

Frank J. Millero

Reflections on My Career as a Marine Physical Chemist, and Tales of the Deep

Frank J. Millero

Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida 33149; email: fmillero@rsmas.miami.edu

Annu. Rev. Mar. Sci. 2015. 7:1-20

First published online as a Review in Advance on July 25, 2014

The Annual Review of Marine Science is online at marine.annualreviews.org

This article's doi: 10.1146/annurev-marine-010814-015946

Copyright © 2015 by Annual Reviews. All rights reserved

Keywords

thermodynamics, kinetics, speciation, ocean cruises

Abstract

This is a personal review of how one can apply the principles of physical chemistry to study the ocean and other natural waters. Physical chemistry is the study of chemical thermodynamics, kinetics, and molecular structure. My long-term interest in the chemistry of seawater is an extension of my early work on water and the interactions that occur in aqueous electrolyte solutions, which I began as part of my PhD research on the thermodynamics of organic acids in water. Over the years, I have attempted to apply the tools of physical chemistry to elucidate the structures of seawater, brines, lakes, and rivers. I have developed and continue to work on ionic interaction models that can be applied to all natural waters. Here, I reflect on how my students, postdocs, research assistants, and scientific colleagues have influenced my life, my career, and the field of marine physical chemistry. My hope was and is to use these tools to understand the molecular structures of natural waters.

INTRODUCTION

As I near retirement, this is a good time for me to look back on my career and to thank those who have worked with me. This is a tale of how a young physical chemist became interested in the chemistry of the oceans and other natural waters and spent 50 years having fun. It is a unique story of many interesting people who have aided me in my career and the interesting scientific cruises I made over the years.

After receiving my BS in physical chemistry from Ohio State University in 1961, I received my MS and PhD degrees from the Carnegie Institute of Technology in 1964 and 1965, respectively. My major professor at Carnegie was Loren Hepler, who had come from Gilbert N. Lewis and Merle Randall's thermodynamics group at the University of California, Berkeley. It is interesting to note that this science group can be traced backward by a "scientist's genealogy" to Nicolo Leoniceno (1428–1524), who received his MD and PhD degrees in 1453 at the University of Padua in Italy and was a professor at the University of Ferrara.

My long-term interest in the chemistry of seawater is an extension of my early interest in water and the interactions that occur in aqueous electrolyte solutions, which I worked on as part of my PhD research on the thermodynamics of organic acids in water. Most of the studies involved the heats of ionization of these acids (such as phenols and barbiturates), with the heats of the equilibrium reactions measured using a solution calorimeter. I used the results to attempt to understand the relationships between the structures of the acids and their thermodynamic properties (enthalpy, entropy, and free energy).

After a brief stay at Esso working on automobile air pollution, I moved to the Marine Laboratory at the University of Miami. My initial studies there dealt with determining the equations of state of water and seawater. I also examined the thermochemical properties of seawater and the major sea salts. I was and still am interested in developing ionic interaction models that can be applied to natural waters. I later became involved in researching how the rates of oxidation and reduction of metals were affected by their speciation, and spent some time measuring the rates of oxidation of H₂S in anoxic waters around the world. In my latter years, I have been examining the carbon dioxide system in the world's oceans and the effects of ocean acidification on chemical processes in the oceans. In this article, I review some of these studies and the interesting scientific cruises that I went on.

A SKETCH OF MY LIFE HISTORY

I was born in Greenville, Pennsylvania, on March 16, 1939. My Italian grandfathers had settled in this town in the early 1900s. My grandfather on my father's side, Leonardo Mottola, originally came from Sauvignon, Italy, to the east of Naples; his father (my great-grandfather) had moved the family to Pennsylvania in the late 1800s. For some reason, my grandfather changed the family name to Miller; he later felt bad about the change and added the *o*, giving me the family name Millero.

We moved to Warren, Ohio, before I started grade school. After grade school, I went to West Junior High School, where I played football, ran track, and pole vaulted. I continued these sports at Warren Harding High School and graduated in 1957 as president of my class. We still have a reunion of the class every five years. I had a keen interest in chemistry in high school, decided to get a degree in this field, and applied to several colleges during my senior year. I was accepted by quite a few, but most did not offer me a full scholarship, without which I could not afford the tuition. I did get a full scholarship to play football at Thiel College, a small school in Greenville. I was on the wrestling team and played football until I injured my knee in a game. I still remember my math instructor teaching calculus by examining the physics of how *Sputnik* was launched into orbit.

The next year, I transferred to Ohio State University and began work on a degree in chemical engineering. After suffering through a math course for engineers taught by a graduate student who knew nothing about physics, I transferred to pure chemistry. I enjoyed my time at Ohio State, particularly the football games and Sunday pasta with friends. In my senior year, I had an opportunity to work at a local racetrack as a ticket checker. A friend's father worked at the track and got both of us the jobs. Since I had no classes in the afternoon, I took the job. We won four daily doubles during the season, making enough money to buy my first car after graduation in 1961.

I was accepted to graduate school at the Carnegie Institute of Technology and started there in the fall of 1961. I had applied for a summer job in Washington, DC, at the National Bureau of Standards (now the National Institute of Standards and Technology). The job was in the Electrochemical Division, headed by Dr. Roger Bates, and it changed my career. I gave up my thoughts of studying nuclear chemistry and decided to study the chemistry of solutions. I made density and viscosity measurements on *N*-methylpropionamide with added electrolytes. Bates later released the data, and I published my summer work after going to Miami (Millero 1968). At the bureau, I made the density measurements with an early version of a magnetic float densitometer; later, at Miami, I built a similar system and made density measurements of seawater and other electrolytes (Millero 1967). I also developed a high-pressure magnetic float system that I used to study the density of water and seawater to 1,000 bar (Millero et al. 1972).

My advisor at Carnegie, Loren Hepler, was a graduate of the University of California, Berkeley. His advisor had been Wendell M. Latimer, who wrote the book *Oxidation Potentials* (Latimer 1952) and was in the thermodynamics group of Lewis and Randall, who wrote the book *Thermodynamics* (Lewis & Randall 1961; this work was originally published in 1923, with a second edition then revised by Kenneth S. Pitzer and Leo Brewer and published in 1961). Loren taught me how to make careful physical chemical measurements and write up the results on a typewriter, which made it very easy for me when computers came into play. I fondly remember my days in Pittsburgh and hearing discussions about the structure of water by Henry Frank, Felix Franks, and Robert Kay at meetings at the Mellon Institute of Industrial Research (now part of Carnegie Mellon). I continued work on the structure of water throughout my career as part of my interest in seawater and other natural waters.

Much of this research was supported by the Office of Desalination in the Department of the Interior. I will never forget going to one of their meetings in Pittsburgh. Ray Fuoss from Yale was giving a paper on the conductivity of electrolytes. Peter Debye stood up and debated with Fuoss about the paper. Debye sat down after saying that he would wait until Fuoss tried to publish this paper, quieting the room.

I had planned on doing some of my PhD work on the volume properties of solutions, but Loren Hepler went on sabbatical in Australia and built the system I had planned to construct. I should point out that my interest in molal volumes came early in my career, when I gave a seminar based on a paper by Hepler (1957). During my last two years at Carnegie, I also worked in the evenings as a bartender at a place called the Fox Cafe. It was a local bar in the daytime and a college bar in the evenings. Hepler found out about my bartending job and wrote me a letter saying that I should give it up. I did for a few months but then went back to it. I was able to save \$3,000 from this job, and after graduating in March 1965, I used it to spend three months in Europe—a trip I had planned for many years. That tale will be published elsewhere.

After returning to Pittsburgh, I had some time before moving to my job at Esso in New Jersey. The owner of the bar hurt his back and asked me to run it for a month or so. Since the bar had some of the best ham and pastrami sandwiches in Pittsburgh, Hepler would frequently come in for lunch, and while sipping on beer, we would talk about reviewers' comments on our coauthored papers. I also met my wife, Judy, in Pittsburgh. She was a nurse who worked in the area and frequently came to the bar with her friends. I fell in love with her from our initial meeting and have enjoyed my 50 years with her since. She has put up with my watching football games on most days of the week in the fall, with a laptop nearby to write papers during the commercials.

Before leaving Esso to go to Miami, I had their library make me copies of all the papers dealing with the volume properties of aqueous solutions. This gave me the information that I needed to work on the volume properties of seawater. I later wrote a review article on the topic (Millero 1971) and a book chapter (Millero 1972).

Dr. Walter Drost-Hansen had brought me to the Marine Laboratory at the University of Miami to prove his theory that water has unique temperature transitions at 5°C, 15°C, and 25°C. After building the magnetic float system (Millero 1967), I studied the partial molal volumes of several chlorides as functions of temperature (Millero & Drost-Hansen 1968). I found no transitions, and after reading an unpublished review by Otto Redlich from Berkeley, decided to give up this work. This resulted in a split with Drost-Hansen, who went to the main campus chemistry department while I stayed at the Marine Laboratory. I was initially supported by funds from the US Office of Saline Water, but as these funds dried up, I wrote proposals for funding to support my salary and research. After being turned down for a year or two, I finally received some National Science Foundation funds to examine ionic interactions in seawater, thanks to program manager Kilho Park, who supported my earlier proposals that Ricardo Pytkowicz had turned down.

