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PROFILES IN SCIENCE



Dr. Theodore R. Folsom

Dr. Theodore R. Folsom is an oceanographer at Scripps Institution of Oceanography whose studies have been supported by ONR for the past 20 years.

He has pioneered in the development of instruments and methods for following radioactive contaminants in the ocean so as to provide better understanding of water mass movement and the rate of dispersal of radioactivity and other pollutants. He directs Scripps Institution's new Mount Soledad Laboratory for the Study of Marine Radioactivity.

Dr. Folsom has contributed numerous papers and has been consulted continually on matters of radiation hazards, ionizing dosage burdens, and analytical and oceanographic surveying procedures. He has given special attention to the behavior of global fallout in the ocean, and in modeling the upper moving layers of the North Pacific Ocean.

He has contributed to advancement of oceanographic thermometry, plankton sampling, behavior of the rare alkalies in the oceanic environment, particularly the precise determination of natural cesium; also to understanding the behavior of silver and cobalt nuclides from fallout and those of polonium and plutonium in the ocean environment.

Foreword

The Ocean Sciences Program of the Office of Naval Research supports a diverse research effort aimed at improved understanding of the varied and complex marine environments which form the Navy's primary operational areas. Chemical Oceanography is an important part of this research because it bears directly on many Navy problems such as corrosion and deterioration of materials in the marine environment; the monitoring, assessment, and possible control of pollutants in the sea; the interchange of materials across the air-sea and sea-bottom boundaries; the effect of chemical processes on the properties of sound transmission, absorption, and scattering in the marine environment; an improved understanding of the bulk thermodynamic and transport properties of seawater; as well as the use of tracers for the identification of water masses in studying ocean circulation and mixing mechanisms. All of these problems share a common basis in chemistry.

Traditionally, chemical oceanography has been almost completely descriptive, with emphasis on analytical chemistry. In the majority of cases, these studies have been directed solely at identifying water masses to gain insight into their movements and mixing, and at assisting biological investigations, such as productivity studies. More recently, however, the chemical oceanographer has been seeking to elucidate the entire spectrum of physical and chemical processes responsible not only for the composition of the ocean itself, but also for the reactions occurring at the various interfaces (i.e., air-sea, sediment- and land-sea, and suspended material-sea). These considerations embrace the occurrence and distribution of the elements in the ocean and the types of reactions that occur between the various chemical species in solution, as well as the rates and mechanisms of supply and removal of each oceanic component (i.e., the routes and reservoirs).

A major programmatic area in the ONR Chemical Oceanography Program, which is addressing basic research problems related to Navy operational considerations, is concerned with the processes and mechanisms controlling the inorganic composition of seawater. Since this control is determined to a great extent by the physical properties of the medium, investigations on the physical chemistry of seawater form an integral part of the program. The boundaries of physical chemistry are not sharp; they overlap physics on the one side and all branches of chemistry on the other, incorporating many different aspects of chemistry which superficially appear unrelated. The physical chemist draws his facts from many fields of knowledge and

correlates them by means of word descriptions, graphical representations, and mathematical equations to describe, explain and predict natural phenomena.

One fundamental field which underlies much of this aspect of chemistry is thermodynamics, which is the concern of the following discussion by Dr. Millero. Thermodynamics deals with the inter-conversion of various forms of energy and makes it possible to answer the question "How far will this particular reaction go before equilibrium is reached?" A second fundamental field is kinetics, Dr. Atkinson's and Gilligan's interests, which involves the time factor and deals with the problem of how fast chemical reactions occur. A third consideration is oxidation and reduction phenomena, the subject of Dr. Kester's considerations, whereby elements can change their oxidation state (i.e. the number of orbital electrons surrounding the nucleus) and thereby possibly alter the chemical reactions in which they participate. These are three of the important approaches being supported with the objective of gaining an improved understanding of the phased chemistry of the sea.

The following discussions serve as examples not only of work in their specific subject areas, but also as illustrations that individual research tasks which comprise a significant programmatic thrust in the Chemical Oceanography Program of ONR addressing Navy relevant problems, are not being conducted in separate vacuums. Rather, together they are providing the Navy with an improved knowledge base to cope with a number of operational problems, some of which are mentioned in the individual discussions.

TNT is Biodegradable

The Navy continues to search for ways to dispose of its explosives which are economical, safe, and non-polluting. Sometimes it is possible to reclaim the explosive ingredient. With some explosives, such as TNT, it is much cheaper to dispose of the small residues which are left. However TNT is a pollutant.

TNT-contaminated areas at ammunition plants were cleaned by flushing them with water which then flowed into and polluted the streams at the discharge point. Because of the Environmental Protection Agency's water quality standards, this method had to be stopped. Passing the water through charcoal to remove the dissolved TNT by adsorption is an expensive process, but it is one method under consideration.

The Naval Ordnance Laboratory in White Oak, Silver Spring, Maryland, is working on a system to biodegrade TNT. NOL's experimental process uses an

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Chemistry of Iron in Marine Systems

D. R. Kester*
University of Rhode Island

Introduction

A knowledge of chemical equilibria in an aqueous system is a prime factor in defining significant chemical processes within the marine environment. In this discussion, several aspects of the chemistry of iron in the ocean will be considered. Iron was selected as a metallic element for a case study for a variety of reasons. Until recently analytical measurements of iron in seawater provided an unsatisfactory picture of the behavior of this metal in the ocean. Adjacent parcels of deep ocean water which one would expect to be chemically uniform on the basis of oceanographic knowledge have frequently shown differences of a factor of ten in their iron content. The amount of iron in these waters also exceeded the solubility limit estimated for iron hydroxide solid phases. These two observations led to the concept that iron in the ocean existed as very small particles (less than 1×10^{-5} cm in diameter) known as colloids. In order to make reliable evaluations of the behavior of iron in the marine environment, the circumstantial evidence for iron colloids must be replaced by systematic information on the chemical form of this metal in the ocean.

An understanding of the chemistry of iron is important because of its diverse roles in the marine system. There are many natural processes in which iron is a key factor. Under some conditions the growth of marine organisms can be limited by the lack of iron in an appropriate chemical form. Iron is a major component of the economically significant ferro-manganese nodules which form on the seafloor. Suspended particles in the ocean coated with iron may be important in removing other natural or man-made metals from seawater by absorption processes. Finally, iron is a primary component in many of the structural materials used by man in the ocean. The corrosion of these

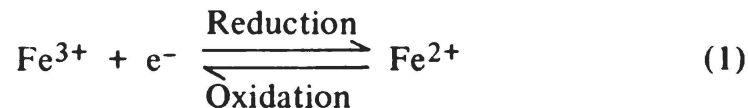
*Dr. Dana R. Kester is an Associate Professor of Oceanography in the Graduate School of Oceanography of the University of Rhode Island, Kingston, Rhode Island. Dr. Kester's research interests have been primarily concerned with oxidation-reduction phenomena in the ocean, using iron as a model. However, he has also made significant contributions to understanding the bases for observed oxygen and fluoride distributions in the marine environment.

metals is influenced by the chemical behavior of iron in seawater. In this discussion the term "iron" will be used to refer to the chemical atom, Fe, which may exist in a large variety of chemical forms such as dissolved ions, Fe^{3+} , sedimentary minerals, Fe_3O_4 , corrosion products, Fe_2O_3 , or a structural steel. As the particular chemical form of the iron becomes important it will be specified.

Several types of chemical processes will be included in this discussion of iron in seawater. The first of these will be redox reactions which determine the oxidation state and hence much of the behavior of the metal. Next, the chemical forms of iron which exist dissolved in seawater under a variety of environmental conditions will be considered. The solid phases of iron will then be examined. The discussion will be concluded with two illustrations of how this chemical knowledge can be related to two problems in the ocean: corrosion and the magnetic properties of marine sediments.

Predox Equilibria

One of the aspects of iron chemistry in the environment and in biological systems is its oxidation-reduction reaction in which ferric, Fe^{3+} , and ferrous, Fe^{2+} , iron interact with electrons:



Whether this equilibrium favors the ferric or the ferrous form depends on the availability of electrons in the system. The redox potential, Eh, is a convenient way of expressing the availability of electrons:

$$\text{Eh} = - \frac{RT}{F} \ln a_e \quad (2)$$

The R is the universal gas constant, T is absolute temperature, F is the Faraday constant, and a_e refers to the thermodynamic activity of electrons in the system. Eh is expressed as a potential in volts, and it can be measured with a suitable electrical circuit or it may be calculated from a_e .

Electrons do not exist freely in seawater; their availability (as measured by Eh or a_e) for a reduction process such as reaction (1) is provided at the expense of some other chemical process in the system. One of the current areas of research is to establish what Eh

of seawater is, and what chemical processes determine it. Theoretical considerations indicate that when seawater contains dissolved oxygen, the availability of electrons for iron will be determined by the reaction:



In some portions of the marine environment, such as organic rich sediments, some Norwegian fjords, and the Black Sea, oxygen is completely consumed from the seawater by biological processes and the availability of electrons is then determined by:



Reactions (3) and (4) are two examples of Eh controlling mechanisms which determine the relative amounts of Fe^{3+} and Fe^{2+} in reactions (1).

A second parameter which is significant in iron chemistry is the acidity of the system. This property is expressed as $\text{pH} = -\log a_{\text{H}}$ where a_{H} is the thermodynamic activity of hydrogen ions in the system.

In considering the behavior of iron in seawater, Eh and pH may be regarded as independent variables which will be determined by the overall chemical characteristics of the environment. A graphical representation of these variables may be formulated and specific chemical reactions and environmental conditions on the Eh-pH diagram can be identified (Figure 1). For an aqueous system there is an upper limit to the Eh which is determined by the chemical properties of water molecules. In Figure 1 this limit is represented by the upper dashed line. Above this line, water is converted to oxygen gas and hydrogen ions. There is also a lower limit for water molecules on the Eh-pH diagram which is shown by the second dashed line. Below this line, water is converted to hydrogen gas and hydroxyl ions. All aqueous environments will occur between these two dashed lines on the Eh-pH diagram.

The effect of reaction (3) in determining Eh is shown by the cross-textured band for oxygen concentrations which are typical of most ocean waters. Eh is relatively insensitive to fairly large variations in oxygen concentration. The Eh-pH stability band which is set by reaction (4) is shown as the stipled region for typical ranges of sulfide concentrations.

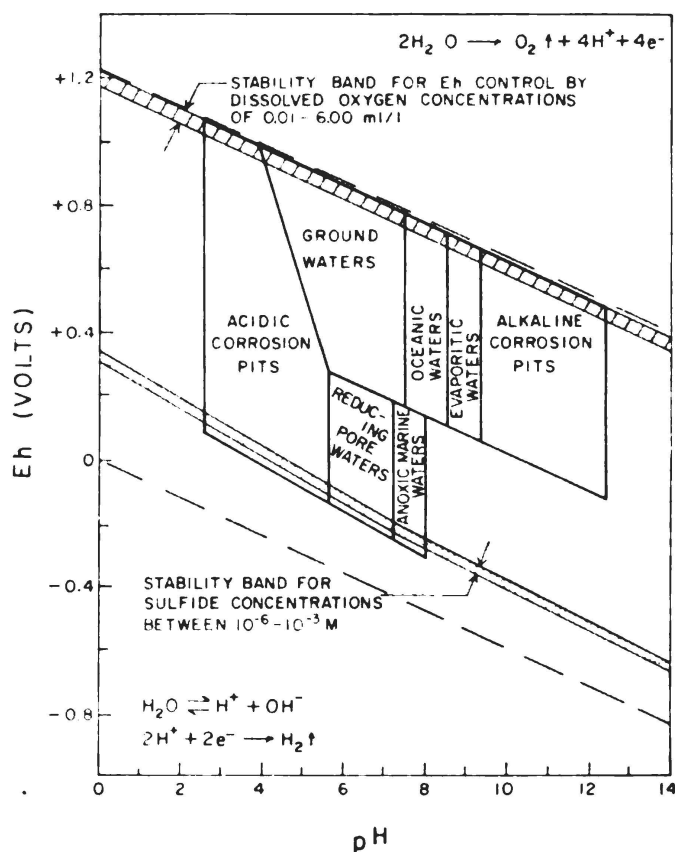


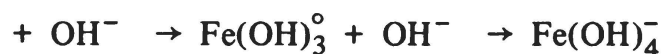
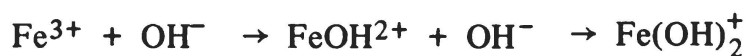
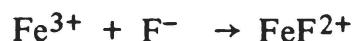
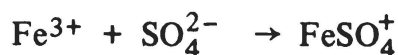
Figure 1 – The Eh-pH diagram for various types of aqueous environments

Superimposed on this Eh-pH diagram are several types of marine and related environments. Most ocean waters have pH values between 7.6-8.3 and have an Eh greater than 0.2 volts. Under evaporative conditions, the pH may increase by about one unit. Anoxic (oxygen-poor) marine waters have a lower Eh and pH than normal ocean water, and the pore water of reducing sediments may be even more extreme. The domain of oxygenated continental ground waters is also shown on the diagram. Later in this discussion, some of the chemical characteristics of the micro-environments associated with pit corrosion in seawater, which may be very acidic and very alkaline relative to normal seawater, will be considered.

Chemistry of Dissolved Iron in Seawater

Having identified the redox potential (Eh), and acidity (pH), as two of the primary variables which influence iron chemistry, the chemical forms of this metal dissolved in seawater may now be considered. Iron is a highly reactive metal with many of the components

in seawater. For example, it forms complexes with the chloride, sulfate, fluoride, and hydroxyl ions in seawater:



One of the objectives of studying the physical chemistry of iron in seawater is to determine the relative significance of these various chemical forms. The present concept of this system is illustrated in an Eh-pH diagram (Figure 2) in which the regions of dominance of specific iron species are delineated. Chemical and instrumental techniques are being used to identify the chemical forms and to determine the location of the domain boundaries on the Eh-pH diagram. The domain boundaries which are speculative are indicated by question marks.

The following conclusions may be obtained from this analysis of iron species. If iron is added to normal ocean water (pH = 7.6 – 8.3) in which the Eh is established by oxygen, it will exist as an electrically neutral Fe(OH)_3° species. In anoxic ocean water, the ferric hydroxide species will be transformed to the ferrous hydroxide species Fe(OH)_2° . It is possible that, under extremely alkaline oxidizing conditions which may exist in micro-environments, the iron may be the negatively charged hydroxide complex Fe(OH)_4^{-} . When corrosion occurs under acidic conditions the iron released will form positively charged chloride and hydroxide complexes. Thus, the chemical and electrostatic characteristics of dissolved iron in seawater may vary greatly under different environmental conditions.

