation A.3.1 and the change in the surface history of \( \text{TCO}_2 \), \( c_0(t - t') \). Calculation of the surface history of \( \text{TCO}_2 \) is discussed in section 5.2.2.

A.3.3 Uncertainties in the TTD Anthropogenic \( \text{CO}_2 \)

1. Assumed surface saturations

When calculating \( \Delta \) and \( \Gamma \), it is assumed there is a constant surface saturation or under-saturation of the transient tracer, but observations of the surface CFCs saturations show this is not true. Seasonal variations in temperature and ice cover lead to under-saturations differing by as much 40% in Antarctic marginal seas [Rodehacke et al., 2010]. Tanhua et al. [2008] analyzed the mean surface saturations of CFC-12 and SF\(_6\) in the North Atlantic from the GLODAP [Key et al., 2004] and CARINA [Tanhua et al., 2009] data bases and find recent (from 1999 and on) surface saturations of CFC-12 are close 100%. The change in average percent saturation is attributed to decrease in atmospheric CFC concentrations, allowing surface saturations of CFCs to fully equilibrate with the atmosphere. Based on these results, it is assumed the surface saturation is 95% [Hartin et al., 2011], and is reflective of the long term average surface percent saturation, but may not
be reflective of the seasonal saturation [Hall et al., 2004].

2. **Tracer age accuracy**

Due to the decreasing concentrations of CFCs in the atmosphere the use of CFC-12 as a proxy for anthropogenic CO$_2$ is limited, and the error associated with the calculation of anthropogenic CO$_2$ from TTDs in the surface ocean is increasing. Tanhua et al. [2008] estimate an error of 8 $\mu$mol kg$^{-1}$ for samples collected between 2007 - 2010 with CFC-12 ages of less than $\sim$ 15 years. This error can be minimized by using SF$_6$, which has atmospheric concentrations that are still increasing.

3. **Differences in gas solubility**

CO$_2$ and CFCs have a different solution chemistry and respond differently to changes in temperature. As the temperature decreases, the solubility of gases increase. However, due to the buffering effect of the ocean warm tropical waters are able to dissolve greater concentrations of anthropogenic CO$_2$. Álvarez and Gourcuff [2010] suggest the differences in atmospheric histories and ocean uptake of anthropogenic CO$_2$ and CFCs is responsible for the observed difference in the transport of the tracers in the North Atlantic.

4. **Universal surface source**

The TTD assumes a single source region from which water is transported to the interior ocean. When the TTD anthropogenic CO$_2$ is calculated with cruise data, as described in section 5.2, the data is taken from the same location the TTD is estimated. It is assumed the water masses are isopycnack lly transported to the interior region from the source region, and the same anthropogenic CO$_2$ should be determined if the anthropogenic CO$_2$ is calculated using data taken from the water mass source region and the local TTD.
A.3.4 P06 TTD Anthropogenic CO₂

The following figures show the either the total or difference in the calculated anthropogenic CO₂ on the CLIVAR P06 using the TTD method. The calculations were performed with a code written in MATLAB and provided by Dr. Samar Khatiwala.

Figure A.3.5: The total increase in anthropogenic CO₂ calculated on BEAGLE (2003) P06 from the TTD method. The solid lines are the potential density isopycnal surfaces.
Figure A.3.6: The total increase in anthropogenic CO$_2$ calculated on WOCE (1992) P06 from the TTD method. The solid lines are the potential density isopycnal surfaces.

Figure A.3.7: The difference in anthropogenic CO$_2$ between BEAGLE (2003) and WOCE (1992) P06 from the TTD method. The solid lines are the potential density isopycnal surfaces.
Figure A.3.8: The total increase in anthropogenic CO$_2$ calculated on CLIVAR (2010) P06 from the TTD method. The solid lines are the potential density isopycnal surfaces.

Figure A.3.9: The difference in anthropogenic CO$_2$ between CLIVAR (2010) and WOCE (1992) P06 from the TTD method. The solid lines are the potential density isopycnal surfaces.
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