CHEMICAL THERMODYNAMICS

Fundamental to the chemical thermodynamics of solutions is the free energy (G) function given by (Millero 2001b)

$$\mathrm{d}G = (\partial G/\partial T)_{P,n_i,n_2}\mathrm{d}T + (\partial G/\partial P)_{T,n_i,n_2}\mathrm{d}P + (\partial G/\partial n_1)_{T,P,n_2}\mathrm{d}n_1 + (\partial G/\partial n_2)_{T,P,n_i}\mathrm{d}n_2.$$

The change in the free energy (dG) is related to the change with respect to temperature (T), pressure (P), and composition (n_i) . A given system is studied by keeping two of the variables constant—T and P, T and n_i , or P and n_i —while varying the third. I have used these basic principles to study chemical processes in aqueous electrolyte solutions and natural waters. The effect of pressure on the free energy is related to the volume ($V = \partial G/\partial P$), the effect of temperature is related to the enthalpy ($H = \partial G/\partial T$), and the effect of composition is related to the chemical potential ($\mu = \partial G/\partial n$).

Early in my time at Miami, I started a series of measurements of the thermodynamic properties of water, seawater, and the major sea salts. My long-term interest was to be able to account for all the ionic interactions in seawater and brines as a function of temperature ($t = 0-100^{\circ}$ C), pressure (P = 0-1,000 bar), and composition ($n_i = 0-6$ m). We started by examining the pressurevolume-temperature (PVT) properties of H₂O, D₂O, seawater, and the major sea salts. The PVT properties of H₂O (Chen et al. 1977a,b) and D₂O (Fine & Millero 1975, Chen & Millero 1981) were determined from density and sound speed measurements (Millero 1967, Millero et al. 1972). We also measured the PVT properties of the major sea salts as functions of temperature and pressure (Chen et al. 1977a, 1978). More recent density and sound speed studies have been made on the major sea salts over a wider range of concentrations (Connaughton et al. 1986, Millero et al. 1987c).

We made our initial density and compressibility measurements of seawater at 1 atm (Lepple & Millero 1971; Millero et al. 1976a,b). The 1980 equation of state of seawater was based on the 1-atm density work of Millero & Poisson (1981) and the high-pressure studies of Millero, Chen, Bradshaw & Schleicher (Millero et al. 1980). I have described the historical development of the equation of state of seawater elsewhere (Millero 2010b).

In recent years, we have measured the 1-atm densities and sound speeds of seawater from 0°C to 90°C (Millero & Huang 2009, 2011). These measurements were used to extend the equation of state of seawater to high temperatures. Safarov et al. (2009, 2012) have done further PVT studies to extend the salinity, temperature, and pressure range of the equation of state of seawater. We have also performed several studies on the thermochemical properties of seawater, including measuring the enthalpy (Millero et al. 1973a) and heat capacity (Millero et al. 1973b) of seawater; summaries of these results have been given elsewhere (Millero & Leung 1976, Millero 1983b). These results were used to test multicomponent electrolyte theories (Duer et al. 1976) and were fitted to the Pitzer equations (Millero & Pierrot 2005). The seawater PVT and thermochemical properties constitute the fundamental thermodynamic properties of seawater used in the new thermodynamic equation of state for seawater called TEOS-10 (Intergov. Oceanogr. Comm. et al. 2010).

The microcalorimeter used to measure the enthalpy of seawater and other electrolytes was also used to examine the heat produced by the uptake of glucose by the bacteria *Vibrio alginolyticus* (Gordon et al. 1982). We found that the heat released was a linear function of the added glucose over a wide range of concentrations. We also found that the addition of Cu^{2+} to the solution lowered the heat and became toxic at high enough concentrations (Schreiber et al. 1985). The toxic concentration was the same as the maximum adsorbed on the surface of living or dead bacteria (Gordon & Millero 1987). Schreiber left the bacteria in the calorimeter overnight, and we were surprised the next morning to see that the bacteria finished off the glucose, apparently by creating a ligand that complexed Cu^{2+} and prevented the toxic effect (Schreiber et al. 1990). We also examined uptake by attached and unattached bacteria using a flowing microcalorimeter (Gordon & Millero 1983).

CHEMICAL KINETICS

I became interested in the rates of chemical processes in seawater in the late 1980s. This started with an attempt to estimate the lifetime of superoxide (O_2^-) in seawater (Millero 1987). As shown by Zika (1981), O_2^- can be produced by photochemical processes:

$$Org + hv = Org^*,$$
$$Org^* = Org^+ + e^-,$$
$$O_2 + e^- = O_2^-.$$

The O_2^- produced by this pathway can also produce peroxide (H₂O₂):

$$H^+ + O_2^- = HO_2$$

$$\mathrm{HO}_2 + \mathrm{HO}_2 = \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2.$$

Both O_2^- and H_2O_2 along with O_2 can react with metals in natural waters. Moffett & Zika (1977) showed that Cu^+ and Fe^{2+} can be oxidized with O_2 as well as H_2O_2 formed photochemically. They suggested that the Cu^+ found in surface seawater could be formed by the reduction of Cu^{2+} with H_2O_2 (Moffett & Zika 1983):

$$Cu^{2+} + H_2O_2 = Cu^+ + HO_2 + H^+.$$

One of the reviewers of my first kinetic proposal said that because I dealt only with thermodynamics, I could not study kinetic processes in the oceans. I got some funding anyway, and did several studies of the oxidation of Cu^+ , Fe^{2+} , and H_2S in seawater. Our first studies were on the oxidation of Fe^{2+} with O₂ in seawater (Millero et al. 1987b):

$$-d[Fe(II)]/dt = k[Fe^{2+}][O_2].$$

The rate was a second-degree function of pH. We attributed this to the rate constant being related to the speciation of Fe²⁺ in water:

$$Fe^{2+} + H_2O = FeOH^+ + H^+,$$

 $Fe^{2+} + 2H_2O = Fe(OH)_2 + 2H^+$

The overall rate constant (k) was related to the fraction of the forms of Fe(II) in solution:

$$k = k_0 \alpha_{\mathrm{Fe}^{2+}} + k_1 \alpha_{\mathrm{FeOH}^+} + k_2 \alpha_{\mathrm{Fe(OH)}_2},$$

where the α variables are, respectively, the fractions of Fe²⁺, FeOH⁺, and Fe(OH)₂ in solution. We later examined how the rate was affected by ionic interactions with the major components of seawater (Millero et al. 1989a). This work was one of the first to demonstrate that the speciation of metals in natural waters controls the rates of oxidation and reduction (Millero 1985). We made similar studies of the oxidation of Fe²⁺ with H₂O₂ (Millero & Sotolongo 1989), and later studies examined oxidation at low concentrations of Fe²⁺ (King et al. 1995, González-Dávila et al. 2005) and the competition between O₂ and H₂O₂ in the oxidation of Fe²⁺ (González-Dávila et al. 2006).

Our second kinetic study on metals dealt with the oxidation of Cu(I) with O_2 (Sharma & Millero 1988) and H_2O_2 (Sharma & Millero 1989) and the reduction of Cu(II) with H_2O_2 . We found that the speciation of Cu(I) with inorganic solutes affected the oxidation rate. The rate of reduction of Cu(II) with H_2O_2 (Millero et al. 1991) was also affected by the formation of complexes with inorganic and organic ligands in natural waters. The reduction slowed down when CO_3^{2-} or ethylenediaminetetraacetic acid (EDTA) was added to form complexes. Later, we showed that lowering the pH of ocean waters and decreasing CO_3^{2-} accelerates the formation of Cu(I) in seawater (Millero et al. 2009b, Millero & DiTrolio 2010). These studies demonstrated how the speciation of metals in natural waters can affect both the oxidation and reduction of metals in seawater.

My interest in the kinetics of the oxidation of H_2S in natural waters came from our studies of anoxic waters. Our first laboratory studies were on the oxidation of H_2S in seawater with O_2 and H_2O_2 as a function of pH and salinity (Millero et al. 1987a, Millero & Hershey 1989). We found that the rates of oxidation of HS^- were faster than those of H_2S . The half-lives for the oxidation were approximately 50 h in water and 25 h in seawater. We then examined the effects of metals on the oxidation of H_2S (Vazquez et al. 1989). Iron (at nanomolar levels) and manganese (at micromolar levels) were the only metals found to accelerate the oxidation rates at low concentrations. Since these metals were quite common in anoxic waters, we decided to examine the oxidation of H_2S with O_2 in the field.