Solid Phases of Iron in the Marine Environment

If the concentration of dissolved iron in seawater is increased sufficiently, a point will be reached at which a precipitate forms between iron and other components of the seawater. This type of

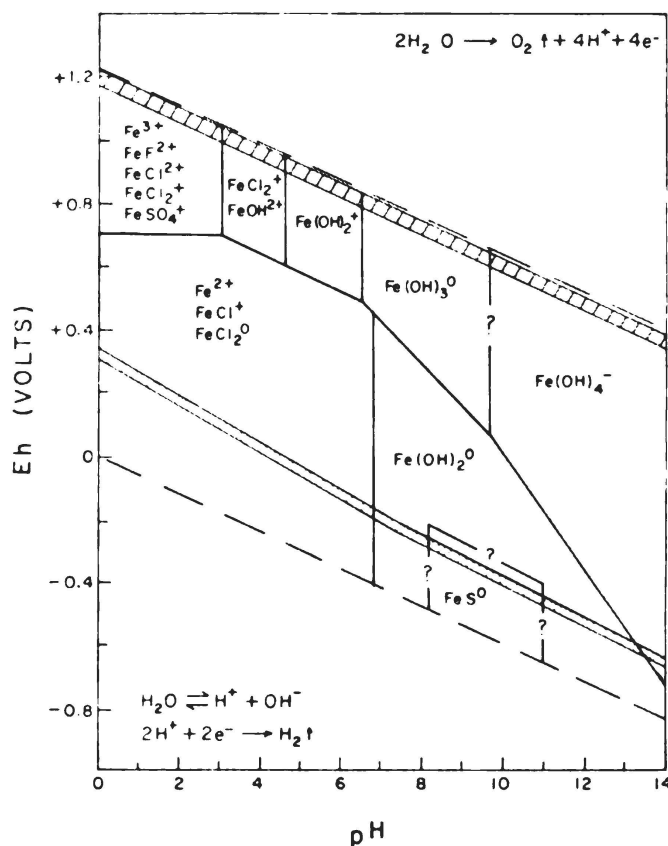


Figure 2—The chemical forms of dissolved iron in seawater. The textural bands are from Figure 1, and the boundaries indicate the regions within which most of the soluble iron exists as the designated species.

process may occur where rivers enter the ocean or where iron-rich acid wastes are disposed of in the ocean. The formation of these solid phases is also evident in the rust and scale corrosion products.

The relationship between the chemical characteristics of iron solid phases and the conditions found in the marine environment can be illustrated with Eh-pH diagrams. For marine systems, there are three types of solid phases which form when the dissolved iron concentration exceeds their solubility limit (Figure 3). Under oxidizing conditions, the Fe^{3+} will precipitate to form a hydrous ferric oxide ($\text{FeOOH} \cdot \text{H}_2\text{O}$). The precipitation of Fe^{2+} occurs in two chemical forms; FeS_2 which will normally be the dominant phase if sulfide is present in the marine environment, and Fe(OH)_2 which may form in the absence of sulfide.

The hydrous oxides of iron which form initially upon precipitation undergo chemical alteration to form oxides which are chemically more stable such as Fe_2O_3 and Fe_3O_4 . The effect of these processes

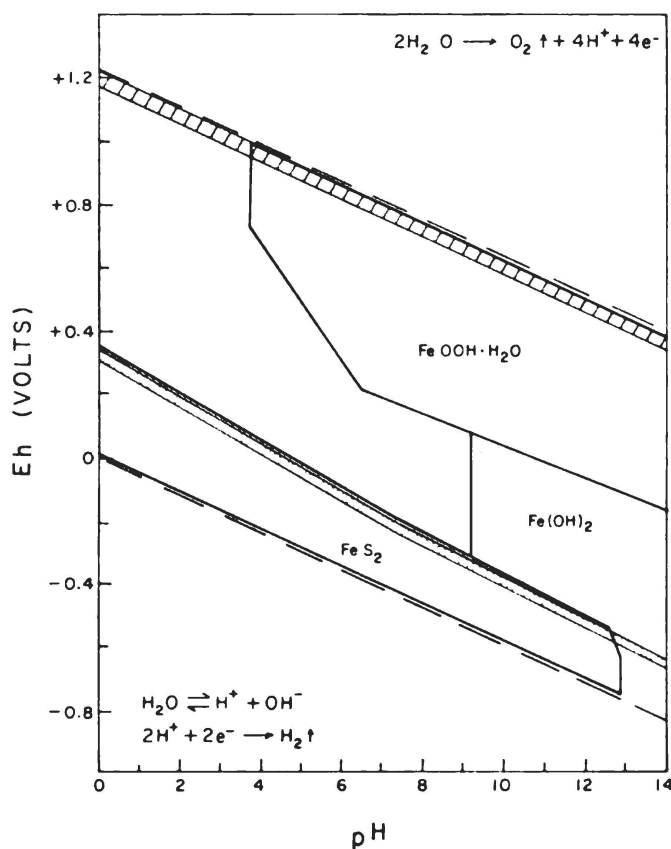


Figure 3—The solid phases of iron precipitated from seawater under various Eh-pH conditions. To the left of the hydrous oxide domains iron has a solubility greater than 10^{-6} molar.

on the dominance of the solid phases in the Eh-pH diagram is shown in Figure 4. Ferric oxide (Fe₂O₃) prevails over most of the environmental conditions, unless sulfide is present. There is a small range of conditions in which the mixed ferric-ferrous oxide, Fe₃O₄, is the chemically stable form of solid iron. Nowhere on these Eh-pH diagrams is elemental iron, Fe, the stable form; it is for this reason that steel containing Fe corrodes to produce rust (Fe₂O₃). In the next two sections of this article, the preceding information about the chemistry of iron will be applied to specific problems in the ocean.

Application of Iron Chemistry to Processes in the Marine Environment of Naval Concern

Pit Corrosion

The chemical reactivity of structural materials in seawater creates substantial problems for man's activities in the marine environment.

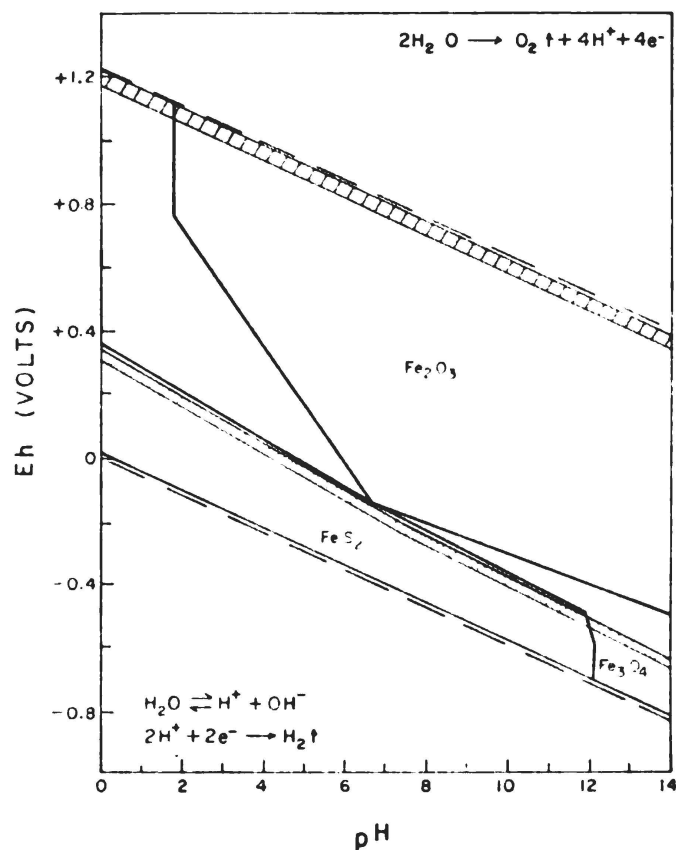


Figure 4—The stable solid phases of iron which form under various Eh-pH conditions from the hydrous iron oxides in Figure 3. The solubility of iron exceeds 10^{-6} molar to the left of the Fe_2O_3 domain.

In some instances there is localized deterioration of a metal surface which results in the formation of pits. This pit corrosion provides a micro-environment near the metal which may have chemical properties drastically different from bulk ocean water.

Some of the processes occurring in pit corrosion have been simulated by a group of ocean engineers at the University of Rhode Island⁽¹⁾ by constructing a test cell from a section of a steel pipe with the ends sealed by plexiglass windows which permit optical monitoring. When the cell was about 2/3 filled with seawater and pressurized with oxygen gas, a series of spontaneous corrosion processes occurred over a period of several days. This system intensifies and accelerates some of the chemical reactions of pit corrosion on a macroscopic scale so that chemical measurements may be made conveniently in various portions of the system. Some of the characteristics of this experiment are illustrated in Figure 5. A two layer system develops due to the electrochemical reactivity of iron exposed to

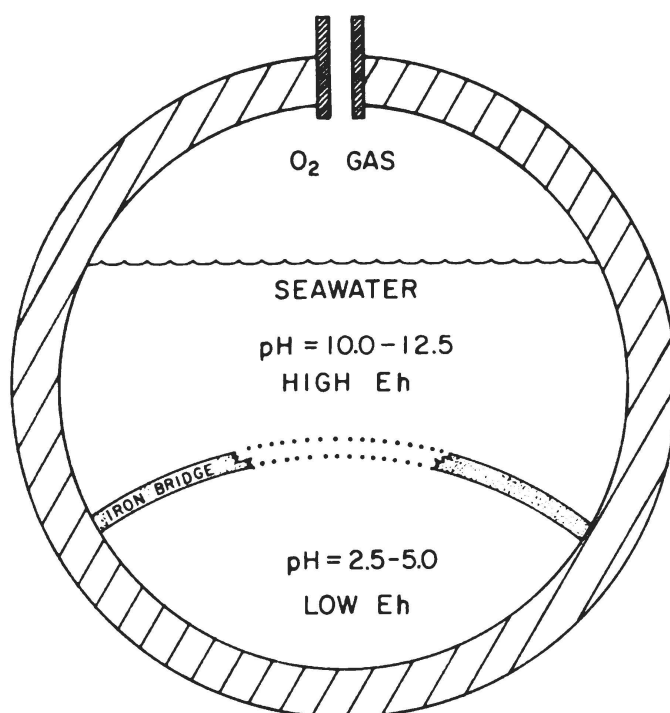


Figure 5—Schematic illustration of the macroscopic pit corrosion experiment of Petersen et al. (1973).

seawater in an oxygen gradient. The upper portion has a high pH and Eh while the lower portion is acidic and reducing. At the interface between these two layers an iron “bridge” forms consisting of Fe_3O_4 , Fe_2O_3 , and FeOOH . The bridge gradually grows out from the sides of the steel ring until it completely seals off the lower layer from the upper one.

Some of the chemical processes occurring in this system may be recognized using the previously constructed Eh-pH diagrams. Figure 2 illustrates that the dissolved iron will exist as Fe^{2+} , FeCl^+ , and FeCl_2^0 in the lower portion of the cell; in the upper part the dissolved iron will most likely be $\text{Fe}(\text{OH})_4^-$. No sulfide was reported in this system, probably because the time scale and environment were not suitable for the bacterial reduction of sulfate in the seawater to form sulfide. Ferrous iron at pH 2.5-5.0 in a chloride medium is soluble to fairly high concentrations, so the iron which is released to the bottom of the pit by the corrosion process will produce a vertical concentration gradient and will diffuse upward toward the oxygenated layer. In Figure 3 this diffusion path corresponds to a diagonal trajectory (for example, from Eh = 0.0, pH = 4.0 to Eh = +0.6, pH = 11.0). During this diffusion the Eh-pH conditions will reach a point at which $\text{FeOOH} \cdot \text{H}_2\text{O}$ is the stable form and the ferrous iron will precipitate as a hydrous ferric oxide. With time, this solid

phase will be transformed to Fe_2O_3 and apparently conditions are also suitable for the formation of Fe_3O_4 . These products then become incorporated into the iron bridge.

There are undoubtedly factors other than those which have been considered here which are important in pit corrosion. For example, observations of pit corrosion on ships in San Diego harbor indicated that sulfate reduction occurs under natural conditions and that the iron bridge in these cases also contains FeS_2 , as we would expect from Figure 4. It is likely that, as the conditions of the micro-environments associated with corrosion processes become known better, it will be possible to apply a knowledge of basic chemical reactions to the improved performance of materials in the ocean.

Magnetic Properties of Sediments

The magnetic characteristics of marine sediments provide a second example of the application of iron chemistry to an oceanic problem with which the Navy is concerned. When sediment particles settle to the seafloor, those which have a magnetic moment will tend to be oriented by the earth's magnetic field. This statistical orientation of a large number of individual particles produces a net magnetic component in the deposited sediment which is aligned with the earth's field at the time of deposition and compaction. During the last millions of years the earth's magnetic field has reversed its north-south polarity a number of times. These reversals have been recorded in deep-sea sediments and igneous rocks which formed during this period of time. These magnetic properties have been extremely important in dating sediment and rock sequences and in supporting the sea-floor spreading theory.

Under some conditions the magnetic signature of sediments may be erased by the geochemical cycling of iron minerals. This realization was based on the unusual magnetic results of some Italian sediments which were initially deposited in the Mediterranean Sea and on a consideration of the chemical behavior of iron minerals in these sediments. One magnetic observation was that, even though these sediments were deposited during a time of reversed earth's field, they are now magnetically oriented in line with the present earth's field. The second characteristic of these sediments was that, when they were heated to temperatures less than 350°C , a superparamagnetic component was produced in the sediment; at temperatures above 350°C there was a second transformation to a solid phase with a high degree of magnetization.

The magnetic properties of these sediments may be understood by considering the response of iron minerals to variations in environmental Eh-pH conditions. The chemical processes involved are illustrated in Figure 6 along with the preceding Eh-pH diagrams for iron. Iron minerals may exhibit several types of magnetic behavior which are summarized in Table 1. One of the primary magnetic components of sediments is magnetite (Fe_3O_4). The fate of a magnetite particle which, being ferrimagnetic, is deposited in a sediment column aligned with the earth's field at the time of deposition may be considered. If the Eh-pH conditions of the sedimentary pore waters shift toward the acidic range, aqueous ferrous ions will be released from the Fe_3O_4 . At this point four things may happen (Figure 6): the Fe^{2+} may diffuse out of the pore waters, it may form pyrite if

Table 1
Types of magnetic behavior shown by some common iron minerals

Type	Minerals	Characteristics
Paramagnetic	Pyrite Lepidocrocite	There is no permanent magnetic component, but it is possible to induce a weak magnetic moment with an applied field.
Ferrimagnetic	Magnetite Maghemite	There is a permanent magnetic moment which aligns in the same direction as an applied field.
Antiferromagnetic	Hematite Goethite	There is no permanent magnetic component, because within the mineral crystal there are opposing magnetic domains; a small applied field will not produce a magnetic moment.
Superparamagnetic	Hydrous ferric oxide	There is no permanent magnetic component, but an applied field will readily induce a magnetic moment; this behavior is associated with small particles which are less than the domain size of the mineral.