In 1988, we participated in the first field study in the Black Sea. Some of the interesting events during this cruise are discussed below. We studied the oxidation of H₂S by mixing deep waters with surface waters and found that the rates were much faster than expected (Millero 1991c). Later measurements were made in the Framvaren Fjord (Millero 1991b; Yao & Millero 1995a,b), Chesapeake Bay (Millero 1991a), and the Cariaco Trench (Zhang & Millero 1993). We found that, in all the anoxic waters we studied, the rates of oxidation of H₂S were the same as our laboratory values determined at the same Fe²⁺ concentrations. We also determined the oxidation rates of sulfite (Zhang & Millero 1991), which allowed us to define the mechanism for the oxidation of H₂S in natural waters. The kinetic rate constants for the oxidation of H₂S with O₂ found in the

field were similar to those found in the laboratory studies at the same Fe^{2+} concentrations. So, in summary, the iron concentrations in anoxic basins control the rates of oxidation.

IONIC INTERACTION MODELS

The thermodynamic and kinetic measurements made over the years have been useful in developing ionic interaction models for seawater and other mixed electrolyte solutions. Two types of models have been pursued: those that can be used to estimate the physical chemical properties of natural waters (Millero 1974b) and those that can be used to estimate equilibrium constants in natural waters (Millero 1977). Both models need to be able to make the estimates as a function of temperature, pressure, and composition (Millero & Pierrot 1998, Pierrot & Millero 2000). The models can be used to determine the solubility of gases and solids, the ionization of acids, and the speciation of metals in natural waters (Millero & Pierrot 1998).

The interactions that occur in mixed electrolyte solutions need to account for plus-minus, minus-minus, and plus-plus interactions. The plus-minus interactions are the strongest and may result in an ion complex or ion pair. Earlier work had estimated the physical properties using Young's rule (Young & Smith 1954), which simply says that the property of an electrolyte solution is equal to the property of pure water (P^0) plus terms that are related to the ionic interactions:

 $P = P^0 + A$ (cation-anion) + B (cation-cation) + C (anion-anion).

The *A* term is determined from the major salts (NaCl, MgCl₂, NaSO₄, and MgSO₄) in the solution; the *B* and *C* terms are determined by mixing the major salts (NaCl + MgCl₂, Na₂SO₄ + MgSO₄, MgCl₂ + MgSO₄, and NaCl + Na₂SO₄). I first used this simple model to estimate several properties of seawater (Millero 1974b). In recent years, we have used it to estimate the density and compressibility of seawater from 0°C to 100°C (Rodriguez & Millero 2013b). Pitzer (1991) has also developed a model that can be used to estimate the physical properties of seawater over a wide range of temperatures and pressures (Pierrot & Millero 2000; Millero & Pierrot 2005; Rodriguez & Millero 2013a,b).

An activity coefficient model is needed to examine the equilibrium constant (K^*) in a mixed electrolyte solution. For dissociation of acid HCl,

$$HCl = H^+ + Cl^-.$$

The stoichiometric equilibrium constant K^* is given by

$$K^* = [\mathrm{H}^+][\mathrm{Cl}^-]/[\mathrm{H}\mathrm{Cl}] = K^0\{(\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}})/(\gamma_{\mathrm{H}\mathrm{Cl}})\}.$$

 K^0 is the value in pure water, square brackets denote concentrations, and the γ variables are the activity coefficients of the ions and nonelectrolytes in the media. The activity coefficients estimated from the Pitzer equations (Pitzer 1991) are in the form

 $\ln \gamma_i = DH + \Sigma(\text{cation-anion term}) + \Sigma(\text{cation-cation term}) + \Sigma(\text{anion-anion term}).$

The summation is made over all of the ions in the solution.

We first used the Pitzer activity coefficient model to estimate the activity coefficients of ions in seawater (Millero & Schreiber 1982) and brines (Millero 1999) and to examine the speciation of the major ions (Millero & Pierrot 2007). A QuickBASIC program called CO2sys (Millero 1982b, Millero & Roy 1997, Millero & Pierrot 1998, Waters & Millero 2013) was developed to estimate the equilibrium constants needed to examine the CO₂ system in natural waters over a wide range of salinities and temperatures (Gleitz et al. 1995). All of the equations needed for the computer

code have been published (Pierrot & Millero 2000, Waters & Millero 2013). An Excel version of the program was also written to determine the speciation of metals in seawater or any natural water of known composition (Millero & Pierrot 2002). We have used our version of the Pitzer equations to examine the speciation of metals in natural waters over a wide range of temperatures and pressures (Millero 1979a,b, 1999; Millero & Pierrot 2007; Sharma et al. 2007; Millero & Woosley 2009; Woosley & Millero 2010, 2013). Recently, we have used the model to examine the effects of ocean acidification on the speciation of metals (Millero et al. 2009b). Pitzer (1991) also developed programs that can be used to examine the activity coefficients of nonelectrolytes in mixed electrolyte solutions (Millero 2000). We have used this model to examine the solubility of O_2 (Millero et al. 2002) and B(OH)₃ (Chanson & Millero 2006) in seawater.

Finally, I should mention that I have made numerous studies of the volume properties of ions in water and seawater (Millero 1971, 1972; Millero & Huang 2013; Millero & Sharp 2013), which can be used to estimate the effects of pressure on processes in the oceans (Millero 1979a, 1982a, 1983a). I had also hoped that I could use the results of these studies to examine the structure of ions in seawater. This interest was piqued by the pioneering studies by Duedall (1968) and Poisson & Chanu (1975). I examined the earlier studies by Duedall (1968) when studying the structure of ions in seawater (Millero 1969). Recently, I developed a model that can be used to estimate the partial molal volume of ions in seawater as a function of temperature. The results are in good agreement with the measured values. Therefore, it is now possible to estimate the effects of pressure on seawater, brines, and lakes over a wide range of temperatures.

CARBON DIOXIDE STUDIES

Over the years, I have written several reviews on the carbonate system (e.g., Millero 1979b). In my *Chemical Reviews* article (Millero 2007), I attempted to update the more recent work on the carbon cycle in the oceans. My initial (and continued) interest in the CO₂ system related to the thermodynamics of the system in seawater. After the UN Educational, Scientific, and Cultural Organization (UNESCO) panel finished the equation of state of seawater, it formed a committee to examine the carbon dioxide system in seawater. The most reliable measurements for seawater at the time were made by Mehrbach et al. (1973). It is important to note that these measurements were made for salinity S = 15–40. Dickson and I refit the equations for the Mehrbach constants and forced them to the values for pure water (Dickson & Millero 1987). This made them more useful for estuarine systems. Others made measurement of the constants in artificial seawater (Hansson 1973, Goyet & Poisson 1989, Roy et al. 1993). Furthermore, Mojica Prieto & Millero (2002) and Millero et al. (2006) made seawater measurements for absolute salinities (S_A , i.e., the total mass of all salts) of 0–45 g/kg. The results of all of these studies were in reasonable agreement and are available on different pH scales (Millero 2010a).

The carbonate constants and their thermodynamic relationships in the oceans were formalized by Kilho Park (1969). I wrote several QuickBASIC programs that use these thermodynamic equations (Park 1969) and the above constants to examine the components of the CO₂ system in the oceans. The CO2sys program was improved by my students Arthur Chen, Kitack Lee, Jia-Zhong Zhang, and Denis Pierrot. Lewis & Wallace (1998) "prettied up" my original program and called it CO2SYS.BAS. Denis developed an Excel version of this program while he was a graduate student, and he continues to update it as new constants are published. It is publicly available from the Carbon Dioxide Information Analysis Center website (http://cdiac.esd.ornl.gov). We used our original unpublished program to examine the CO₂ system in our earlier cruises in the Mediterranean Sea, the Atlantic and Pacific Oceans, and the Bahama Banks. My student Wensheng Yao also wrote a program that added the appropriate equations needed to study the CO₂ system in anoxic waters (Yao & Millero 1995a,b).

A similar CO2brine program was developed to examine the thermodynamics of the CO₂ system in any natural water with a known composition of the major components or salinity from 0 to 50 g/kg. It calculates all the thermodynamic constants needed to examine the CO₂ system by using a Pitzer equation to calculate all the activity coefficients (Gleitz et al. 1995, Millero & Pierrot 1998). This program predicts values for pK_1 , pK_2 , and other constants in S = 35 salinity seawater that are in good agreement with the measured values.

Research on CO_2 uptake in the oceans has been an important use of the CO_2 data accumulated over the past 30 years during the World Ocean Circulation Experiment (WOCE), Joint Global Ocean Flux Study (JGOFS), and Climate Variability and Predictability (CLIVAR) programs. Several methods have been used to examine the penetration of fossil fuel into the oceans (Millero 2007). The two most popular methods at the present time are (*a*) using measurements of total CO_2 and correcting the amount due to the oxidation of plant material and the dissolution of CaCO₃ using Redfield ratios (Gruber et al. 1996) and (*b*) using measurements of total CO_2 and other chemical parameters (i.e., oxygen and nutrients) as a function of time (multiple linear regression and extended multiple linear regression) (Friis et al. 2005).