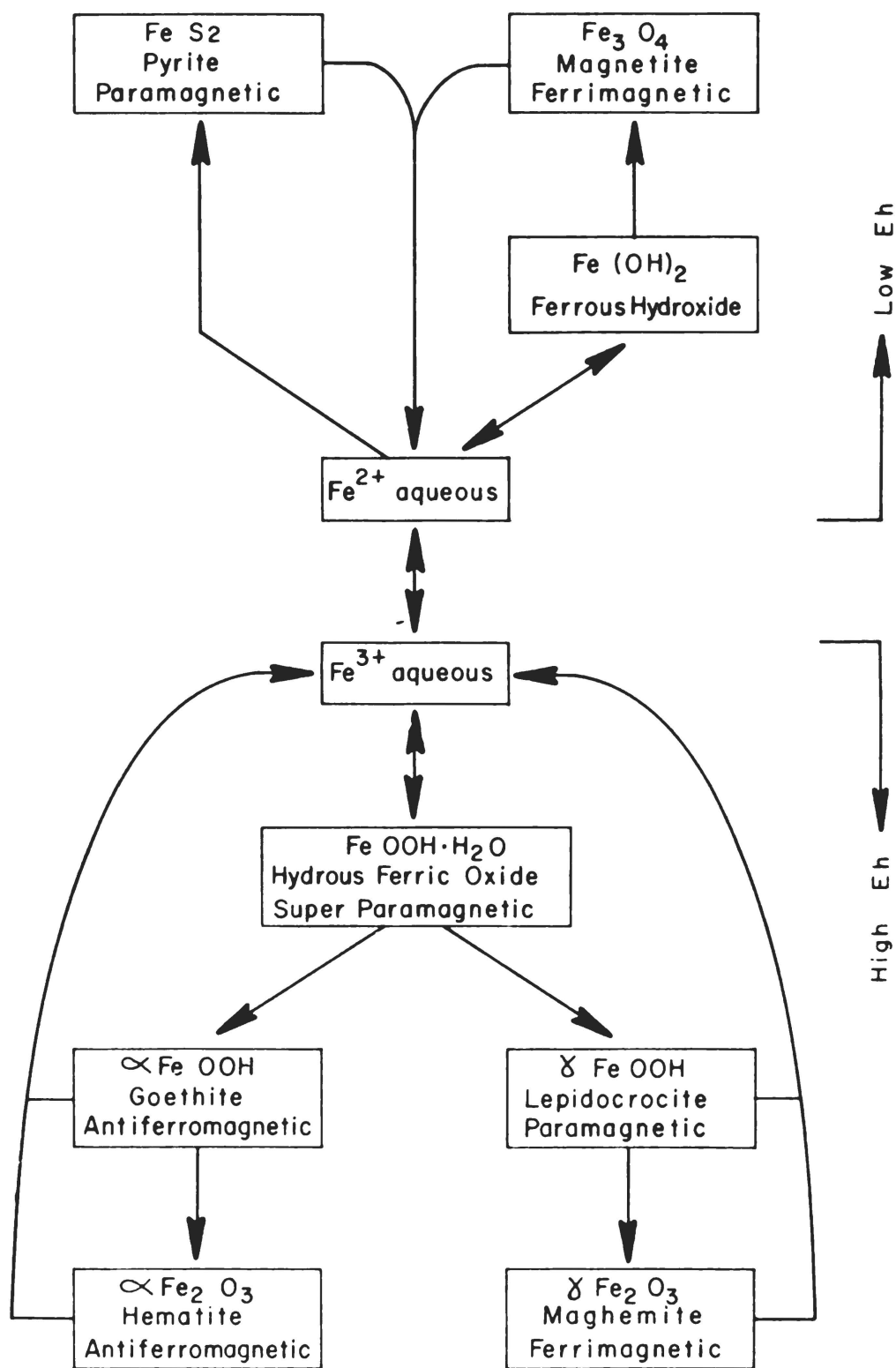


Figure 6 Geochemical cycling of major iron minerals with an indication of the magnetic characteristic of each solid phase. The chemical forms of the aqueous Fe^{2+} and Fe^{3+} depend on the specific Eh and pH as indicated in Figure 2.

sulfide is present, it may form $\text{Fe}(\text{OH})_2$ if the pH shifts to higher values, or it may be oxidized to aqueous Fe^{3+} . If the concentration of aqueous Fe^{2+} exceeds the solubility of hydrous ferric oxide at the time of oxidation the iron will precipitate as $\text{FeOOH} \cdot \text{H}_2\text{O}$. This solid phase may be transformed into either of two types of FeOOH and then on to two types of Fe_2O_3 . (The α and γ forms have the same chemical composition, but their different crystal structure leads to different magnetic properties). Further perturbations in the Eh-pH conditions of the sediment may recycle the ferric solid phases back to ferrous solids.

The magnetic properties of the sediment at any point in time will depend on the particular iron minerals which are present and on the direction of the earth's field at the time of their crystallization. Over periods of millions of years it is possible for the iron to be cycled through this mineralogical cycle many times. Even if only a small percentage of the magnetic minerals is recycled during a single Eh-pH excursion of the sedimentary environment, the cumulative effect of many such excursions would be sufficient to erase the original magnetic record. This process was used to explain the anomalous polarity of the Italian samples. The presence of a superparamagnetic phase upon heating supports this interpretation because that could represent the thermal dehydration of hydrous ferric oxides.

This consideration of the non-permanence of magnetic signatures in sediments has substantial implications to the field of paleomagnetism and to natural magnetic fields in the ocean. The success of paleomagnetism studies in many parts of the world implies that deep ocean sediments have not been subjected to the Eh-pH extremes of the Mediterranean samples. In those cases where the Eh-pH history of the sediments may include significant variations, it would be useful to support paleomagnetic interpretations with independent information of the permanence of the magnetic iron oxide minerals. The oxygen isotope ratios of these minerals could provide evidence of their cycling through the aqueous phase of pore waters.

Conclusion

A chemical understanding of iron in the marine environment involves a variety of types of reactions including oxidation-reduction, complex formation, and solubility equilibria. Many of these processes for a metal such as iron may be summarized through the use of Eh-pH diagrams on which specific types of environments in the marine system may be identified. The information provided by this type of

an analysis is valuable for understanding chemical processes in the ocean such as the corrosion of metals and the alteration in solid phases which may affect their magnetic behavior.

There are several areas of present research related to the physical chemistry of seawater which will increase man's ability to cope with chemical processes in the ocean. Defining the basic properties of seawater as a multicomponent electrolyte medium is one of the first steps in understanding chemical reactions in the ocean (the discussion by Dr. F. J. Millero in this issue of Naval Research Reviews). Determining the magnitude and the control mechanism of the Eh of seawater is a problem which requires further attention. Existing chemical information is often adequate for estimating the most significant chemical forms of a metal such as iron in seawater, but a reliable quantitative evaluation of metal complexes under oceanic conditions will normally require specially designed experimental studies. As the specific chemical processes which control the behavior of a chemical in seawater become evident, one may determine its kinetics (See the discussion by Dr. Gordon Atkinson in this issue of Naval Research Reviews). This general approach will ultimately provide a basis for predicting the paths which will be followed in a chemical cycle such as Figure 6 in response to changing environmental conditions.

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Chemical Kinetics in Seawater

G. Atkinson and T. J. Gilligan*

University of Oklahoma

Introduction

Recent research has added much to our knowledge of the physical and inorganic chemistry of seawater. In particular, the characterization of seawater as an equilibrium chemical system has been explored in a systematic and sophisticated fashion. (See the report by Dr. Millero in this issue). Unfortunately, not as much attention has been given to the dynamic aspects of seawater chemistry. Yet, to characterize a chemical system fully, one must know both the equilibrium states and the rates at which the various processes occur. This kinetic information is important since the rate of approach to a given state may be very slow, even though the state itself is thermodynamically favored.

Since the chemistry of the sea is the primary interest here, the presence of all plant and animal life will be neglected. The major emphasis will be on the inorganic salts and dissolved gases which are present in the greatest amounts in the sea.

There are many different chemical reactions that can occur in the sea and they occur with a tremendous range of rates. The fastest are proton transfer reactions in acid-base equilibria which have half-lives in the nanosecond range (10^{-9} sec.); slightly slower are association reactions with half-lives in the millisecond (10^{-6} sec.) to microsecond (10^{-3} sec.) range; slower still are oxidation-reduction reactions, and finally the precipitation and aging processes. The first two types of kinetic processes, the realm of fast reaction kinetics, will be discussed in this paper. Due to their importance, some attention will be given to the rates of oxidation-reduction reactions including the role played by biological catalysts in enhancing the rates of reaction. (See also the report by Dr. Kester in this issue). The fourth topic, precipitation and aging, is not one that occurs in solutions, but rather at the interface between solid and liquid. Since the present discussion

*Dr. Gordon Atkinson is Professor and Chairman of the Department of Chemistry at the University of Oklahoma, Norman, Oklahoma. Dr. Atkinson is internationally recognized for his research on the kinetics of chemical reactions with particular emphasis on those equilibria which serve to cause anomalous excess sound absorption in seawater. Dr. Thomas J. Gilligan has just completed a post-doctoral appointment with Dr. Atkinson, and is presently conducting research at the University of Zurich. His research interests are concerned with the kinetics of fast reactions in solutions.

is primarily concerned with the solution phase, these reactions plus those that occur at the sea-air interface will be omitted. The available information on the kinetics of the major components will be reviewed, along with some of the important and interesting minor components and the influence of the important variables, temperature and pressure, on seawater kinetics. The temperature of the sea ranges from -2° to 35°C with the average around $+3^{\circ}\text{C}$. The pressure changes with depth are enormous with pressures in the deepest sections of the sea exceeding 1000 atmospheres. Both these variables influence the composition of the seawater and the rate at which different processes occur.

Studies of the composition of seawater show that most of the dissolved salts are in the form of chloride, sodium, magnesium, sulfate, calcium, and potassium ions. Together, these ions account for all but about one percent of the total salinity of seawater. Although not in high concentration, the carbon dioxide system is very important in controlling the acidity of the ocean and in the biological and geological processes.

The concentration of CO_2 depends on several factors: the partial pressure of CO_2 in the air, the rate of growth and decay of plants, and in some cases the presence of inorganic carbonates. Carbon dioxide is interchanged between the seawater and the atmosphere. Photosynthesis converts carbon dioxide into plankton, while the subsequent decay of this organic matter regenerates the carbon dioxide.

It is commonly accepted that the carbon dioxide/water equilibria play a very important role in maintaining the pH of seawater near eight, with the boric acid equilibrium playing a somewhat minor role.

Table 1 lists the major components and their abundances in seawater along with the most prevalent minor components. This article will emphasize the kinetics of association-dissociation reactions between the major components, where association is the combination of two ions to form an ion-pair defined by the law of mass action. For magnesium sulfate, for example,

$$K_{\text{assoc}} = \frac{[\text{MgSO}_4]_{\text{aq}}}{[\text{Mg}^{+2}] [\text{SO}_4^{-2}]} \quad (1)$$

where the brackets denote the activity of the species, and K_{assoc} is the equilibrium constant for the association reaction. The most important reactions in seawater are between sodium, potassium, magnesium, calcium, and the sulfate ions. The association of the same four cations with carbonate and bicarbonate will also be discussed. The

Table 1
Composition of Seawater at 25° ,
 from Riley, J. P. and Skirrow, G. (ed.), Chemical
 Oceanography, Vol. I, Academic Press (1965).

Component	Concentration	
	g/kg of seawater	molality
Water		54.90
Chloride	19.353	0.5483
Sodium	10.76	0.47015
Sulfate	2.712	0.02824
Magnesium	1.294	0.05357
Calcium	0.413	0.01024
Potassium	0.387	0.00996
Bicarbonate	0.142	0.00234
Bromide	0.067	0.00083
Strontium	0.0080	0.0015
Boron	0.0045	0.00043
Fluoride	0.001	0.00007

hydroxides and fluorides of these metals will be considered, although these anions are not in high concentrations. In addition, the influence of minor ionic components such as borate, nitrate, phosphate, bromides and strontium will be considered.

Kinetic Techniques

The approach used to study solution reactions that proceed at high rates is relaxation kinetics. This field has its most elegant exposition in the work of Manfred Eigen [1]. The basic procedure in such studies is to take a system at equilibrium, perturb it, and then observe how the system approaches a new equilibrium state. This is usually done by measuring a variable such as the concentration as a function of time after the perturbation, determine the rates of reaction its behavior. This perturbation of the solution could be a rapid change in the temperature (T-jump) or the pressure (P-jump), an applied electric field (E-jump), a sound wave (ultrasonic absorption) or a flash of light (flash photolysis). The first three methods generally use spectrophotometric detection, although conductance measurements are sometimes employed when favorable.

Kinetic Theory

Expressions for the rate of chemical reactions can be derived in terms of the concentration of the reactant species and the rate constants for the individual steps. For a specific set of conditions, a relaxing equilibrium will exhibit a characteristic relaxation time which will depend on the rate constants and in most instances on the concentration (C). For example,



will have

$$\frac{-dC_A}{dt} = \frac{-dC_B}{dt} = \frac{dC_C}{dt} = k_1 C_A C_B - k_{-1} C_C. \quad (3)$$

Using this rate equation and the mass balance equations for A and B, an expression for the relaxation time, τ , can be obtained, where

$$\frac{1}{\tau} = k_1 (C_A + C_B) + k_{-1} \quad (4)$$

For the above example, a plot of $1/\tau$ versus $(C_A + C_B)$ will give k_1 as the slope and k_{-1} as the intercept. The equilibrium constant for this reaction is then simply

$$K_{eq} = \frac{k_1}{k_{-1}}. \quad (5)$$

If the equilibrium constant, K_{eq} , is too large, the k_{-1} intercept will be very close to zero, making it very difficult to determine the rate constant accurately. If K_{eq} is too small, the slope will be nearly zero and accurate determination of k_1 is impossible. In either case, if the equilibrium constant is known, then only one rate constant needs to be determined experimentally and the other can be obtained from equation (5).

The effects of temperature and pressure on the thermodynamic equilibrium constants do not indicate how the rates of reactions will be affected by changes in these variables. The behaviors of the thermodynamic quantities with respect to temperature and pressure are fairly well established. The van't Hoff equation,

$$\left(\frac{\partial \ln K_{eq}}{\partial T}\right)_P = \frac{+\Delta H^0}{RT^2}, \quad (6)$$

where K_{eq} is the equilibrium constant, ΔH^0 is the enthalpy or heat constant change at infinite dilution, T is the temperature, P is pressure and R the universal gas constant, gives the temperature dependence of the thermodynamic equilibrium constant. The pressure analog of the van't Hoff equation

$$\left(\frac{\partial \ln K_{eq}}{\partial P}\right)_T = \frac{-\Delta V^0}{RT}, \quad (7)$$

where ΔV^0 is the volume change at infinite dilution, gives the pressure dependence. ΔH and ΔV for the reaction will determine the thermodynamic temperature and pressure dependence, but to determine their effects on the kinetics, one must employ a more detailed picture of the process.

To characterize the effects of temperature and pressure on the kinetics of a process, their influence on the activated complex as well as the products and reactants must be known. The above van't Hoff equations can be expressed in terms of the temperature and pressure dependence of the individual rate constants such that

$$\left(\frac{\partial \ln k_i}{\partial P}\right)_T = \frac{-\Delta V_i^\ddagger}{RT}; \quad \left(\frac{\partial \ln k_i}{\partial T}\right)_P = \frac{+\Delta H_i^\ddagger}{RT^2} \quad (8)$$

(See Figure 1 for a graphical illustration of the effect of an increase in temperature.) If $\Delta H^\ddagger$ or $\Delta V^\ddagger$ for the formation of the activated complex increases with temperature or pressure, then the forward rate constant for that process will be slowed. If ΔH or ΔV for the overall reaction also increases with temperature or pressure, then the equilibrium constant will increase. This means then, that the backward rate will have to be slowed even more than the forward rate if the equilibrium constant is to increase.

Unfortunately, little information is available on the influence of temperature and pressure on the systems of interest for seawater studies. The pressure dependence of the rate constants is a particularly barren field with little thermodynamic data and no kinetic data available. For seawater systems, this pressure factor could be of greater importance than the temperature factor, since the pressure change variations cover three orders of magnitude while the temperature variations rarely exceed 10% of the absolute temperature.