I was indirectly involved in the development of the first method. This work started with a paper by Peter Brewer and colleagues in which they used the Redfield model to understand the dissolution of $CaCO_3$ in seawater (Brewer et al. 1975). Arthur Chen (1978) put some math into their results and described how to use the model to examine the CO_2 system. At a dinner meeting with Peter and Arthur at my home, we discussed this method and thought that it could be used to study the uptake of CO_2 in the oceans. Peter wrote a paper on using the method (Brewer 1978), and Arthur wrote a similar paper, making me a coauthor (Chen & Millero 1979). Arthur continued to use this method to examine the input of CO_2 into various oceans and made, I believe, the first global estimate of CO_2 uptake in the ocean (Chen 1993). Although it was quickly criticized by some (Broecker et al. 1985), the Brewer and Chen method is still used in a modified form to examine CO_2 uptake in the major oceans (Gruber et al. 1996).

My review of the CO₂ system (Millero 2007) gave a summary of some of the earlier estimates of CO₂ uptake by Sabine et al. (2004). Wanninkhof et al. (1999) made a comparison of the ΔC^* method (Gruber et al. 1996) and the multiple linear regression method (Friis et al. 2005) for estimating the input of anthropogenic CO₂ into the oceans. The methods give similar overall results but have substantial differences in the distributions in the water column. Most of the present estimates are made using both methods. The CO₂ studies of the CLIVAR program have allowed us to examine the changes in CO₂ uptake and decreases in pH as a function of time (Waters et al. 2013) and the penetration into deeper waters.

OCEAN CRUISES

Over the years, I have gone on a number of scientific cruises that have been important in developing my work in marine chemistry and chemical oceanography. My first cruise, in 1968, was from Miami to Bermuda on the R/V *Pillsbury*. The cruise was planned by Associate Dean Richard Bader to introduce newcomers to ocean measurements. I made some pH measurements as a function of depth on the cruise with pH electrodes (not very eloquent, but the profiles were similar to modern measurements). As it turned out, the cruise became quite famous because it started a love affair between a chemical oceanography student, Ruth Eisemann-Schier, and a marine technician, Gary Krist, who later kidnapped a young heiress and buried her in a ventilated wooden box that had

been constructed on our campus. They demanded a \$500,000 ransom, and Krist used one of the school's small boats to pick up the money. When confronted by police near where he had parked their car, he dropped the money, and he and Eisemann-Schier took off in different directions. Krist asked for another drop of the ransom money and picked it up, then bought a boat and attempted to get away by traveling across Florida. He was later caught near Tampa and went to prison for 20 years. Eisemann-Schier had the honor of being the first woman to appear on the FBI's Ten Most Wanted list, and was found a few months later in Oklahoma working as a carhop; she had applied for a nursing job that required fingerprints, which by then were known by the FBI. After serving several years in prison, she was paroled and deported to her home in Honduras. When Krist was released from prison, he settled in Alabama, and he later served another prison term after being found guilty of importing drugs and humans from Columbia and growing marijuana underground at his farm. While in prison, he wrote a book that further discusses his life.

John Morse and Arthur Chen joined me in 1976 on a CO_2 cruise in the Mediterranean Sea. We made some of the early measurements of total alkalinity, pH, and total inorganic carbon near Gibraltar (Millero et al. 1979). Because the border between Gibraltar and Spain was closed, to leave Gibraltar, we had to go to Tangiers and take a boat back to Spain. Arthur could not make the trip because he was from Taiwan and could not get a visa. John and I had an interesting time in Tangiers, enjoying the food and the night life.

A few years later, we returned to the Mediterranean on another cruise. I brought a vibrating tube densitometer and made the first density measurements on a ship, with the goal of determining how the oxidation of plant material affected the composition of seawater (Millero et al. 1978b, 2011). These effects were first suggested by Brewer & Bradshaw (1975). We also made density measurements in the North Atlantic and Pacific Oceans (Millero et al. 1976a, 1978a, 2009a) to examine these effects in the major oceans, and continued to examine them as part of our global studies on the WOCE, JGOFS, and CLIVAR cruises (Millero 2001a; Millero et al. 2008b, 2009a, 2011). Because of the changes in composition, the conductivity measurements are not affected by nonelectrolytes (CO₂, SiO₂, and organics), but the density is. Our work on estuaries (Millero 1984) suggested that the properties of natural waters were due more to the absolute salinity (S_A) in those waters. S_A is important because it directly affects the ocean density and enthalpy used by physical oceanographers. This led to the definition of the S_A of seawater (in grams per kilogram) (Millero et al. 2008a) and the new TEOS-10 equation of state (Intergov. Oceanogr. Comm. et al. 2010), which is a function of S_{iA} . The values of S_A in ocean waters can be estimated using a correlation with the concentrations of SiO₂ in the waters (McDougall et al. 2012).

John Morse and I made several summer cruises to the Bahamas from 1980 to 2009. We were interested in how carbonate whitings formed. On our first cruise, we repeated an earlier study by Broecker & Takahashi (1966). We published several papers on our results (Morse et al. 1984, 2003; Bustos et al. 2009). We found that active precipitation of CaCO₃ occurred slowly during the year, with a maximum in the summer, and occurred only when the saturated waters from the Gulf Stream came over the shelf (Bustos et al. 2009).

Several of the cruises took place at a time when drug boats made frequent trips between the Bahamas and Miami, and on one of the cruises, we were advised at one point to leave an area where planes would be dropping marijuana. Later on the same cruise, I was sunning on the back deck of the R/V *Calanus* one day, enjoying a bottle of beer after a day of diving, when a boat appeared from Andros Island and circled the ship. It finally pulled up to the side, whereupon a man pointed a submachine gun at me. Needless to say, I was shaking. Fortunately, the captain was a Reaganite, and he and the crew came forward with guns pointed at the would-be kidnapper. He decided to flee, and we left the area.

One of the most pleasant cruises I went on was by car, in Italy, studying the Tiber River (Millero et al. 1981, Pettine et al. 1982). I spent my one and only sabbatical leave in Rome in 1980. The cruise started at the beginning of the Tiber in Tuscany, near the birthplace of Michelangelo. We collected samples all along the river to Ostia, where it enters the Mediterranean, and enjoyed fine wines with lunch and dinner at some of the most famous restaurants near the river.

Before I went to Italy on my sabbatical, I went on a cruise from Djibouti through the Red Sea to Gibraltar on the R/V *Columbus Iselin*, which was on its way back to Miami after a series of physical oceanographic cruises in the Red Sea. A large group of Europeans joined me on the cruise (including David Dyrssen, Leif Anderson, Angelo Piro, Michéle Loijens, and C. Brunet, to name a few I remember). After a long plane ride, I arrived in Djibouti only to see the group leaving the ship. It turned out that the ship had only one working engine. On the first evening, one of the crew fell asleep while refueling, causing oil to flow into the lab and lower cabins in the ship.

I bought 14 cases of Kronenbourg beer in Djibouti that came in handy later on the cruise. I lost one case during a storm one evening, so my cabin had a pleasant smell of beer for the remainder of the trip. We could not keep up with a convoy through the Suez Canal with one engine and were put off in the Great Bitter Lake to wait for a tow. The wait lasted for a week, which we spent making CO_2 measurements of the surface waters and drinking beer. I suspect that someone studying the sediments in the lake will someday be surprised to find empty beer bottles on the bottom.

We were towed to Port Said, where they wanted twice as much money for the tow as was originally agreed upon. We stayed in the port for a week under a police guard. They charged us for shore passes but never allowed us to go ashore. We could make contact with Miami only once a day, which made it difficult to get help from there. Finally, the captain used the ship's pay to get us out of the port. We limped our way into the Mediterranean, taking a few stations along the way. We wanted to get the engine fixed in Malta but were refused.

We finally got to Naples to wait for a new engine, and most of the Europeans left to get back to work. Since my family was coming to Italy to join me on my sabbatical leave, I took a train to Rome and surprised them at the airport. They came with five trunks of clothes for all of us. I was able to put all the trunks in the bottom of the bus to Rome by pretending that I did not understand the bus driver, who was not happy with my taking up all the space. After getting off the bus, I hired two taxis to get all of us and our luggage to the Hotel Caprice. Once I had everyone settled into a nice apartment and got the kids in school, I made my way back to Naples, and Angelo Piro and I finished the cruise into the Atlantic. The ship then went on to Miami, and we took a plane back to Rome. During the rest of my stay in Italy, I wrote the first edition of my book *Chemical Oceanography* (Millero & Sohn 1991).