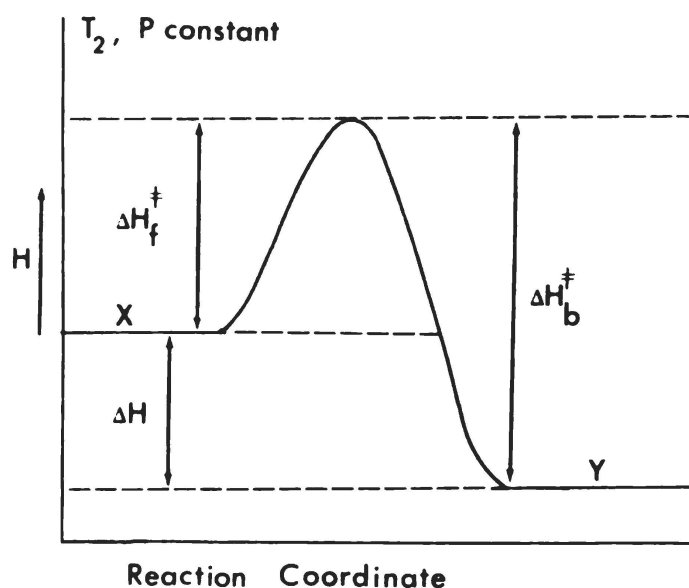
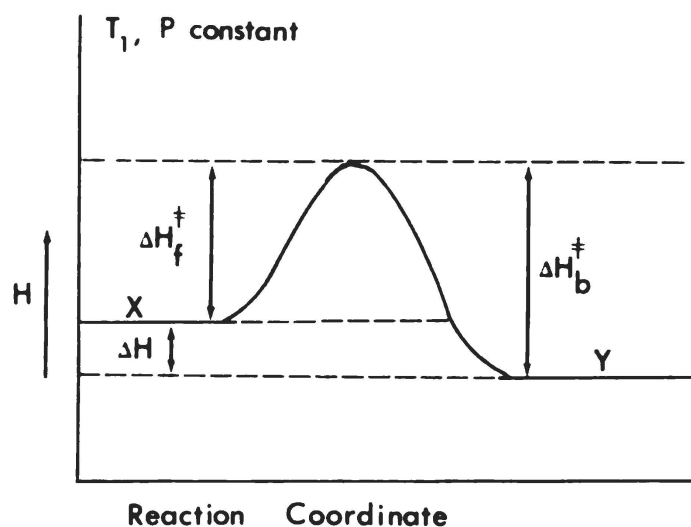


Figure 1—Reaction diagram for X (reactants) Y (products) at T_1 and T_2 , showing the effect of the change in temperature on ΔH and $\Delta H_f^\ddagger$. T_2 is greater than T_1 .

Major Components

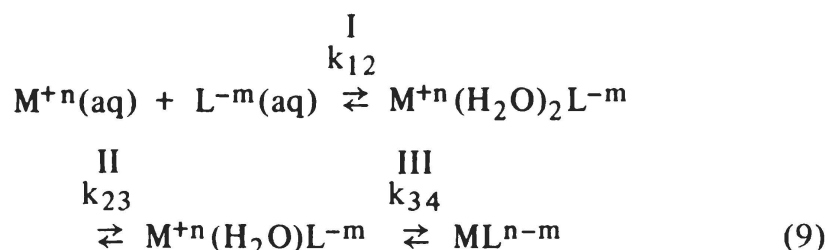
In considering seawater kinetics it is important to note that the major constituents are not salts such as NaCl or MgSO_4 but the ions formed by these salts— $\text{Na}^+(\text{aq})$, $\text{Cl}^-(\text{aq})$; $\text{Mg}^{+2}(\text{aq})$, $\text{SO}_4^{-2}(\text{aq})$. The kinetics that are being considered are the interactions between these hydrated ions to form transient ion pair species.

The first area of available kinetic data that will be covered is that involving ionic association between the major components present in

seawater; chloride, sodium, magnesium, sulfate, calcium, and potassium ions. They make up 99% of all the dissolved salts in seawater. Of the two anions, the chloride ion does not exhibit any association with the cations listed here. Except for its large contribution to the ionic strength of the medium, its presence can be ignored.

The sulfate ion is known to associate with all the major cations, predominantly with magnesium and sodium. Most of the excess ultrasonic absorption of seawater is attributable to the dissociation of magnesium sulfate ion pairs under the influence of the sound wave. ["Excess" refers to the absorption over and above that found in pure water at the same temperature and pressure.]

A number of kinetic studies have been performed on magnesium sulfate. This association is thought to proceed by a multistep mechanism with different characteristic rate constants for each step. The mechanism generally accepted to explain these results is that of Eigen [2, 3] where



M is any cation and L is any anion. All six rate constants for this mechanism and the resulting equilibrium constants for each step have been calculated (Table 2). From these three equilibrium constants, an overall equilibrium constant that compares quite favorably with that determined conductometrically is obtained. The first step in the above mechanism is very rapid, approaching the maximum rate possible for moving two charged particles together in a viscous medium. The particles are the hydrated cation and anion. For magnesium sulfate Eigen used [6] the Debye-Smoluchowski theory of diffusion-controlled reactions to calculate a value of $4 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ for the forward rate constant. Atkinson and Petrucci [4] argue that the rate of the second step is controlled by the rate of dehydration (loss of water) on the anion. The evidence shows that all sulfates for example, show essentially the same forward rate for this step. The third step rate is then attributed to cation dehydration. It varies greatly from cation to cation and can be closely correlated to the water exchange rate characteristic of a given cation.

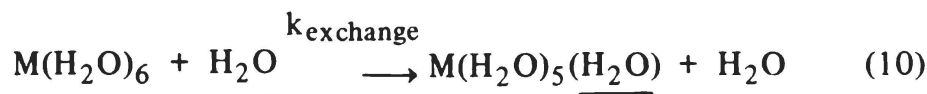
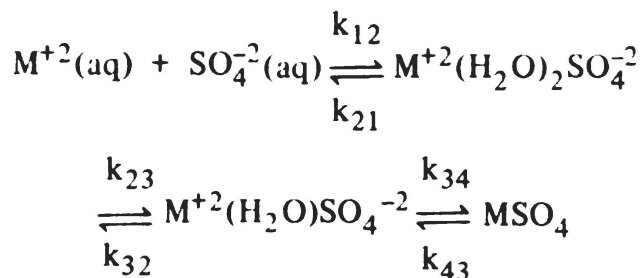


Table 2
Rate Constants and Individual Equilibrium Constants
For Magnesium and Manganese Sulfate

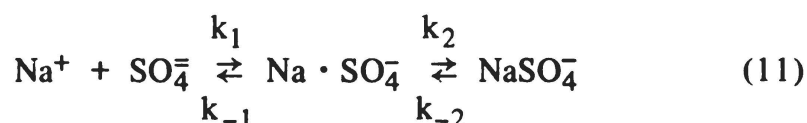


	MgSO ₄	MgSO ₄	MnSO ₄
	Eigen-Tamm ³	Atkinson-Petrucchi ⁴	Atkinson-Kor ⁵
$k_{12} \text{M}^{-1} \text{sec}^{-1}$	4.6×10^{10}	2.8×10^{10}	4.2×10^{10}
$k_{21} \text{sec}^{-1}$	8×10^8	5.6×10^8	8.0×10^8
$K_{12} \text{M}^{-1}$	.017	.020	.019
$k_{23} \text{sec}^{-1}$	1×10^9	7.2×10^7	6.7×10^7
$k_{32} \text{sec}^{-1}$	5×10^8	3.7×10^7	1.9×10^8
K_{23}	0.5	0.51	2.8
$k_{34} \text{sec}^{-1}$	1×10^5	1.4×10^5	4.8×10^7
$k_{43} \text{sec}^{-1}$	8×10^5	8.0×10^5	1.4×10^7
K_{34}	7.5	5.8	.28

In summary, the general mechanism for ion association in water consists of the very fast diffusion together of the hydrated ions followed by the slower step-wise loss of hydration water until the ions are in contact. This model can be simplified at times into a two step process. The first step is the formation of an outer-sphere ion pair (that is, a species where the cation and anion are still separated by a water molecule). This is followed by loss of water to give an inner-sphere or contact ion pair where the anion is in intimate contact with the cation. In this simplified model, the first step is usually very rapid and has association constants in the range 1 to 10. The second step can be much slower and have a very large association constant.

The association of sodium and potassium with sulfate ions has not been extensively studied until now. Ultrasonic studies in Germany

indicated no relaxation below 100 MHz although there appeared to be a small excess absorption. Studies at the University of Oklahoma show that a chemical relaxation does occur at higher frequencies for 0.5 M sodium sulfate at 25°C. This relaxation frequency is in the neighborhood of 200 MHz which gives a relaxation time near 10^{-9} sec. This makes the chemical process being observed near the diffusion controlled limit for sodium and sulfate ions. The mechanism proposed is the formation of an outer-sphere complex which will have an equilibrium constant of about 0.1 to 1.0. The relaxation measured then represents the formation of an inner-sphere complex.



$$K_{\text{os}} = \frac{k_1}{k_{-1}} ; K_{\text{is}} = \frac{k_2}{k_{-2}}$$

and

$$K_{\text{overall}} = K_{\text{os}}(1 + K_{\text{is}})$$

The overall equilibrium constant is 5.2 from conductance work, so the equilibrium constant for the second step can be obtained from a reasonable assumption of the equilibrium constant for outer-sphere association. Since the amplitude of the excess absorption is so small, high concentrations must be used to obtain worthwhile data. The amplitude increases as the temperature decreases so the major emphasis was placed on the temperature range between 0 and 25°C. From the temperature dependence of the rates, it should be possible to determine the activation parameters. For these alkali sulfates, sodium exhibits the largest excess absorption, being about twice that of potassium sulfate. This can probably be attributed to a larger ΔV for the formation of sodium sulfate ion pairs.

At the normal pH of about 8.0 for seawater, the amount of bisulfate present is very small. Therefore, complexation of the major cations with bisulfate is of little consequence. However, as the pH becomes more acidic, these systems could be important. The proton transfer reaction for



has been studied ultrasonically by Eigen and co-workers. [10] A k_b of about 1×10^9 and a k_f of about 1×10^{11} at 20°C and 1.0 M ionic strength was obtained. No work has been done on the association of the major cations with bisulfate. This would require working at a very high pH to get appreciable bisulfate concentrations and to eliminate competition from the sulfate ion associations which would predominate.

Since calcium and strontium are in low concentrations in seawater, their ion pairs with sulfate are of little importance. Their low saturation concentrations make most conventional measurements of their rate constants impossible. Here, one would expect the differences between the rate constants for these sulfates and for magnesium sulfate to resemble the differences reported by Atkinson and Petrucci [4] between magnesium sulfate and manganese sulfate. For the three-step mechanism, calcium and strontium sulfate should have essentially the same k_{23} as magnesium sulfate, $\sim 7 \times 10^7 \text{ sec}^{-1}$ since this is believed to be the anion dehydration. k_{34} is then the dehydration of the cation and reflects the water exchange rate which is characteristic of the cation alone.

One expects k_{34} for strontium and calcium sulfate to be in the neighborhood of 10^8 – 10^9 sec^{-1} . The backward rates, k_{32} and k_{43} , would then reflect the equilibrium constants for each step and would depend on the individual cations, calcium and strontium. The rate constant for the first step, k_{12} , should also approach the diffusion-controlled rate constant calculated by the Debye-Smoluchowski equation. An estimate of the reverse rate constant, k_{21} , would then be available from a calculation of the outer-sphere association constant employing the Eigen-Fuoss equation where

$$K_{os} = \frac{4\pi N a^3}{3000} \exp \left(\frac{Z_a Z_b e^2}{DkTa(1 + \eta a)} \right). \quad (13)$$

Here we have only one adjustable parameter, 'a', the ion size parameter, familiar from conductance equations.

One would expect this outer-sphere constant for calcium and strontium sulfate to be close to the calculated value of 50 for magnesium sulfate. Therefore, the reverse rate constant for calcium and strontium sulfate should be similar to that found for magnesium sulfate. The calculated values of k_{os} and k_{12} would differ only in the ion size parameter used for these three cations and in the diffusion coefficients of these ions. The variables should be quite similar for three cations, especially calcium and strontium, which have nearly identical single ion conductivity. The insolubility problem

arises again with the hydroxides, fluorides, and carbonates of magnesium, calcium and strontium. [5 and 6]

The pressure dependence of the sulfate ion association rates has not been studied. However, there does exist a fair amount of thermodynamic data for magnesium sulfate [7, 8, 9] and one thermodynamic study of sodium sulfate. [7] From the ΔV values obtained thermodynamically, the change in the amplitude of the ultrasonic absorption with pressure can be estimated. The equilibrium constant change can also be estimated from,

$$RT \ln \frac{K_p}{K} = \Delta \bar{V}(P - 1). \quad (14)$$

Kester and Pytkowicz [7] have measured the pressure dependence of the equilibrium constant for sodium sulfate association and they find a decrease in the association constant with increasing pressure at an initial ionic strength of 0.608. One might expect the same behavior for magnesium sulfate since $\Delta \bar{V}(\sim 11)$ is positive although somewhat smaller than $\Delta \bar{V}(\sim 13)$ for sodium sulfate ion pair formation. Why these two salts should have very similar ΔV 's is not at all clear.

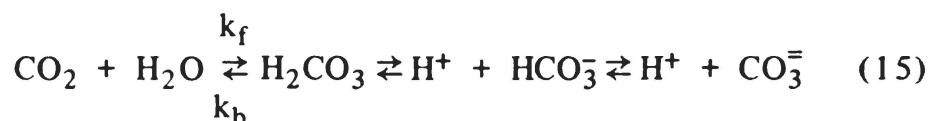
This information is necessary before a kinetic study of the pressure dependence of the rate constant can be done because the equilibrium constant at the desired pressure must be known. The effect of pressure on the activity coefficients will also have to be dealt with if the thermodynamic equilibrium constant is used. Use of the concentration equilibrium constant would avoid this problem, but the data would then be limited to specific concentrations and the rate constants then could not be determined.

The effect of low temperature on the equilibrium state of these sulfate systems has also been studied experimentally by Kester and Pytkowicz at 2°C. [7] They also give the thermodynamic data for sodium, magnesium, and calcium sulfate ion pairs collected from the literature.

Minor Components

Most important of the lower concentration species are those generated by the presence of CO_2 and its equilibrium species. The concentrations of these ions are not in approximate constant proportion to the salinity as is the case for the major ions. The growth and decay of plant life controls the overall concentration of the carbonate species and these factors vary with depth. This is also true

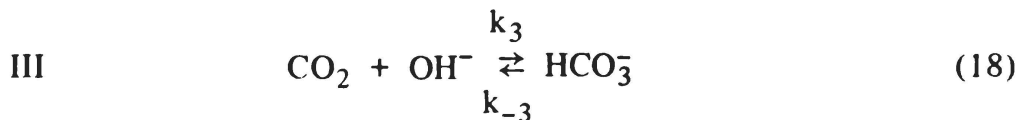
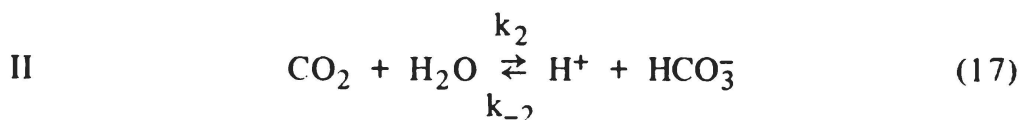
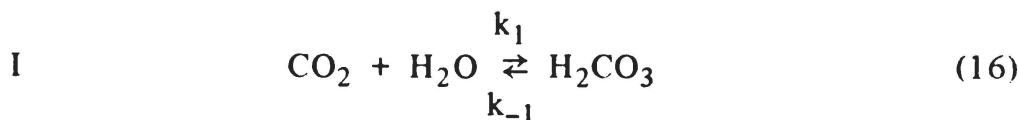
of nitrate, phosphate and dissolved oxygen, which are participants in the growth-decay cycle. The equilibrium distribution of the various carbonate species depends strongly on the pH of the solution. In neutral or acidic media the overall equilibrium is the following:



The saturation concentration of CO_2 in this medium is fairly low which can cause experimental difficulties. In addition to this equilibrium system, one must also consider the formation of ion pairs between the major component cations and the bicarbonate and carbonate anions.

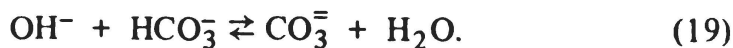
The hydration-dehydration step for CO_2 is the slowest step in the mechanism. k_f has a pseudo first order rate constant of 0.03 sec^{-1} while k_b is about 10 sec^{-1} . This is the rate determining step for any carbon dioxide equilibrium since the next two steps are proton transfers which are known to proceed much more rapidly.

Eigen et al. [10] arrive at slightly different rate constants. They propose three possible first steps whose relative importance will depend on the pH of the solution:



k_1 and k_2 are the same and have a value of 0.043. k_{-1} is 15, k_{-2} is 5.6×10^4 and for mechanism III, k_3 is 1.4×10^4 and k_{-3} is 1×10^{-4} .

The rate constant for dissociation of carbonic acid to give bicarbonate is about $8 \times 10^6 \text{ sec}^{-1}$ and the rate constant for recombination is 4.7×10^{10} . [10] It is not possible to measure the rate constants for the formation of carbonate from bicarbonate except in very basic solutions where the only appreciable reaction is



If large concentrations of hydroxide are not present, then equilibrium will lie well on the side of the bicarbonate-carbonic acid equilibrium with a very low concentration of carbonate being formed. This means any attempt at measuring the second protolytic equilibrium will be swamped out by the much larger contribution of the first protolytic equilibrium. Eigen, et al. [10] have measured a forward rate constant for this reaction in 1.0 molar sodium carbonate of about $6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ using ultrasonics.

A systematic study of the dehydration step has been done recently as a function of temperature, ionic strength and isotope effect using a wide variety of fast kinetic techniques. Patel and co-workers [11] obtained the following rate constants for the dehydration step $\text{H}_2\text{CO}_3 \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O}$, from which the associated activation parameters can be obtained (See Table 3). Patel and Atkinson [12] have

Table 3
A. Rate Constants for the Hydration and Dehydration of CO_2 at Various Temperatures

Temp ($^{\circ}\text{C}$)	$k_{-1} (\text{sec}^{-1})$	$k_1 (\text{sec}^{-1})$
3.5	2.25	0.35
13.2	5.86	1.21
21.3	15.2	3.00
29.5	28.1	6.61
39.5	59.7	17.27

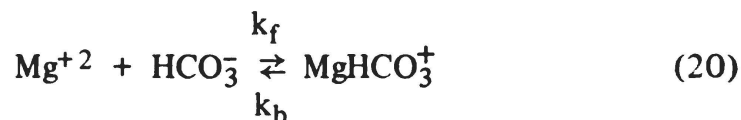
Ionic strength (μ) = 0.5 M NaCl

B. Dehydration Rate Constants as a Function of Ionic Strength at Various Temperatures

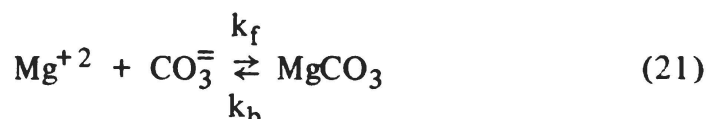
Temp ($^{\circ}\text{C}$)	Ionic Strength (NaCl)	$k_{-1} (\text{sec}^{-1})$
3.5	0.005	3.55
3.5	0.5	2.25
3.5	3.0	2.85
21.5	0.005	16.3
21.3	6.5	15.2
21.5	3.0	16.4
38.5	0.005	63.7
38.5	0.5	59.7
38.5	3.0	63.7

also reported values for the temperature dependence of the hydration step (See Table 7). The dehydration rate is independent of ionic strength up to 3 M sodium chloride. As a result, the value obtained for the dehydration rate should be directly applicable to seawater which has an ionic strength of 0.7.

Patel and Atkinson [13] have also studied the association of magnesium with bicarbonate in methanol. Methanol is used as a solvent to promote ionic association and then the results are subsequently extrapolated to water as the solvent. For the reaction



at 25°C, a k_f of $5 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ and a k_b of 7 sec^{-1} are obtained in methanol. Although not of great importance to the study of seawater itself, due to the low carbonate concentration, the



equilibrium is of considerable interest since large amounts of magnesium carbonate minerals are formed in the sea in the form of magnesite (pure MgCO_3) and dolomite (mixed carbonates of calcium and magnesium, $\text{CaMg}(\text{CO}_3)_2$). Patel and Atkinson [13] reported rate constants for this reaction at 25°C in both methanol and water. For methanol, k_f is $6.8 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ and k_b is 3.4 sec^{-1} and for water k_f is greater than 3×10^5 while k_b is about 2×10^3 .

These rate constants are for the formation of the inner-sphere complex. There will be a much faster set of rate constants for the formation of outer-sphere complexes. It is unlikely that this system can be treated experimentally since the high pH's necessary for appreciable carbonate concentrations would precipitate the magnesium as the hydroxide ($\text{pK}_{sp} \approx 10-11$). The rate constants for the formation of the outer-sphere complex could be obtained in the same manner suggested for calcium and strontium sulfate, employing the equations for diffusion controlled rate constants and outer-sphere association constants.

The effect of pressure on the first and second association constants of carbonic acid at 1000 atm has been studied. It was found that both pK 's are lowered at 1000 atm. ΔV values from glass electrode emf shifts at 1000 atm from the values at 1 atm were obtained. For

the first ionization an ΔV° of -25.4 was obtained and for the second ionization ΔV° was measured as -25.6 at 22°C . There has not been any work done on the pressure dependence of the kinetics of the various processes involved in the carbonate system.

Interestingly, model system calculations indicate there is appreciable association of magnesium with fluoride ions. The kinetics of this displacement of water from the inner coordination sphere of magnesium has been studied using temperature jump experiments. A second order rate constant for this displacement of $3.7 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ was obtained. The remaining rate constants would then come from the known overall equilibrium constant and a good assumption for the outer-sphere equilibrium constant. This case is much like that encountered for the alkali sulfates where the overall equilibrium constant is small and only one relaxation time is measured experimentally. This is not unexpected, since the MgF^+ is a 2-1 ion pair and NaSO_4^- is a 1-2 ion pair. As mentioned before, insolubility problems prevent the study of calcium and strontium fluoride. They would be present in extremely low concentrations anyway.

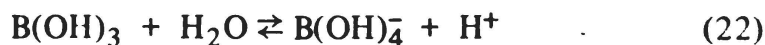
The reactions of transition metal ions with various anions such as sulfate have been reasonably well studied. The rate-determining step is normally the formation of the inner-sphere complex. The concentration of these metals in seawater is generally low and probably controlled by the very low solubility of their hydroxides at the pH of seawater. An extreme example is iron (see the report by Dr. Kester in this issue) which forms $\text{Fe}(\text{OH})_3$ with a K_{sp} of about 10^{-37} . The transition element ions that do not precipitate probably exist predominantly as ion pairs and uncharged complexes with OH^- , HCO_3^- , SO_4^{2-} , and Cl^- . This is predictable from known equilibrium data and is verified generally by polarographic measurements on seawater. The details of transition element speciation need much more research because of their importance as tracers and essential elements in biochemistry.

There are numerous oxidation-reduction reactions that occur in seawater. It has a high oxidation potential that results from the presence of dissolved oxygen. As a result most of the trace transition elements are found in their highest oxidation state in seawater having oxygen concentrations greater than about 0.12 ml/l. The major oxidation reaction is the conversion of dead plants back to carbon dioxide and water. Under some conditions this dead organic matter can sink to a depth where the oxygen has been depleted. Then the oxygen in nitrates is utilized to oxidize the organic matter. When this supply is exhausted, the oxygen in sulfates is utilized to continue the oxidation with simultaneous production of sulfide. These are

the anerobic conditions that exist in the depths of the Black Sea and other areas where there is little circulation to bring oxygen from the surface. Normally these redox reactions are quite slow, but there do exist biological catalysts, mostly in bacteria, that can greatly accelerate them.

The actual rates for these redox reactions have not been measured quantitatively. However, the rate constants for bimolecular redox reactions are known to have a wide range of rate constants and are generally much smaller than the rate constants for association reactions. There is some correlation between the formation of an outer-sphere complex and redox reactions that proceed rapidly. When an inner-sphere complex must be formed before a redox reaction can occur, the rate constant is generally smaller, controlled by the slower formation of the inner-sphere complex.

The final two minor component systems that are of interest are the borates and silicates. Both of these systems are involved in maintaining the pH of the seawater. Boron is primarily in the form of H_3BO_3 and $\text{B}(\text{OH})_4^-$, the latter being the result of the reaction,



The kinetics of this reaction have not been studied, but the rate constants should be comparable with other acid-base proton transfers. The ion pair formation of the borate with the major cations should be similar to the kinetics for the bicarbonate-cation associations. At the pH of seawater, higher charged anions will not be of appreciable concentration.

The concentration of silicates is quite low in seawater. This is a result of the low solubility of the numerous silicates that make up a large part of the sediment. A major component of these minerals are aluminosilicates with various common cations composing the rest of the lattice. The exact chemical formula for these silicates depends on the concentration of the various cations in the seawater, since most silicates do have ion-exchange capabilities. These ion-exchange reactions occur primarily at the solid-solution interface and probably have rather slow rates. However, no kinetic data are available and most of the systems are even ill-defined from a thermodynamic point of view. Sillen [14] proposed that these silicates are instrumental in maintaining the pH of seawater at about 8. It is true that this system has a very large potential for moderating changes in acidity because there are large amounts of solid silicates in the sediment. However, the action of this silicate system is kinetically quite slow

since it requires either reactions at the solid-solution interface or the dissolution of some of the solid before the pH can be adjusted. Both of these processes are slow compared to the ability of the dissolved carbonates to moderate pH changes. The most reasonable conclusion is that the carbonate system controls the short time fluctuations in the pH while the silicate equilibria exert the long term influence. Of course, the boric acid system does make a small contribution to pH control, but due to its much lower concentration and higher pK_a , it is not as important as the carbonic acid system.

Mixed Electrolytes

In the previous discussion we have limited ourselves to considerations of the kinetics of two component systems (water and one electrolyte). However, the sea is a multicomponent system where the two ions present in highest concentration, sodium and chloride, act mostly as inert electrolyte.

The high ionic strength of seawater will affect both the equilibrium parameters and the rate parameters. The different approaches to the modification of the equilibrium parameters have been discussed previously. Each approach has its advantages and disadvantages. In the case of the rate parameters, the general treatment of salt effects is covered in basic texts. [15] Unfortunately, very little data is available on the effect of ionic strength on the reactions of interest.

Sound Transmission in the Sea

To illustrate the utility of kinetic information in marine chemistry, one need only examine sound transmission in the sea. Figure 2 summarizes the high frequency sound absorption data gathered by many investigators in the 40's and 50's. [16] Although it was shown by a number of investigators that the excess absorption was due to $MgSO_4$, it remained for Kurtze and Tamm [17] to make the quantitative interpretation described earlier. The Marsh-Schulkin formula [18] is a good regression fit to the seawater data.

However, as more low frequency data accumulated, the $MgSO_4$ explanation was clearly shown to be insufficient. Figure 3A illustrates the fact that the absorption is consistently higher at low frequencies than the high frequency data would predict. Although various non-chemical explanations were advanced, most investigators feel that a chemical explanation is quite likely. Figure 3B shows a

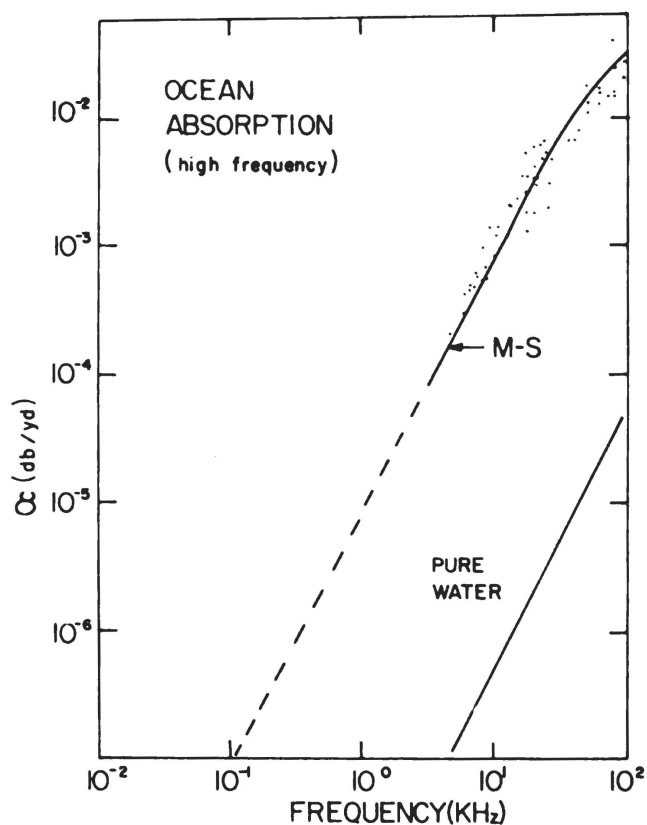


Figure 2—High frequency absorption in seawater and Marsh-Schulkin Fit

Figure 3—(A) Low frequency absorption in seawater showing deviation from Marsh-Schulkin Fit.

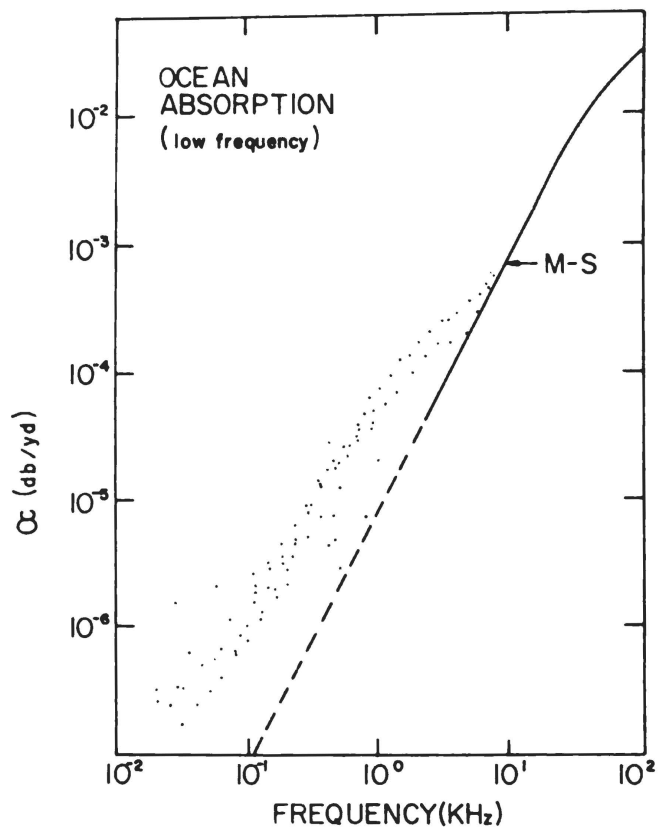
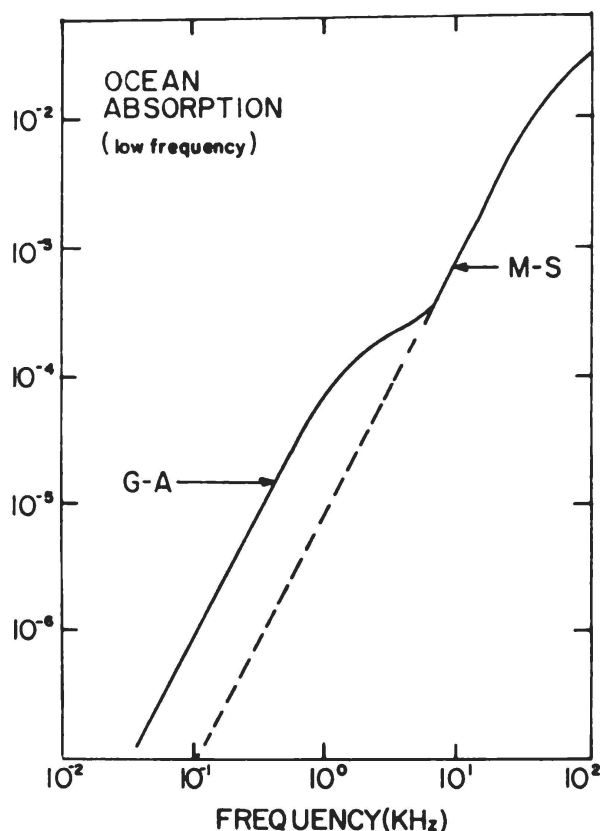
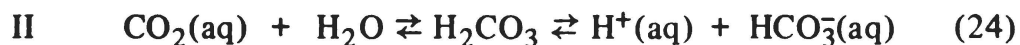
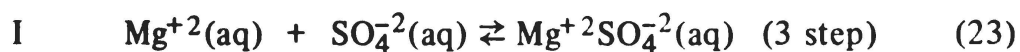


Figure 3-(B) Low frequency absorption in seawater showing KHz relaxation fit. G-A is Garland-Atkinson relaxation fit.



relaxation fit through the low frequency data. Generally, the fit is quite convincing. However, the scatter of the data allows a substantial variation in the relaxation parameters.