I was fortunate to go on the first Iron Enrichment Experiment (IronEx I) cruise on the R/V *Columbus Iselin* in the Pacific. Wensheng Yao and I made all the CO_2 measurements on the cruise. It was quite exciting to see the total CO_2 and nutrients go down (Millero 1997a,b) and the chlorophyll go up after the iron addition (Martin et al. 1994, Watson et al. 1994). The experiment lasted only three days owing to the appearance of a salinity front that sunk the surface water to a depth of around 30 m.

As part of the IronEx I experiment, we made continuous measurements of pCO_2 and NO_3^- around and between the Galapagos Islands (Millero et al. 1998). The measurements between the islands yielded waters with near-zero NO_3^- and decreases in pCO_2 of 100 µatm (Millero et al. 1998, Sakamoto et al. 1998), which were apparently caused by Fe(II) coming from the anoxic sediments. This was a natural iron addition experiment.

We later participated in the second Iron Enrichment Experiment (IronEx II) south of the Galapagos Islands (Coale et al. 1996). This experiment lasted for more than 20 days, during

which the pCO_2 decreased by 73 µatm and the NO₃⁻ decreased by 4 µM. We made continuous measurements of pCO_2 and nutrients and used them to examine the composition of the diatoms formed after the addition. The results were quite different from the Redfield model (Steinberg et al. 1998):

We also later participated in the Southern Ocean Iron Experiment (SOFeX), which added iron in northern and southern patches in the Southern Ocean (Coale et al. 2004). The SiO₂ concentrations are low in the north and high in the south, near Antarctica. Experiments in the Southern Ocean (Boyd et al. 2000, Bakker et al. 2001) gave similar results for the pull-down of nutrients and CO₂ in this ocean (Hiscock & Millero 2005).

Hein de Baar and colleagues published a synthesis paper on the results of all the iron fertilization experiments (de Baar et al. 2005). The experiments showed a maximum in chlorophyll and a minimum in dissolved inorganic carbon (DIC). The overall DIC/Fe efficiency scaled inversely with the depth of the mixed layer as defined by the light environment. The patch dilution, sea surface irradiance, temperature, and grazing played additional roles.

Our early kinetic studies dealt with the oxidation of H_2S in anoxic basins. We first studied the oxidation in the laboratory by adding small amounts of H_2S to water and seawater with various levels of O_2 and H_2O_2 in a closed container. The measurements were made as functions of pH, temperature, and concentration (Millero et al. 1987a,b, 1989b; Zhang & Millero 1994). These results indicated that HS^- was easier to oxidize than H_2S . We then examined the effects of trace metals on oxidation rates and found that iron at nanomolar levels and manganese at micromolar levels affected the rates of oxidation of H_2S in seawater (Vazquez et al. 1989).

In further studies, we examined the rates of oxidation of sulfites in seawater and were able to develop a mechanism for the oxidation of H_2S to SO_3^{2-} and SO_4^{2-} (Zhang & Millero 1991). The first cruise I went on to test the laboratory results was in the Black Sea in 1988. A Russian ship made a daily run at our ship to harass us. But the Russian crew appeared to be happy one day when we had a swim call, and about 40 of them also jumped into the water when we swam. I was able to measure the oxidation rates of deep waters and surface waters in a system we used in the lab and found that they were much higher for deeper waters (Millero 1991c). We also did some kinetic measurements on the adsorption of rare earths (Schijf et al. 1994). My student Bill Hiscock went on a later cruise to the Black Sea and measured carbon and nutrients in the waters (Hiscock & Millero 2006).

My next field study was in the Framvaren Fjord. The H_2S concentrations in the deep waters of the fjord are as high as 6,000 μ M, which is similar to the pore water levels of anoxic sediments. Since the concentrations of iron and manganese are high in the deep waters, the oxidation rates are also very high (Millero 1991b). Wensheng Yao and I had another chance to go to the Framvaren Fjord in 1990 (Yao & Millero 1995a,b).

The next fieldwork took place in Chesapeake Bay. In the summer, the deep river waters near the US Naval Academy become anoxic. Again, the high levels of iron and manganese coming out of the sediments made the rates of oxidation of H_2S very high (Millero 1991c).

The last field study was in the Cariaco Trench, where my student Jia-Zhong Zhang went on a cruise into the trench and carried out CO_2 and nutrient studies. A comparison over time showed that H_2S was increasing. The basin appears to have been reoxygenated in the past by the sloughing off of shelf sediments, perhaps because of earthquakes (Zhang & Millero 1993).

AFTERTHOUGHTS

It is important for me to acknowledge all of the students, postdocs, research assistants, and scientific colleagues who have worked with me over the years. Many of my students have become successful scientists, teachers, doctors, and environmentalists, and my interactions with them have been exciting and fulfilling for me as a scientist and as a human being.

The development of my thoughts on chemical oceanography and marine chemistry was influenced by books edited by John Riley and Geoffrey Skirrow (Riley & Skirrow 1965, 1975). My books on chemical oceanography (e.g., Millero 2013) were patterned on those works, with a bit of added physical chemistry. Early in my career, I had a pleasant visit with John Riley and stayed at his home. Andrew Dickson, his student and a longtime friend of mine, showed me around Liverpool pubs that were frequented by the Beatles.

Many of the geochemists working in the field when I started were very helpful in my early development. They include Bob Garrels, Werner Stumm, Jim Morgan, and Bob Berner. Harmon Craig was helpful in my early work on the thermodynamics of seawater. Wally Broecker gave me a chance to write a review article on the physical chemistry of seawater (Millero 1974a), and Ed Goldberg gave me a chance to write some chapters in Volumes 5 and 6 of *The Sea* (Millero 1974b, 1977), which let me show how ionic interaction models could be used to estimate the thermodynamic properties of seawater and the speciation of metals. Karl Turekian gave me a chance to write some reviews on the physiochemical controls on seawater (e.g., Millero 2003). Kilho Park funded my first National Science Foundation proposal to study ionic interactions in seawater after I had quite a few proposals turned down by reviewers who did not want me to enter the field.

Lastly, I want to acknowledge the late John Morse, a dear friend who taught me the fundamentals of the kinetics of dissolution and precipitation of CaCO₃ in natural waters. Early in my career, I had the opportunity to go to the 1975 Dahlem Conference on the Nature of Seawater, in West Berlin. At this meeting, I met scientists from around the world who were interested in seawater. As with most scientific meetings, a lot of time was spent discussing science over a few beers. One



Figure 1

A free ion in an aqueous solution.



Figure 2

A complex between a cation and an anion.

evening, the meeting organizers let us go to dinner at any restaurant in the city we chose, telling us that they would pick up the tab. Bob Berner and I ended up in a French restaurant, and after we drank a number of their best wines, the meeting paid the \sim \$750 bill.

Finally, I leave you with my young son's versions of a free ion and a complex or ion pair, which have been seen by all the undergraduates in my marine chemistry classes who have suffered through my book *Chemical Oceanography* (Millero 2013) (**Figures 1** and **2**).

DISCLOSURE STATEMENT

The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

I thank Craig Carlson for inviting me to contribute this review on my work over the years. I am grateful to all my coauthors, including students, technicians, and colleagues from around the world, who have been important contributors to my scientific contributions. The students include 8 high school students, 22 undergraduate students, and 43 graduate students, all of whom have gone on to successful careers. My early funding on the equation of state of seawater was supported by the Navy and Oceanographic Section of the National Science Foundation (NSF). The NSF has provided continued funding over the years, and after the Navy stopped supporting chemical oceanography, the National Oceanic and Atmospheric Administration funded our CO₂ work, including studies performed as part of the WOCE, JGOFS, and CLIVAR programs. The NSF also supported our work on IronEx I and II in the South Pacific and SOFeX in the Southern Ocean.

LITERATURE CITED

- Bakker DCE, Watson AJ, Law CS. 2001. Southern Ocean iron enrichment promotes inorganic carbon drawdown. Deep-Sea Res. II 48:2483–507
- Boyd PW, Watson AJ, Law CS, Abraham ER, Trull T, et al. 2000. A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. *Nature* 407:695–702
- Brewer PG. 1978. Direct observation of the oceanic CO2 increase. Geophys. Res. Lett. 5:997-1000
- Brewer PG, Bradshaw A. 1975. The effect of non-ideal composition of seawater on salinity and density. J. Mar. Res. 33:157-75
- Brewer PG, Wong G, Spenser E. 1975. An oceanic calcium problem? Earth Planet. Sci. Lett. 26:81-87
- Broecker WS, Takahashi T. 1966. Calcium carbonate precipitation on the Bahama Banks. J. Geophys. Res. 71:1575-602
- Broecker WS, Takahashi T, Peng T-H. 1985. Reconstruction of the past atmospheric CO₂ contents of the chemistry of the contemporary ocean: an evaluation. Tech. Rep. DOE/OR 857, US Dep. Energy, Washington, DC
- Bustos H, Morse JW, Millero FJ. 2009. The formation of whitings on the Little Bahama Banks. *Mar. Chem.* 113:1–8
- Chanson M, Millero FJ. 2006. The solubility of boric acid in electrolyte solutions. J. Solut. Chem. 35:689-703
- Chen C-TA. 1978. Decomposition of calcium carbonate and organic carbon in the deep oceans. Science 201:735-36
- Chen C-TA. 1993. The oceanic anthropogenic CO2 sink. Chemosphere 27:1041-64
- Chen C-TA, Chen L-S, Millero FJ. 1978. The speed of sound in NaCl, MgCl₂, Na₂SO₄, and MgSO₄ aqueous solutions as functions of concentration, temperature, and pressure. *J. Acoust. Soc. Am.* 63:1795–800
- Chen C-TA, Emmet RT, Millero FJ. 1977a. The apparent molal volumes of aqueous solutions of NaCl, KCl, MgCl₂, Na₂SO₄, and MgSO₄ from 0 to 1000 bars at 0, 25, and 50°C. *J. Chem. Eng. Data* 22:201–7
- Chen C-TA, Fine RA, Millero FJ. 1977b. The equation of state of pure water determined from sound speeds. *J. Chem. Phys.* 66:2142–44
- Chen C-TA, Millero FJ. 1979. Gradual increase of oceanic CO2. Nature 277:205-6
- Chen C-TA, Millero FJ. 1981. The equation of state of D₂O determined from sound speeds. *J. Chem. Phys.* 75:3553–58
- Coale KH, Johnson KS, Chavez FP, Buesseler KO, Barber RT, et al. 2004. Southern Ocean Iron Enrichment Experiment: carbon cycling in high- and low-Si waters. *Science* 304:408–14
- Coale KH, Johnson KS, Fitzwater SE, Gordon RM, Tanner S, et al. 1996. A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean. *Nature* 383:495– 501
- Connaughton LM, Hershey JP, Millero FJ. 1986. PVT properties of concentrated electrolytes. V. The density of NaCl, Na₂SO₄, MgCl₂ and MgSO₄ from 0 to 100°C. *J. Solut. Chem.* 15:989–1002
- de Baar HJW, Boyd PW, Coale KH, Landry MR, Tsuda A, et al. 2005. Synthesis of iron fertilization experiments: from the iron age in the age of enlightenment. *J. Geophys. Res.* 110:C09S16
- Dickson AG, Millero FJ. 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Res.* 34:1733–43
- Duedall IW. 1968. Partial molal volumes of 16 salts in seawater. Environ. Sci. Technol. 2:706-7
- Duer WC, Leung WH, Oglesby GB, Millero FJ. 1976. Seawater—a test for multicomponent electrolyte solution theories. II. Enthalpy of mixing and dilution of the major sea salts. J. Solut. Chem. 5:509–28
- Fine RA, Millero FJ. 1975. The high pressure PVT properties of deuterium oxide. 7. Chem. Phys. 63:89-95
- Friis K, Körtzinger A, Pätsch J, Wallace DWR. 2005. On the temporal increase of anthropogenic CO₂ in the subpolar North Atlantic. *Deep-Sea Res. I* 52:681–98
- Gleitz M, Rutgers M, Loeff VD, Thomas DN, Dieckmann GS, Millero FJ. 1995. Seasonal changes of inorganic carbon, oxygen and nutrient concentrations in Antarctic Sea ice brines. *Mar. Chem.* 51:81–91
- González-Dávila M, Santana-Casiano JM, Millero FM. 2005. Oxidation of iron (II) nanomolar with H₂O₂ in seawater. *Geochim. Cosmochim. Acta* 69:83–93
- González-Dávila M, Santana-Casiano JM, Millero FM. 2006. Competition between O_2 and H_2O_2 in the oxidation of Fe(II) in seawater. *J. Solut. Chem.* 35:95–111

- Gordon AS, Millero FJ. 1983. Measurement of attached bacteria using a sorption microcalorimeter. J. Microbiol. Methods 1:291–96
- Gordon AS, Millero FJ. 1987. Sorption of copper by a marine vibrio in seawater. Va. J. Sci. 38:194-99
- Gordon AS, Millero FJ, Gerchakov SM. 1982. Microcalorimetric measurements of glucose metabolism by marine bacterium Vibrio alginolyticus. Appl. Environ. Microbiol. 44:1102–9
- Goyet C, Poisson A. 1989. New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity. *Deep-Sea Res. A* 36:1635–54
- Gruber N, Sarmiento J, Stocker T. 1996. An improved method for detecting anthropogenic CO₂ in the oceans. *Glob. Biogeochem. Cycles* 10:809–37
- Hansson I. 1973. A new set of acidity constants for carbonic acid and boric acid in seawater. Deep-Sea Res. Oceanogr. Abstr. 20:461–78
- Hepler LG. 1957. Partial molal volumes of aqueous ions. J. Phys. Chem. 61:1426-28
- Hiscock W, Millero FJ. 2005. Nutrient and carbon parameters during the Southern Ocean Iron Experiment (SOFeX). Deep-Sea Res. I 52:2086–108
- Hiscock W, Millero FJ. 2006. Alkalinity of the anoxic waters in the western Black Sea. Deep-Sea Res. II 53:1787–801
- Intergov. Oceanogr. Comm., Sci. Comm. Ocean. Res., Int. Assoc. Phys. Sci. Ocean. 2010. The international thermodynamic equation of seawater—2010: calculation and use of thermodynamic properties. Man. Guides No. 56, Intergov. Oceanogr. Comm., UN Educ. Sci. Cult. Organ., Paris
- King DW, Lounsbury HA, Millero FJ. 1995. Rates and mechanism of Fe(II) oxidation at nanomolar concentrations. *Environ. Sci. Technol.* 29:818–24
- Latimer WM. 1952. Oxidation Potentials. Englewood, NJ: Prentice Hall. 2nd ed.
- Lepple FK, Millero FJ. 1971. The isothermal compressibility of seawater near one atmosphere. *Deep-Sea Res.* Oceanogr. Abstr. 18:1233–54
- Lewis E, Wallace DWR. 1998. Program developed for CO₂ system calculations. Rep. ORNL/CDIAC-105, Oak Ridge Natl. Lab., Oak Ridge, TN
- Lewis GN, Randall M. 1961. Thermodynamics. Revis. KS Pitzer, L Brewer. New York: McGraw-Hill. 2nd ed.
- Martin JH, Coal KH, Johnson KS, Fitzwater SE, Gordon RM, et al. 1994. Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean. *Nature* 371:123–29
- McDougall TJ, Jackett DR, Millero FJ, Pawlowicz R, Barker PM. 2012. A global algorithm for estimating absolute salinity. Ocean Sci. 8:1117–28
- Mehrbach C, Culberson CH, Hawley JE, Pytkowicz RM. 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.* 18:897–907
- Millero FJ. 1967. High precision magnetic float densimeter. Rev. Sci. Instrum. 38:1441-44
- Millero FJ. 1968. Relative viscosity and apparent molal volume of N-methylpropionamide solutions at various temperatures. *J. Phys. Chem.* 72:3209–14
- Millero FJ. 1969. The partial molal volume of ions in seawater. Limnol. Oceanogr. 14:376-85
- Millero FJ. 1971. The molal volumes of electrolytes. Chem. Rev. 71:147-76
- Millero FJ. 1972. The partial molal volumes of electrolytes in aqueous solution. In *Structure and Transport* Processes in Water and Aqueous Solutions, ed. RA Horne, pp. 519–95. New York: Wiley-Interscience
- Millero FJ. 1974a. The physical chemistry of seawater. Annu. Rev. Earth Planet. Sci. 2:101–150
- Millero FJ. 1974b. Seawater as a multicomponent electrolyte solution. In *The Sea: Ideas and Observations on Progress in the Study of the Seas*, Vol. 5: *Marine Chemistry*, ed. ED Goldberg, pp. 3–80. New York: Wiley-Interscience
- Millero FJ. 1977. Thermodynamic models for the state of metal ions in seawater. In *The Sea: Ideas and Observations on Progress in the Study of the Seas*, Vol. 6: *Marine Modeling*, ed. ED Goldberg, IN McCave, JJ O'Brien, JH Steele, pp. 653–93. New York: Wiley-Interscience
- Millero FJ. 1979a. Effects of pressure and temperature on activity coefficients. In Activity Coefficients in Electrolyte Solutions, Vol. 2, ed. RM Pytkowicz, 63–151. Boca Raton, FL: CRC Press
- Millero FJ. 1979b. The thermodynamics of the carbonate system in seawater. *Geochim. Cosmochim. Acta* 43:1651-61
- Millero FJ. 1982a. The effect of pressure on the solubility of minerals in water and seawater. Geochim. Cosmochim. Acta 46:11–22