Unfortunately, it is exceptionally difficult to make low frequency acoustic measurements on seawater in the laboratory. In principle, however, one can obtain the needed equilibrium and kinetic parameters by other methods and calculate the acoustic properties of the seawater. The methods for doing this are straightforward and have been described. [19] In this article, best candidates were given for explaining the whole spectrum of chemical relaxation in seawater:



The slow step in reaction III is primarily responsible for the relaxation in seawater in the kilohertz frequency range.

Another explanation has been advanced by Fisher and Yeager [20] in which this relaxation is attributed to the borate equilibrium



A more complete consideration of this would presumably also include interactions of the B(OH)_4^- with Na^+ and Mg^{+2} ions.

Finally Knoche [21] has suggested AlSO_4^+ ion pair formation as the cause of the kilohertz relaxation. However, the concentration of Al^{+3} in the sea is far too small to make this plausible. Other work on sound transmission in bodies of water such as Lake Tanganyika and the Red Sea have not really been analyzed quantitatively using a chemical model.

A more definitive modeling requires additional laboratory data on kinetics of the important equilibria as a function of temperature, pressure and salinity as well as careful seawater studies. In particular, measurements of transmission in seawater as a function of temperature and pressure are needed.

Conclusions

From the above discussion, it is evident that the state of knowledge of the kinetics of reactions important to seawater is quite limited. Several major association reactions have been extensively studied, but by and large, most of the associations are small and the rates are difficult to determine accurately. The influence of temperature and pressure on the reaction rates needs extensive study, especially the pressure aspects. Since most of the kinetic studies are done at 25°C , low temperature studies are needed, especially in the region of $0-5^\circ\text{C}$, which is the range for most of the ocean.

Table 4 is a compilation of the available kinetic data for the five most prevalent cations and the five most concentrated anions present in seawater. Included are the overall association constant and the rate constant for each step if there is association. All the data are at 25°C . As can be clearly seen, even in this limited area which is the most extensively studied for the kinetic processes occurring in the sea, there is not a great deal of information available. Continuing advances in kinetic techniques, especially in the field of relaxation kinetics, should help fill in these gaps. The influence of pressure is an experimentally more complicated problem but such studies too should yield valuable results in the near future. The other variable, temperature, could be handled quite easily if experimenters would take the additional time to work at the lower temperatures that are common to the sea. Since much of the thermodynamic information is available at 25°C , one must of course, work at that temperature,

Table 4
Rate Constants for Reactions Between the Major Components of
Seawater at 25°C and 1 Atmosphere.

Ion Pair Formed	k_f	k_b
KSO_4^-	$>1 \times 10^9 \text{M}^{-1} \text{sec}^{-1}$	$>1 \times 10^8 \text{sec}^{-1}$
NaSO_4^-	$>1 \times 10^9 \text{M}^{-1} \text{sec}^{-1}$	$>2 \times 10^8 \text{sec}^{-1}$
$\text{Mg}^{+2}(\text{H}_2\text{O})_2\text{SO}_4^{-2}$	$2.8 \times 10^{10} \text{M}^{-1} \text{sec}^{-1}$	$5.6 \times 10^8 \text{sec}^{-1}$
$\text{Mg}^{+2}(\text{H}_2\text{O})\text{SO}_4^{-2}$	$7.2 \times 10^7 \text{sec}^{-1}$	$3.7 \times 10^7 \text{sec}^{-1}$
MgSO_4	$1.4 \times 10^5 \text{sec}^{-1}$	$8.0 \times 10^5 \text{sec}^{-1}$
$\text{Sr}(\text{H}_2\text{O})_2\text{SO}_4, \text{Ca}(\text{H}_2\text{O})_2\text{SO}_4$	$\sim 2 \times 10^{10} \text{M}^{-1} \text{sec}^{-1}$	$\sim 5 \times 10^8 \text{sec}^{-1}$
$\text{Sr}(\text{H}_2\text{O})\text{SO}_4, \text{Ca}(\text{H}_2\text{O})\text{SO}_4$	$\sim 7 \times 10^7 \text{sec}^{-1}$	
$\text{SrSO}_4, \text{CaSO}_4$	$\sim 10^8 - 10^9 \text{sec}^{-1}$	
KHCO_3	Association Slight	
NaHSO_4	Association Slight	
MgHCO_3^+	$\sim 5 \times 10^5 \text{M}^{-1} \text{sec}^{-1}$	$\sim 1 \times 10^5 \text{sec}^{-1}$
$\text{SrHCO}_3^+, \text{CaHCO}_3^+$	much greater than MgHCO_3^+	
KCO_3^-	$>1 \times 10^9 \text{M}^{-1} \text{sec}^{-1}$	
NaCO_3^-	$>1 \times 10^9 \text{M}^{-1} \text{sec}^{-1}$	
$\text{Mg}^{+2}\text{CO}_3^{-2}(\text{Outer Sphere})$	$\sim 2 \times 10^{10} \text{M}^{-1} \text{sec}^{-1}$	$\sim 4 \times 10^8 \text{sec}^{-1}$
$\text{MgCO}_3(\text{Inner Sphere})$	$>3 \times 10^5 \text{sec}^{-1}$	$\sim 2 \times 10^3 \text{sec}^{-1}$
MgF^+	$3.7 \times 10^4 \text{M}^{-1} \text{sec}^{-1}$	
$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{--}$	$\sim 1 \times 10^{11} \text{sec}^{-1}$	$1 \times 10^9 \text{M}^{-1} \text{sec}^{-1}$
$\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3$	$.043 \text{sec}^{-1}$	15sec^{-1}
$\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	$.043 \text{sec}^{-1}$	$5.6 \times 10^4 \text{M}^{-1} \text{sec}^{-1}$
$\text{OH}^- + \text{CO}_2 \rightleftharpoons \text{HCO}_3^-$	$1.4 \times 10^{11} \text{M}^{-1} \text{sec}^{-1}$	$1 \times 10^{-4} \text{sec}^{-1}$
$\text{OH}^- + \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{--} + \text{H}_2\text{O}$	$6 \times 10^9 \text{M}^{-1} \text{sec}^{-1}$	
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	$4.7 \times 10^{10} \text{sec}^{-1}$	$8 \times 10^6 \text{M}^{-1} \text{sec}^{-1}$

but the lower temperatures should not be neglected (See the article by Dr. Millero in this issue).

The oceans of the earth are enormous, but our knowledge of them is still quite limited. The discipline of kinetics is but one aspect of the physical chemistry of the sea which is in need of much investigation.

Glossary of Symbols

a , mean distance of approach for two ions

C_i , concentration of an individual reactant or product species

D, dielectric constant
 e, electronic charge
 ΔH , enthalpy or heat content change when a reaction proceeds from reactants to products in units of kcal/mole
 ΔH° , ΔV° , the infinite dilution values of ΔH and ΔV .
 $\Delta H^\ddagger$, activation enthalpy which is analogous to the activation volume
 K, equilibrium constant
 K_{os} , outer sphere association constant
 K_{is} , inner sphere association constant
 K_{sp} , solubility product
 k, Boltzman's constant
 k_i , rate constant for a specific step in a reaction mechanism
 M, molarity which is moles of solute per liter of solution
 N, Avogadro's number
 Q, Debye-Hückel constant, .509 for water at 25°C
 ΔV , volume change when a reaction proceeds from reactants to products
 $\Delta V^\ddagger$, activation volume which is the difference between the volume of the activated complex and the volume of either the products or the reactants
 Z_i , charge on an ion
 α , absorption coefficient for a sound wave passing through an absorbing medium
 κ , the reciprocal of the average radius of the ionic atmosphere
 τ , relaxation time which is the time it takes a reaction to reach 1/e or 1/2.7303 of its new equilibrium value

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(Continued from Page 2)

activated sludge treatment system, similar to those used by some industries and municipalities to biodegrade organic wastes. Microorganisms, working in an aerobic environment, digest the wastes and appear to do the same with TNT.

NOL's pilot plant, which operates as a continuous system, is of 4,000 gallons capacity. Microorganisms present in sludge are fed TNT in a water solution, together with a supplemental nutrient, and the mixture is circulated and aerated in an oxidation ditch. The TNT is biodegraded, the solution passes into a settling tank, and the effluent is now essentially free of TNT. The sludge with its microorganisms is returned to the ditch, more nutrients and TNT water are added, and the process goes on.

A larger demonstration system of approximately 100 thousand gallons capacity is planned for construction at the Naval Ammunition Depot in McAlester, Oklahoma, where it will be put to actual use to biodegrade the TNT that is flushed from the areas where ammunition is handled. If the process proves itself on this larger scale, it will offer an alternate method of disposal of TNT at ammunition plants. Conceivably, the discharged water could be used for irrigation of surrounding grounds.

The success of this method poses the question—can it be used for other explosive materials? Although no experiments have been run at this time, NOL is investigating the possibility of biodegrading other high energy materials in this fashion.

The Equation of State of Seawater

F. J. Millero

University of Miami

In both oceanography and meteorology, the variables span only a small fraction of their possible range, and very accurate absolute measurements are necessary, even in a crude description. For example, a 10 percent error in atmospheric pressure corresponds to identifying a high pressure area as an intense hurricane! The ocean requires even more precision if measured parameters such as temperature and salinity are to be related to acoustic ray paths, the determination of accurate circulation and mixing processes and calculation of the vertical stability of a water column. In order to accomplish this, accurate relationships are necessary between the measured parameters and the physical parameters of seawater, such as density and compressibility, which determine its movements. An equation of state of seawater relates these parameters, and therefore, its accuracy is similarly a necessity. It is a mathematical expression of the P-V-T (Pressure-Volume-Temperature) properties. It is being studied to elucidate it in terms of the ionic components that make up its composition, for at a given concentration, any physical chemical property of seawater can be visualized as being equal to that of water, plus the sum of the ion-water interactions, plus the sum of the ion-ion interactions. However, although many workers have studied the P-V-T properties of seawater over the past 80 years, large discrepancies in the data obtained exist.

To derive a reliable equation of state for seawater, two different approaches were employed: 1) one involving the use of direct experimental P-V-T data, and 2) the derivation of P-V-T properties from measurements of the speed of sound in seawater. This research has produced a reliable equation of state for seawater that is consistent with the speed of sound in seawater. Moreover, the thermodynamic considerations that are an integral part of this ongoing research program are directly applicable in other research on the physical chemistry of seawater. (See the discussion by Drs. Atkinson and Gilligan)

*Dr. Frank J. Millero is Professor of Chemistry and Chemical Oceanography at the School of Marine and Atmospheric Science of the University of Miami, Miami, Florida. Dr. Millero's leadership in research on the thermodynamics of chemical equilibria in seawater is internationally recognized.

Historical Review

Many early workers thought that water was incompressible. They arrived at this conclusion following the experiments in the fourteenth century by the Florentine Academy. In these experiments a sphere of lead was filled with water, sealed and then flattened between the jaws of a press until the water was forced out. Measurement of the distortion of lead showed no loss in volume in the cavity to the accuracy available in the fourteenth century. The actual one percent change in volume was too small to be detected.

Canton in 1762 using a piezometer (see Figure 1) was the first investigator to show that water was compressible. He also found that the compressibility decreased when the temperature was raised (from 0 to 45°C), and that the compression of rain water was greater than seawater, and less than wine. Perkins in 1826 showed that at 10°C the compressibility decreased with pressure, quickly at first and then more slowly at higher pressures. Many early workers incorrectly contested these results.

In 1888 the first serious measurements were made by Tait on the compressibility of water and seawater collected from the HMS Challenger Expedition (1). He used six piezometers in his work, three with pure water and three with seawater. His work covered the pressure range of 0 to 450 bars (1.013 bar = 1 atm) and the temperature range of 0 to 15°C. He reported that the compressibility of water at 1 atm ($P=0$ applied pressure) goes through a minimum at 60°C, and that the minimum temperature was lowered by an increase in pressure. As is apparent from Figure 2, which shows the results of some of the author's recent work, the minimum actually occurs at 45°C at 1 atm ($P = 0$) and 50°C at $P = 1000$ bars applied pressure.

Tait represented his results for the mean compression by an equation of state. However, it has been recently revealed (2) that for the last 60 years the Tait equation has been misquoted. The Tait equation was first misquoted by Tamman in 1907. The misquoted equation has been used over the years resulting in many inaccurate interpretations pertaining to water and seawater P-V-T data.

Since 1969 considerably more precise determinations have been made on the P-V-T properties of water and seawater. Examples of this work are Bradshaw and Schleicher in 1970 (2) and Lepple and Millero in 1970 (3). Recently, the author and his team at the University of Miami have selected the second degree secant bulk modulus as the reliable form for the equation of state of seawater.

$$K = \frac{V^0 P}{V^0 - V^P} = K^0 + A_1 P + A_2 P^2 \quad (1)$$

Glass Piezometer

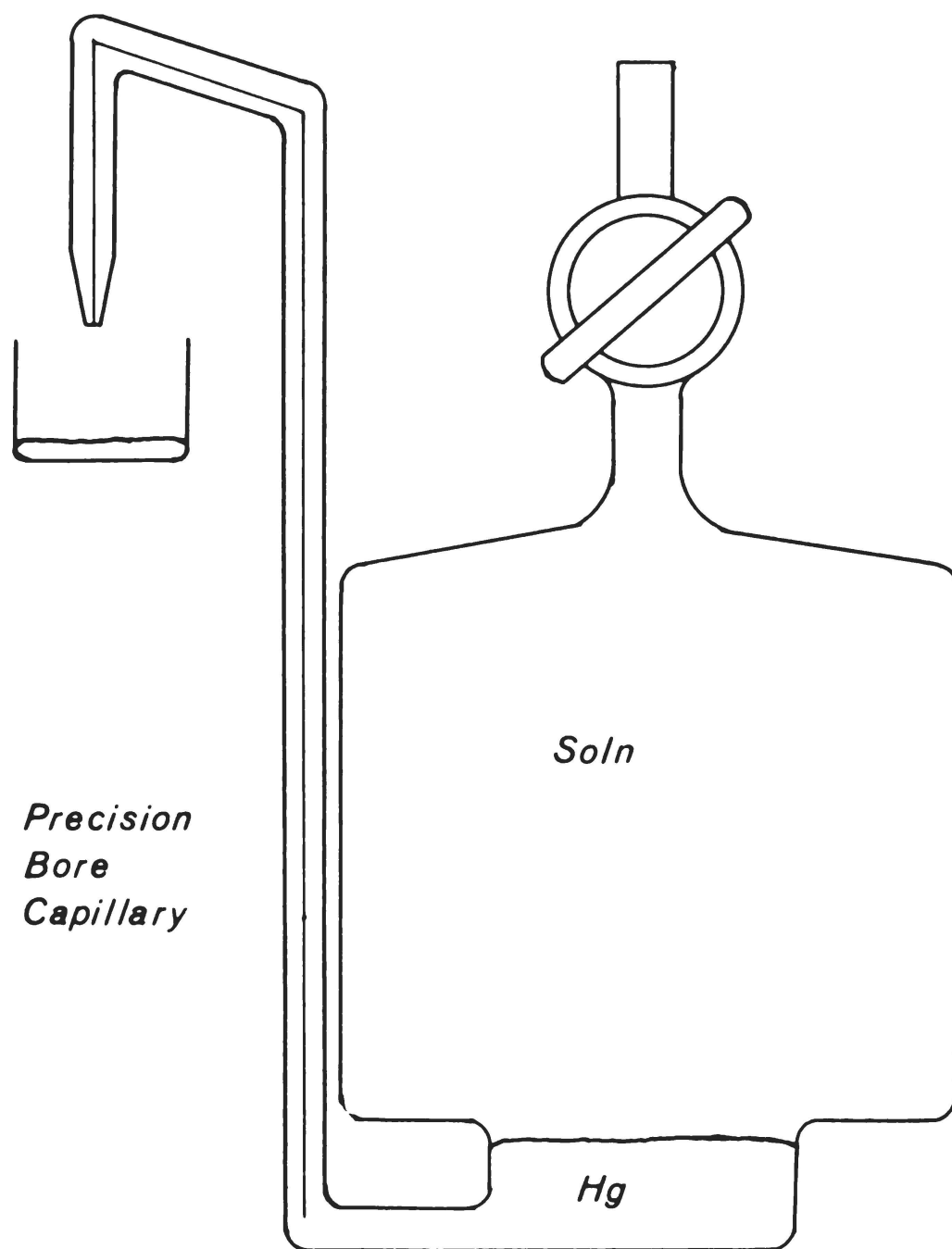


Figure 1 -- Sketch of a typical piezometer used in compressibility studies.

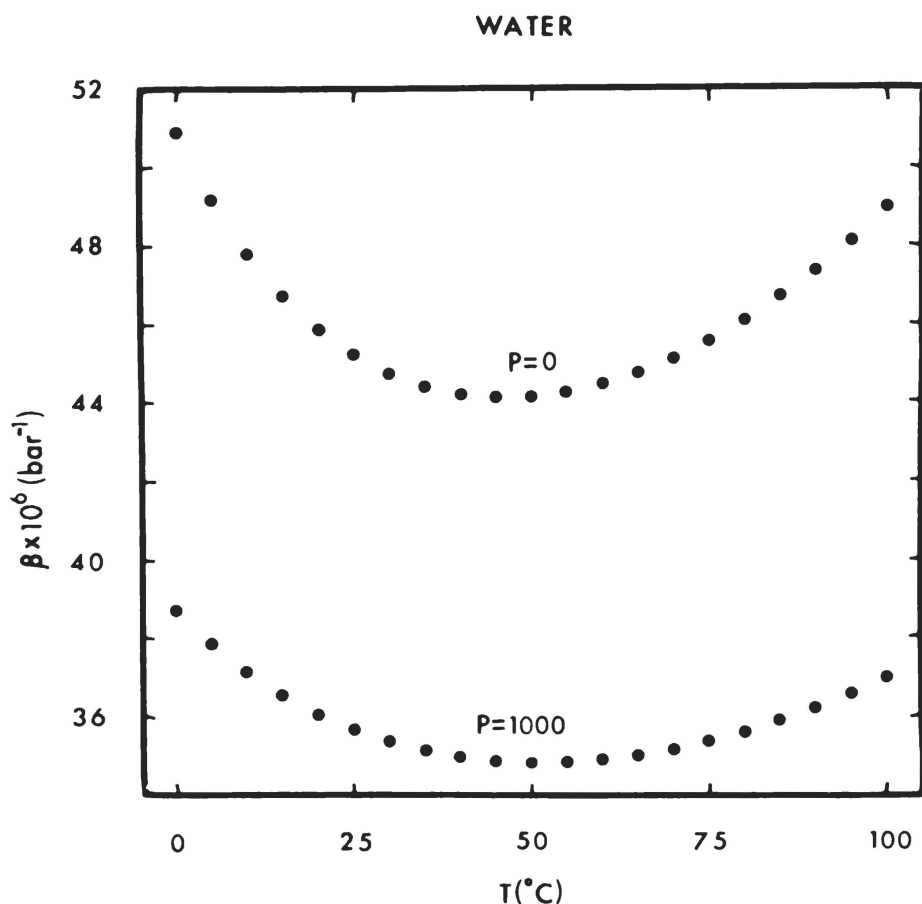


Figure 2 – Compressibility (β) of pure water at $P = 0$ and $P = 1000$ bars applied pressures plotted vs. temperature.

As can be seen from Figures 3 and 4 the secant bulk modulus of seawater is nearly linearly related to pressure (i.e., A_2 is very small and only needed for very precise PVT data). The slopes (A_1) in these Figures appear to be nearly independent of temperature and salinity, which shows the value of treating the high pressure PVT data of seawater in terms of the secant bulk modulus.

Since the K is equal to the reciprocal of β at $P = 0$, the salinity dependence of K^0 is given by

$$K^0 = K_W^0 + A'_K S + B'_K S^{3/2} \quad (2)$$

where the secant bulk modulus of water $K_W^0 = 1/\beta_W^0$.

In the following sections, two general approaches to obtaining a reliable equation of state for seawater using P-V-T properties (a) measured directly and (b) derived from sound speed data, will be discussed in detail.

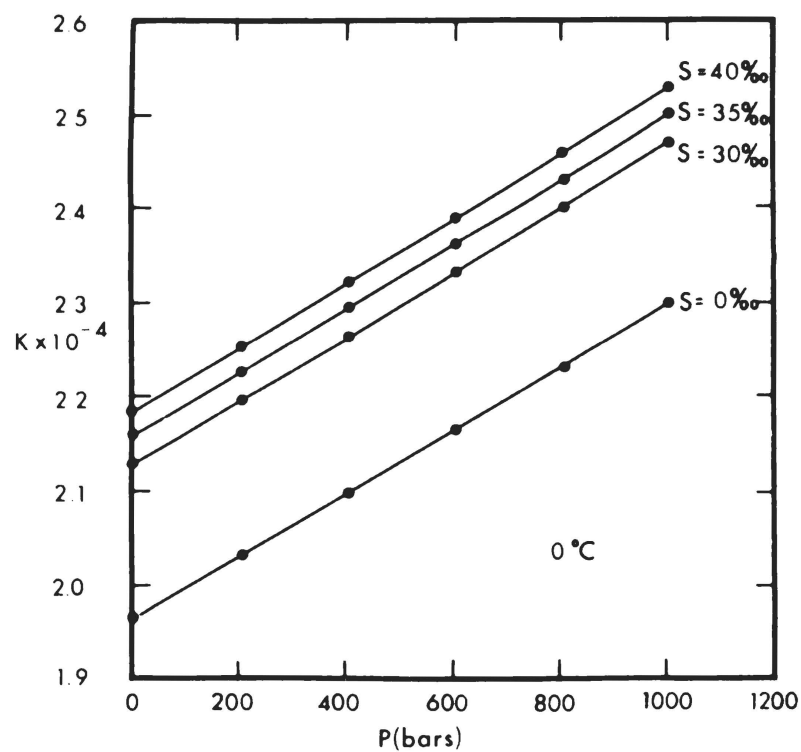


Figure 3 – The secant bulk modulus (k) of sea water of various salinities at 0°C plotted vs. pressure.

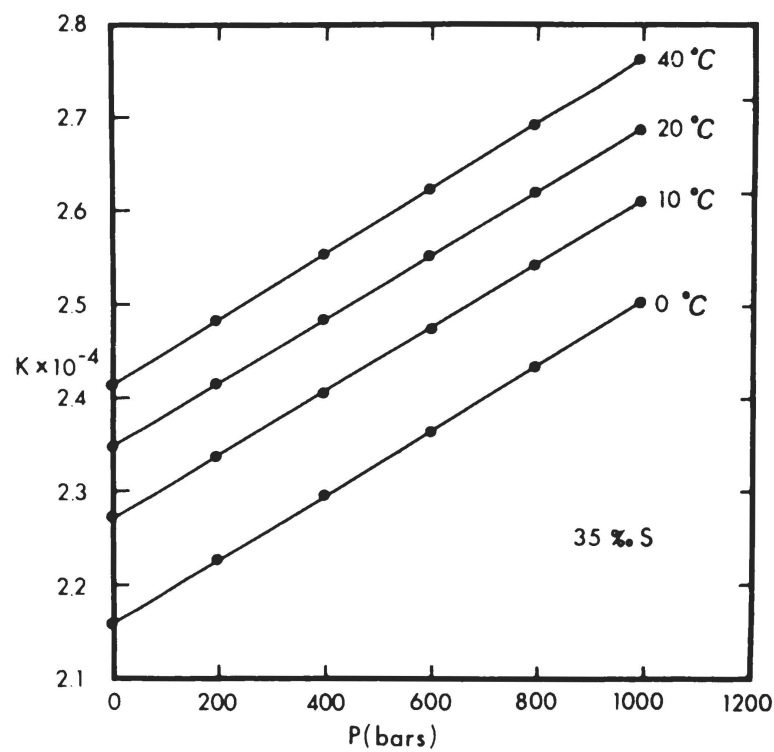


Figure 4 – The secant bulk modulus (k) of sea water at 35°‰ salinity at various temperatures plotted vs. pressure.

Direct PVT Measurements

The most direct method of determining reliable PVT properties for seawater is to measure the specific volume as a function of pressure and temperature. Three methods that have been used in recent years to determine the specific volumes of solutions; (1) the piezometer or dilatometer method; (2) the volumometer method and (3) the magnetic float method.

In the piezometer or dilatometer method the volume change produced by a given pressure change is followed by monitoring the change in volume of mercury that is in contact with the solution in a glass container (confined in a metal pressure vessel). The change in volume of Hg can be determined visually or by indirect methods (such as the use of a capacity detector). In the earlier dilatometers the apparatus was disassembled after each measurement and the displaced Hg was weighed. The volumometer method is similar to the dilatometer method except the solution container which is made of metal also serves as the pressure vessel. The volume change is measured by adjusting a calibrated screw piston. In both methods the volume of the container is determined by a calibration with a fluid of known specific volume (usually Hg). The accuracy is thus limited to how well the PVT properties of calibrating fluid are known. The precision of the method is dependent upon the sensitivity of the volume change measurements (usually careful work can yield V's to within 5 ppm). A magnetic float method which has been used in our laboratory at the University of Miami to measure the density or specific volume of liquids is briefly discussed in the next section.

Magnetic Float Densitometry

The use of the floatation method to measure densities of liquids is a development of the hydrostatic weighing method. However, in the floatation method the float has no suspension thread or wire. Earlier workers adjusted the buoyancy of the float by mixing two liquids, adding platinum weights and by changing the temperature but these methods normally took a long time to reach a steady state. By using an external current through a solenoid to adjust the buoyancy of a float (containing a permanent magnet) the steady state problem is solved. This electromagnetic method of weighing is very sensitive and can yield a precision of one part in 10^7 in the density of a solution. Although the magnetic float method of measuring densities was first described in 1913, it has not received widespread use until

recent years and was not applied at high pressures. A high pressure magnetic float densimeter (see Figure 5) that has a precision of 1 ppm to pressures of 1000 bars has been developed in the laboratory at the University of Miami. This system is presently being used to study the high pressure PVT properties of seawater and sea salts.

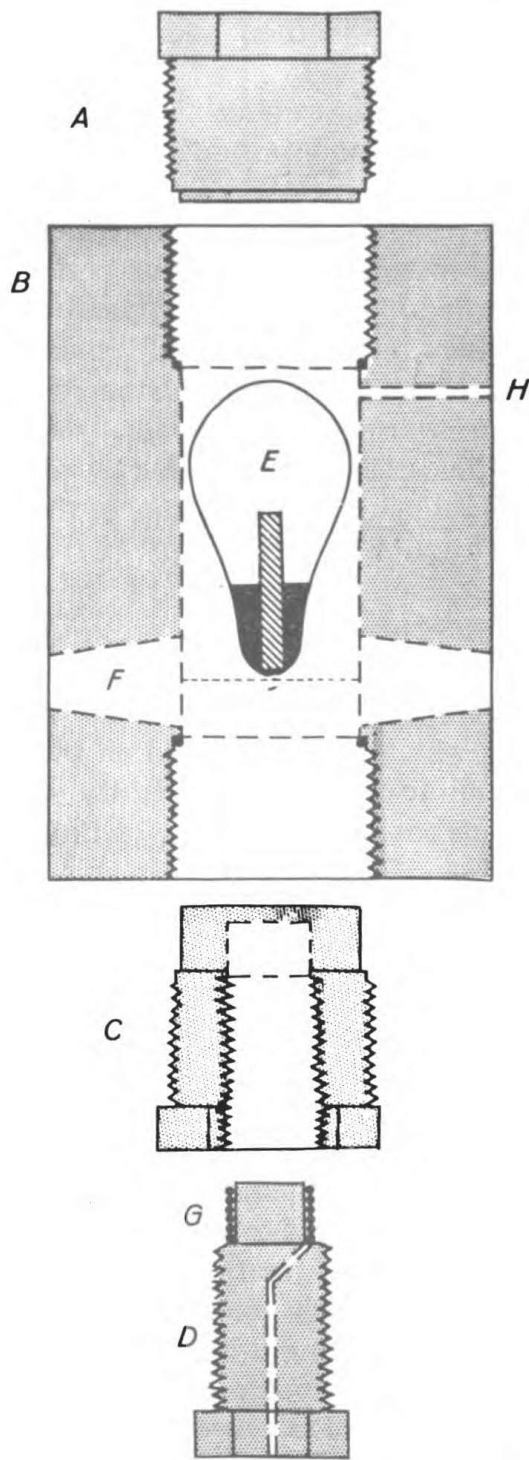


Figure 5—Sketch of the high-pressure magnetic float densimeter. A) Top plug, B) Cylindrical Pressure Bomb, C) Bottom plug, D) Solenoid insert plug, E) Magnetic float, F) Plexiglas window, G) Solenoid.

The principles of operation of the magnetic float densimeter are quite simple. If a weighted float is completely immersed at equilibrium in a solution of density $\underline{d}$, the weight of the volume $\underline{V}$ of the float and the volume $\underline{v}$ displaced by the platinum weights is equal to the weight of the float, W , plus the weight $\underline{w}$ of platinum. If a magnetic force is used to just barely hold the float on the bottom of the densimeter (or any other fixed position), the force is increased by $\underline{f}$ times $\underline{i}$ or a constant times the current through the solenoid. Thus, one obtains

$$d(V_f + v) = W + w + f \times i \quad (3)$$

or

$$d\left(V_f + \frac{w}{d_{Pt}}\right) = W + w + f \times i \quad (4)$$

where d_{Pt} is the density of Pt.

The densimeter is calibrated by measuring the hold-down current when various Pt weights are added to the float in pure water. By rearranging equation (4), we have

$$w\left(1 - \frac{d_{H_2O}}{d_{Pt}}\right) = -f \times i + (d_{H_2O} V_f - W) \quad (5)$$

The weight added to the float is a linear function of current at a given temperature and pressure (Figure 6). The interaction constant $\underline{f}$ can be determined from the slope of equation (5), and the volume of the float can be obtained from the intercept. Calibrations on the high pressure densimeter have shown that the precision is 1 ppm and accuracy is 5 ppm.

The density of seawater is presently being measured over a wide range of salinity (5 to 40‰, at 5‰ increments), pressure (0 to 1000 bars, at 100 bar increments) and temperature (0 to 40°C, at 5°C intervals) with the high pressure magnetic float densimeter. Preliminary results confirmed earlier work at 1 atm and indicate that the presently used equation of state of seawater based on Ekman's work is in error.