- Millero FJ. 1982b. Use of models to determine ionic interactions in natural waters. Thalass. Jugosl. 18:253-91
- Millero FJ. 1983a. Influence of pressure on chemical processes in the sea. In *Chemical Oceanography*, Vol. 5, ed. JP Riley, R Chester, 1–88. London: Academic. 2nd ed.
- Millero FJ. 1983b. The thermodynamics of seawater, part II. Thermochemical properties. Ocean Sci. Eng. 8:1-40
- Millero FJ. 1984. The conductivity-density chlorinity relationship for estuarine water. *Limnol. Oceanogr.* 29:1317–21
- Millero FJ. 1985. The effect of ionic interactions on the oxidation of metals in natural waters. *Geochim. Cosmochim. Acta* 49:547-53
- Millero FJ. 1987. Estimate of the life time of superoxide in seawater. Geochim. Cosmochim. Acta 51:351-53
- Millero FJ. 1991a. The oxidation of H₂S in Chesapeake Bay. Estuar. Coast. Shelf Sci. 33:521-27
- Millero FJ. 1991b. The oxidation of H₂S in Framvaren Fjord. *Limnol. Oceanogr.* 36:1007–14
- Millero FJ. 1991c. The rates of oxidation of H₂S in Black Sea waters. Deep-Sea Res. A 38 (Suppl. 2):S1139-50
- Millero FJ. 1997a. The effect of iron on carbon dioxide in the oceans. Sci. Prog. 80:147-68
- Millero FJ. 1997b. The influence of iron on carbon dioxide in surface seawater. In Marine Chemistry: An Environmental Analytical Chemistry Approach, ed. A Gianguzza, E Pellizzetti, S Sammartano, pp. 381–98. New York: Kluwer Acad.
- Millero FJ. 1999. Modeling the effect of ionic interactions on radionuclides in natural waters. In Actinide Speciation in High Ionic Strength Media, ed. D Reed, SB Clark, L Rao, pp. 39–61. New York: Kluwer Acad.

Millero FJ. 2000. The activity coefficients of non-electrolytes in seawater. Mar. Chem. 70:5-22

Millero FJ. 2001a. Effect of change in the composition of seawater on the density-salinity relationship. *Deep-Sea Res. I* 47:1583–90

Millero FJ. 2001b. Physical Chemistry of Natural Waters. New York: Wiley-Interscience

- Millero FJ. 2003. Physico-chemical controls on seawater. In *The Oceans and Marine Geochemistry*, ed. H Elderfield, pp. 1–21. Treatise Geochem. Vol. 6. Oxford, UK: Elsevier
- Millero FJ. 2007. The marine inorganic carbon cycle. Chem. Rev. 107:308-41
- Millero FJ. 2010a. Carbonate constants for estuarine waters. Mar. Freshw. Res. 61:130-43
- Millero FJ. 2010b. History of the equation of state of seawater. Oceanography 23(3):18-33
- Millero FJ. 2013. Chemical Oceanography. Boca Raton, FL: CRC Press. 4th ed.
- Millero FJ, Chen C-TA, Bradshaw A, Schleicher K. 1980. A new high pressure equation of state for seawater. Deep-Sea Res. A 27:255–64
- Millero FJ, DiTrolio B. 2010. Use of thermodynamics in examining the effects of ocean acidification. *Elements* 6:293–97
- Millero FJ, Drost-Hansen W. 1968. Apparent molal volumes of monovalent salt solutions at various temperatures. J. Chem. Eng. Data 13:330–33
- Millero FJ, Feistel R, Wright DG, McDougall TJ. 2008a. The standard composition of seawater: the definition of a reference salinity scale. *Deep-Sea Res. I* 55:50–72
- Millero FJ, Forsht D, Means D, Gieskes J, Kenyon K. 1978a. The density of North Pacific Ocean waters. *7. Geophys. Res.* 83:2359–64
- Millero FJ, Gonzalez A, Brewer PG, Bradshaw A. 1976a. The density of North Atlantic and North Pacific deep waters. *Earth Planet. Sci. Lett.* 32:468–72
- Millero FJ, Gonzalez A, Ward GK. 1976b. The density of seawater solutions at one atmosphere as a function of temperature and salinity. J. Mar. Res. 34:61–93
- Millero FJ, Graham T, Huang F, Bustos H, Pierrot D. 2006. Dissociation constants for carbonic acid in seawater as a function of temperature and salinity. *Mar. Chem.* 100:80–94
- Millero FJ, Hansen LD, Hoff EV. 1973a. The enthalpy of seawater from 0 to 30°C and 0 to 40‰ salinity. *7. Mar. Res.* 31:21–39
- Millero FJ, Hershey JP. 1989. Thermodynamics and kinetics of hydrogen sulfide in natural waters. In *Biogenic Sulfur in the Environment*, ed. ES Saltzman, WJ Cooper, pp. 282–313. Washington, DC: Am. Chem. Soc.
- Millero FJ, Hershey JP, Johnson G, Zhang JZ. 1989a. The solubility of SO₂ and the dissociation of H₂SO₃ in NaCl solutions. *J. Atmos. Chem.* 8:377–89
- Millero FJ, Huang F. 2009. The density of seawater as a function of salinity (5 to 70 g kg⁻¹) and temperature (273.15 to 363.15 K). Ocean Sci. 5:91–100

- Millero FJ, Huang F. 2011. The compressibility of seawater from 0 to 95°C at 1 atm. Mar. Chem. 126:149-54
- Millero FJ, Huang F. 2013. The partial molal volume and compressibility of salts in seawater. Geochim. Cosmochim. Acta 104:19–28
- Millero FJ, Huang F, Laferriere AL. 2002. The solubility of oxygen in the major sea salts and their mixtures. Geochim. Cosmochim. Acta 66:2349–59
- Millero FJ, Huang F, Williams N, Waters J, Woosley R. 2009a. The effect of composition on the density of South Pacific Ocean waters. Mar. Chem. 114:56–62
- Millero FJ, Huang F, Woosley R, Letcher R, Hansell D. 2011. Effect of dissolved organic carbon and alkalinity on the density of Arctic Ocean waters. *Aquat. Geochem.* 17:311–26
- Millero FJ, Hubinger S, Fernandez M, Garnett S. 1987a. The oxidation of H₂S in seawater as a function of temperature, pH and ionic strength. *Environ. Sci. Technol.* 21:439–43
- Millero FJ, Knox JH, Emmet RT. 1972. A high-precision, variable-pressure magnetic float densimeter. J. Solut. Chem. 1:173–86
- Millero FJ, Laferriere AL, Fernandez M, Hubinger S, Hershey JP. 1989b. Oxidation of hydrogen sulfide with hydrogen peroxide. *Environ. Sci. Technol.* 23:209–13
- Millero FJ, Leung WH. 1976. The thermodynamics of seawater at one atmosphere. Am. 7. Sci. 276:1035-77
- Millero FJ, Macchi G, Pettine M. 1981. The speciation of ions in Tiber river estuary waters. *Estuar. Coast.* Sbelf Sci. 13:517–34
- Millero FJ, Means D, Miller CM. 1978b. The densities of Mediterranean Sea waters. Deep-Sea Res. 25:563-69
- Millero FJ, Morse JW, Chen C-TA. 1979. The carbonate system in the western Mediterranean Sea. Deep-Sea Res. A 26:1395–404
- Millero FJ, Perron G, Desnoyers JE. 1973b. Heat capacity of seawater solutions from 5 to 35°C and 0.5 to 22% chlorinity. J. Geophys. Res. 78:4499–507
- Millero FJ, Pierrot D. 1998. A chemical model for natural waters. Aquat. Geochem. 4:153-99
- Millero FJ, Pierrot D. 2002. Speciation of metals in natural waters. In Chemistry of Marine Water and Sediments, ed. A Gianguzza, E Pellizzetti, S Sammartano, pp. 193–220. Berlin: Springer-Verlag
- Millero FJ, Pierrot D. 2005. The thermochemical properties of seawater fit to the Pitzer equations. *Mar. Chem.* 94:81–99
- Millero FJ, Pierrot D. 2007. The activity coefficients of Fe(III) complexes with hydroxide in NaCl and NaClO₄ solutions. *Geochim. Cosmochim. Acta* 71:4825–33
- Millero FJ, Poisson A. 1981. International one-atmosphere equation of state of seawater. *Deep-Sea Res. A* 28:625–29
- Millero FJ, Roy RN. 1997. A chemical equilibrium model for the carbonate system in natural waters. *Croat. Chem. Acta* 70:1–38
- Millero FJ, Schreiber DR. 1982. Use of the ion pairing model to estimate activity coefficients of the ionic components of natural waters. *Am. J. Sci.* 282:1508–40
- Millero FJ, Sharma VK, Karn B. 1991. The rate of reduction of Cu(II) with hydrogen peroxide in seawater. Mar. Chem. 36:71–83
- Millero FJ, Sharp JD. 2013. Estimation of the partial molal adiabatic compressibility of ions in mixed electrolyte solutions using the Pitzer equations. 7. Chem. Eng. Data 58:3458–63
- Millero FJ, Sohn ML. 1991. Chemical Oceanography. Boca Raton, FL: CRC Press
- Millero FJ, Sotolongo S. 1989. The oxidation of Fe(II) with H₂O₂ in seawater. *Geochim. Cosmochim. Acta* 53:1867-73
- Millero FJ, Sotolongo S, Izaguirre M. 1987b. The kinetics of oxidation of Fe(II) in seawater. Geochim. Cosmochim. Acta 51:793–801
- Millero FJ, Vinokurova F, Fernandez M, Hershey JP. 1987c. PVT properties of concentrated electrolytes. VI. The speed of sound and apparent molal compressibilities of NaCl, Na₂SO₄, MgCl₂ and MgSO₄ solutions from 0 to 100°C. *7. Solut. Chem.* 16:269–84
- Millero FJ, Waters J, Woosley R, Huang F, Chanson M. 2008b. The effect of composition of the density of Indian Ocean waters. *Deep-Sea Res. I* 55:460–70
- Millero FJ, Woosley R. 2009. The hydrolysis of Al(III) in NaCl solutions: a model for Fe(III). *Environ. Sci. Technol.* 43:1818–23

- Millero FJ, Woosley R, DiTrolio B, Waters J. 2009b. The effect of ocean acidification on the speciation of metals in natural waters. *Oceanography* 22(4):72–85
- Millero FJ, Yao W, Lee K, Zhang J-Z, Campbell DM. 1998. Carbonate system in the waters near the Galapagos Islands. *Deep-Sea Res. II* 45:1115–34
- Moffett JW, Zika RG. 1977. Reaction kinetics of hydrogen peroxide with copper and iron in seawater. *Environ. Sci. Technol.* 21:804–10
- Moffett JW, Zika RG. 1983. Oxidation kinetics of Cu(I) in seawater: implications for its existence in the marine environment. Mar. Chem. 13:239–51
- Mojica Prieto FJ, Millero FJ. 2002. The values of pK₁ + pK₂ for the dissociation of carbonic acid in seawater. *Geochim. Cosmochim. Acta* 66:2529–40
- Morse JM, Gledhill DK, Millero FJ. 2003. CaCO₃ precipitation kinetics in waters from the Great Bahama Bank. Geochim. Cosmochim. Acta 67:2819–26
- Morse JW, Millero FJ, Brown TE, Ostlund HG. 1984. The carbonate chemistry of Grand Bahama bank waters: after 18 years another look. *J. Geophys. Res.* 89:3604–14
- Park PK. 1969. Oceanic CO₂ system: an evaluation of ten methods of investigation. *Limnol. Oceanogr.* 14:179–86
- Pettine M, La Noce T, Macchi M, Millero FJ. 1982. Heavy metals in the Tiber river basin. *Mar. Pollut. Bull.* 13:327–29
- Pierrot D, Millero FJ. 2000. The apparent molal volume and compressibility of seawater fit to the Pitzer equations. J. Solut. Chem. 29:719–42
- Pitzer KS. 1991. Ion interaction approach: theory and data correlation. In Activity Coefficients in Electrolyte Solutions, ed. KS Pitzer, pp. 75–153. Boca Raton, FL: CRC Press. 2nd ed.
- Poisson A, Chanu J. 1975. The partial molal volumes of some major ions in seawater. *Limnol. Oceanogr.* 21:853–61
- Riley JP, Skirrow G, eds. 1965. Chemical Oceanography. New York: Academic. 1st ed.
- Riley JP, Skirrow G, eds. 1975. Chemical Oceanography. New York: Academic. 2nd ed.
- Rodriguez C, Millero FJ. 2013a. Estimating the densities and compressibilities of seawater to high temperatures using the Pitzer equations. *Aquat. Geochem.* 19:115–33
- Rodriguez C, Millero FJ. 2013b. Modeling the density and isentropic compressibility of seawater. J. Solut. Chem. 42:303–16
- Roy RN, Vogel KN, Moore CP, Pearson T, Roy LN, et al. 1993. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C. *Mar. Chem.* 44:249–67
- Sabine CL, Bullister JL, Feely RA, Gruber N, Key RM, et al. 2004. The oceanic sink for anthropogenic CO₂. *Science* 305:367–71
- Safarov J, Berndt S, Millero FJ, Feistel R, Heintz A, Hassel E. 2012. (p,ρ,T) properties of seawater: extensions to high salinities. *Deep-Sea Res. I* 65:146–56
- Safarov J, Millero FJ, Feistel R, Heintz A, Hassel E. 2009. Thermodynamic properties of standard seawater: extension to high temperature and pressures. *Ocean Sci.* 5:235–46
- Sakamoto CM, Millero FJ, Yao W, Friederich GE, Chavez FP. 1998. Surface seawater distributions of inorganic carbon and nutrients around the Galapagos Islands: results from the PlumEx experiment using automated chemical mapping. *Deep-Sea Res. II* 45:1055–71
- Schijf J, de Baar HJW, Millero FJ. 1994. Kinetics of Ce and Nd scavenging in Black Sea waters. Mar. Chem. 46:345–59
- Schreiber DR, Gordon AS, Millero FJ. 1985. The toxicity of copper to the marine bacterium Vibrio alginolyticus. Can. J. Microbiol. 31:83–87
- Schreiber DR, Millero FJ, Gordon AG. 1990. Production of an extracellular copper binding protein by the heterotrophic marine bacterium *Vibrio alginolyticus. Mar. Chem.* 28:275–84
- Sharma VK, Millero FJ. 1988. Oxidation of copper(I) in seawater. Environ. Sci. Technol. 22:768-71
- Sharma VK, Millero FJ. 1989. The oxidation of Cu(I) with H₂O₂ in natural waters. *Geochim. Cosmochim. Acta* 53:2269–76
- Sharma VK, Millero FJ, De Stefano C, Crea P. 2007. Dissociation constants of protonated methionine species in seawater. Mar. Chem. 106:453–70

Steinberg PA, Millero FJ, Zhu X. 1998. Carbonate system response to iron enrichment. Mar. Chem. 62:31-43

Vazquez F, Zhang JZ, Millero FJ. 1989. Effect of trace metals on the oxidation rates of H₂S in seawater. Geophys. Res. Lett. 16:1363–66

- Wanninkhof R, Doney SC, Peng T-H, Bullister JL, Lee K, Feely RA. 1999. Comparison of methods to determine the anthropogenic CO₂ invasion into the Atlantic Ocean. *Tellus* 51B:511–30
- Waters J, Millero FJ. 2013. The pH of seawater on the free scale. Mar. Chem. 149:19-28
- Waters J, Millero FJ, Sabine CL. 2013. Synthesis and analysis of the carbonate parameters in the Pacific Ocean. *Glob. Biogeochem. Cycles* 25:GB4011
- Watson AJ, Law CS, Van Scoy KA, Millero FJ, Yao W, et al. 1994. Minimal effect of iron fertilization on sea-surface carbon dioxide concentrations. *Nature* 371:143–45
- Woosley R, Millero FJ. 2010. The hydrolysis of Al(III) in NaCl solutions: a model for M(II), M(III), and M(IV) ions. *Aquat. Geochem.* 16:317–24
- Woosley R, Millero FJ. 2013. Pitzer model for the speciation of lead chloride and carbonate complexes in natural waters. *Mar. Chem.* 149:1–7
- Yao W, Millero FJ. 1995a. The chemistry of anoxic waters in the Framvaren Fjord, Norway. *Aquat. Geochem.* 1:53–88
- Yao W, Millero FJ. 1995b. Oxidation of hydrogen sulfide by Mn(IV) and Fe(III) (hydr)oxides in seawater. In *Geochemical Transformation of Sedimentary Sulfur*, ed. MA Vairavamurthy, MAA Schooner, pp. 260–79. Washington, DC: Am. Chem. Soc.
- Young T, Smith MB. 1954. Thermodynamic properties of mixtures of electrolytes in aqueous solutions. *J. Phys. Chem.* 58:716–24
- Zhang JZ, Millero FJ. 1991. The rate of sulfite oxidation in seawater. Geochim. Cosmochim. Acta 55:677-85
- Zhang JZ, Millero FJ. 1993. The chemistry of the anoxic waters in the Cariaco Trench. Deep-Sea Res. I 40:1023-41
- Zhang JZ, Millero FJ. 1994. The kinetics of oxidation of hydrogen sulfide in natural waters. In *Environmental Geochemistry of Sulfide Oxidation*, ed. CN Alpers, D Blowes, pp. 393–409, Washington, DC: Am. Chem. Soc.
- Zika RG. 1981. Marine organic photochemistry. In *Marine Organic Chemistry*, ed. EK Duursma, R Dawson, pp. 299–326. Amsterdam: Elsevier