Sound Derived PVT Data

The speed of sound (c) in a compressible medium is defined by

$$c^2 = \frac{V}{\beta_S} \quad (6)$$

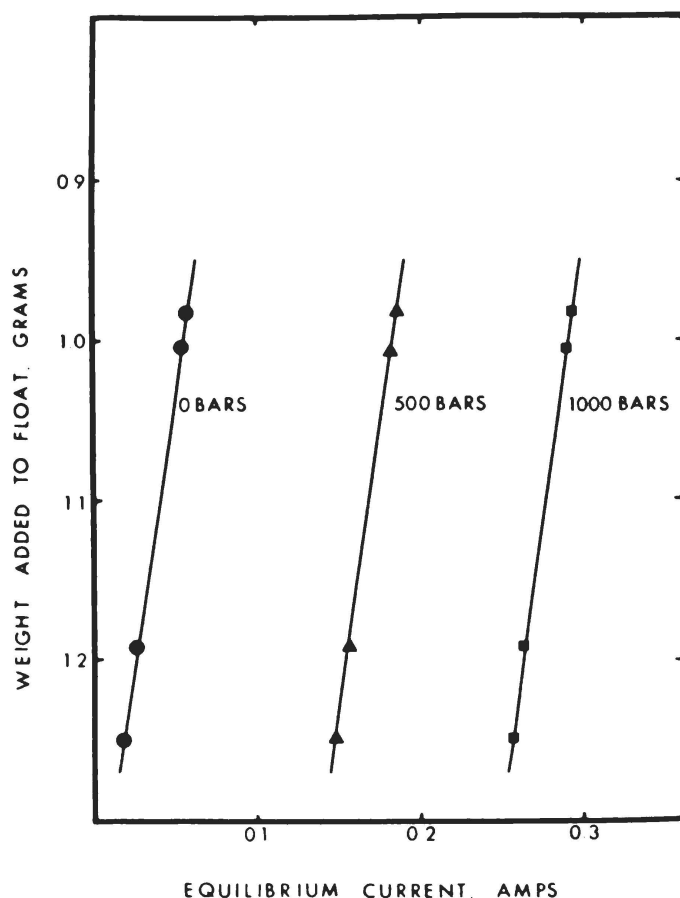


Figure 6 – Plot of weight added to the magnetic floated vs. the hold down current at various pressures.

where β_S is the adiabatic (constant entropy) compressibility

$$\beta_S = \frac{-1}{V} \left(\frac{\partial V}{\partial P} \right)_S \quad (7)$$

Although this equation is difficult to verify by direct experimental measurements, it has been indirectly verified by a number of workers. The adiabatic compressibility is related to the isothermal compressibility by

$$\beta_S = \beta \frac{C_V}{C_P} \quad (8)$$

where C_V and C_P are, respectively, the heat capacity at constant volume and pressure. The difference between C_P and C_V is given by

$$C_P - C_V = \frac{T\alpha^2 V}{\beta} \quad (9)$$

where the expansibility $\alpha = (1/V) (\partial V/\partial T)$ and T is the absolute temperature. By substituting equation (9) into equation (6) and rearranging, we have

$$\beta = \frac{V}{c^2} + \frac{T\alpha^2 V}{C_p} \quad (10)$$

or

$$-\left(\frac{\partial V}{\partial P}\right) = \frac{V^2}{c^2} + \frac{T\alpha^2 V^2}{C_p} \quad (11)$$

Thus, the compressibility (β) or compression ($\partial V/\partial P$) can be determined from sound speeds, providing that heat capacity data is available (α and V must also be known at $P = 0$). Since the second term of equation (11) is small (0.3 ppm) compared to V^2/c^2 (45 ppm), it is possible to determine β or $\partial V/\partial P$ from sound data by treating the correction term as a perturbation to the general equation. That is

$$-\left(\frac{\partial V}{\partial P}\right) = \frac{V^2}{c^2} + \Delta_s \quad (12)$$

where Δ_s is the adiabatic correction. By differentiating equation (1) with respect to pressure we have

$$-\left(\frac{\partial V}{\partial P}\right) = \frac{V^0(K^0 - A_2 P^2)}{(K^0 + A_1 P + A_2 P^2)^2} \quad (13)$$

By combining this equation with equation (11), the constants K^0 , A_1 , and A_2 can be determined from sound speed data at various pressures. The heat capacities at higher pressures needed in this iterative method are calculated from the thermodynamic relationship

$$C_p(P) = C_p(0) + T \int_0^P \left(\frac{\partial^2 V}{\partial T^2}\right) dP \quad (14)$$

Since sound speeds can be measured to a precision of ± 0.1 m/sec, the compressions calculated from sound speeds should be precise to ± 0.006 ppm—a precision that is much superior to that obtained by direct measurements (± 0.02 ppm).

Recently these methods have been used to determine a precise equation of state for water and seawater. It has been shown that

the specific volumes calculated from the sound-derived equation of state agree with directly measured values in the laboratory at the University of Miami (See Figure 7) to 10 ppm over the oceanographic ranges of pressure and temperature. Although one might expect the sound-derived PVT properties to be more reliable than the directly measured values, at present there is some question concerning the reliability of the high pressure sound data. For example at 5°C and 1000 bar (See Figure 8) the sound speeds for 35‰ S seawater measured by Del Grosso (10) differ by as much as 1 m/sec from those measured by Wilson (which would yield an error in $\partial V/\partial P$ of 0.03 ppm (11)). A program is presently being initiated to measure the sound speeds in seawater as a function of pressure, temperature, and salinity. These results should clear up the discrepancy and lead to a reliable equation of state for seawater.

Ion-Water and Ion-Ion Interactions of Sea-Salts

Recently, methods have been developed that can be used to examine the physical properties of seawater in terms of the ion-water and ion-ion interactions of the major ionic components. In this section we will briefly examine some of the results of this work applied to the

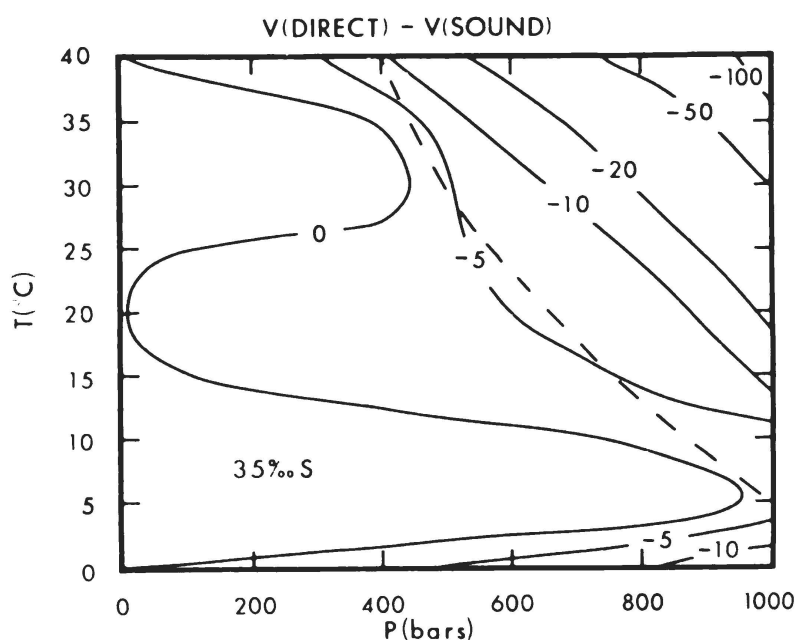


Figure 7 – Contour diagram of the differences in the specific volumes (in ppm) of 35‰ salinity sea water obtained from direct measurements and those obtained from sound speeds from 0 to 40°C and 0 to 1000 bars. The broken line indicates the oceanographic range.

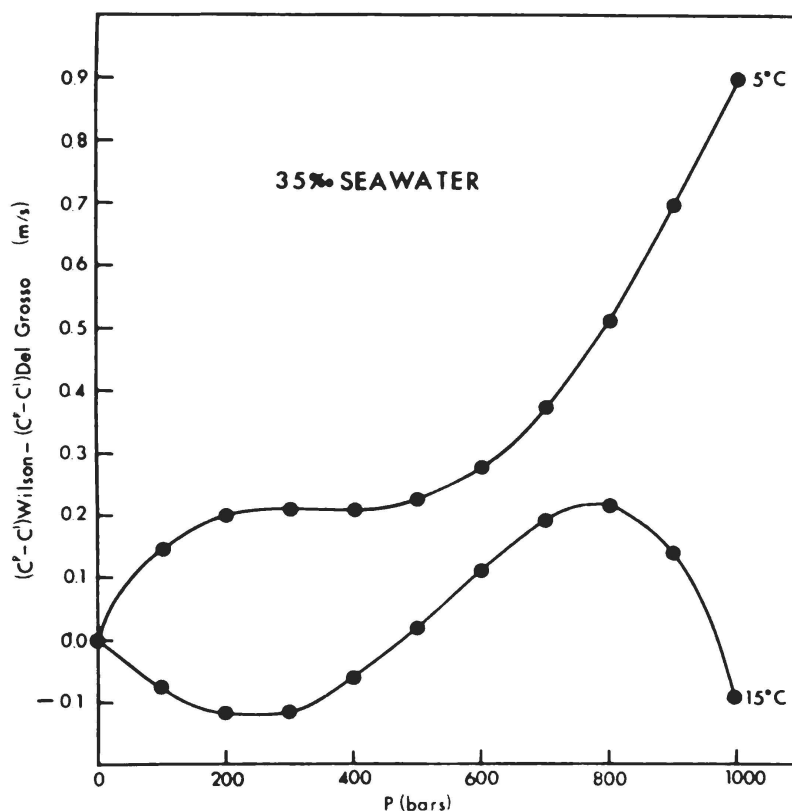


Figure 8 – Comparison of the sound speeds of sea water at 35‰ salinity obtained by Wilson and Del Grosso at various pressures and temperatures.

PVT properties of seawater. (For kinetic considerations see the discussion by Drs. Atkinson and Gilligan.) The volume properties of solutions can be conveniently handled by using the concept of apparent molal properties. The apparent molal volume of seawater is defined by

$$\Phi_v = \frac{(V_{\text{Soln}} - V_{\text{H}_2\text{O}})}{n_T} \quad (15)$$

where V_{Soln} is the volume of the solution, $V_{\text{H}_2\text{O}}$ is the volume of water in the solution and n_T is the total number of equivalents of sea salt added to form the solution. The quantity $(V_{\text{Soln}} - V_{\text{H}_2\text{O}})$ is the volume change that occurs when n_T equivalents of sea salt are added to water to form a solution of seawater at a given salinity. If the total volume of solution is 1000 cm^3 , the Φ_v can be related to quantities by

$$\Phi_v = \frac{1000(d^\circ - d)}{N_T d^\circ} + \frac{M_T}{d^\circ} \quad (16)$$

where $\underline{d}^\circ$ is the density of water, $\underline{d}$ is the density of seawater, N_T is the normality of the solution ($N_T = 0.03128 \times \text{Cl}(\%_\infty) \times d$, $N_T = 0.628$ for 35‰ S seawater) and M_T is the mean equivalent weight (58.049) of sea salt [$(M_T = 1/2 \sum (n_i/n_T)M_i$, where n_i is the number of equivalent and M_i is the equivalent weight of component i]. The Φ_v of sea salt (as well as other electrolytes) has been shown to be a linear function of the total volume ion strength $I_v = 0.03600 \times \text{Cl}(\%_\infty) \times d$, ($I_v = 0.713$ for 35‰ S seawater)

$$\Phi_v = \Phi_v^\circ + S_v \sqrt{I_v} \quad (17)$$

where Φ_v is the infinite dilution apparent molal volume (equal to the partial molal volume, $\bar{V}^\circ$) and S_v^* is a temperature dependent parameter. The infinite dilution partial equivalent volume of an ion is related to ion-water interactions. By using a simple model for ion-water interactions, $\bar{V}^\circ$ (ion) is given by

$$\bar{V}^\circ(\text{ion}) = \bar{V}^\circ(\text{int}) + \bar{V}^\circ(\text{elect}) \quad (18)$$

where the intrinsic partial molal volume $\bar{V}^\circ(\text{int})$ is a positive volume due to the size of the ion ($4/3\pi r^3$, where r is the crystal radius) and packing effects, and the electrostriction partial molal volume $\bar{V}^\circ(\text{elect})$ is the decrease in volume due to the electrostatic interactions between the charged ion and the water dipoles ($\bar{V}^\circ(\text{elect})$ is proportional to Z^2/r , where Z is the charge on the ion). The parameter S_v^* is related to ion-ion interactions which occur as the concentration is increased. These ion-ion interactions can be the classical Debye-Hückel type (i.e., point charges interacting through a dielectric medium) as well as the Bjerrum type (i.e., the formation of cation-anion ion pairs). By combining equations (16) and (17) and noting that n_T and I_v are proportional to the volume of chlorinity ($\text{Cl}_v = \text{Cl}(\%_\infty) \times d$), we have

$$d = d^\circ + A_v \text{Cl}_v + B_v \text{Cl}_v^{3/2} \quad (19)$$

where $A_v = 10^{-3}(d^\circ \Phi_v - M_T) \times 0.03129$ is related to ion-water interactions and $B_v = -10^{-3}d^\circ S_v^* \times 0.00594$ is related to ion-ion interactions.

By appropriate differentiation of equations (15), (16), and (17) with respect to temperature and pressure, one can arrive at similar equations for the expansibility and compressibility

$$\alpha = \alpha^\circ + A_E \text{Cl}_v + B_E \text{Cl}_v^{3/2} \quad (20)$$

where the expansibility of water $\alpha^\circ = (1/d^\circ) (\partial d^\circ / \partial T)$, $A_E = 10^{-3} (\Phi_{e^\circ} - \alpha^\circ \Phi_{v^\circ}) \times 0.03129$ and $B_E = 10^{-3} [S_{E*} - \alpha^\circ S_{V*}] \times 0.00594$ ($\Phi_{e^\circ} = \partial \Phi_v^\circ / \partial T$ and $S_{E*} = \partial S_{V*} / \partial T$) and

$$\beta = \beta^\circ + A_K Cl_V + B_K Cl_V^{3/2} \quad (21)$$

where the compressibility $\beta^\circ = (1/d^\circ) (\partial d^\circ / \partial T)$, $A_K = 10^{-3} (\Phi_{k^\circ} - \beta^\circ \Phi_{v^\circ}) \times 0.03129$ and $B_K = 10^{-3} (S_{K*} - \beta^\circ S_{V*}) \times 0.00594$ ($\Phi_{k^\circ} = -\partial \Phi_v^\circ / \partial P$ and $S_{K*} = S_{V*} / P$). Similar types of equations can be given for other thermodynamics properties of seawater. If we assume that the excess volume of mixing sea salts (to form sea water) is zero, the apparent properties of sea salt can be attributed to the sum of the individual components of seawater.

$$\Phi_v = \sum E_M E_X \Phi_v(MX) + E_B \Phi_v(B) \quad (22)$$

where E_i is the equivalent weighting factors of cation M, anion X and boric acid B, $\Phi_v(MX)$ is the apparent property of MX and $\Phi_v(B)$ is the apparent property of boric acid. By making the summation for each cation over all its possible salts, the total electrolyte term is

$$\begin{aligned} E_M E_X \Phi_v(MX) = & \Phi_v(Na \sum X_i) + \Phi_v(Mg \sum X_i) + \Phi_v(Ca \sum X_i) \\ & + \Phi_v(K \sum X_i) + \Phi_v(Sr \sum X_i) \end{aligned} \quad (23)$$

where each cation contribution $\Phi_v(MX_i)$ is given by

$$\begin{aligned} \Phi_v(M \sum X_i) = & E_M E_{Cl} \Phi_v(MCl) + E_M E_{SO_4} \Phi_v(MSO_4) \\ & + E_M E_{HCO_3} \Phi_v(MHCO_3) + E_M E_{CO_3} \Phi_v(MCO_3) \\ & + E_M E_F \Phi_v(MF) + E_M E_{B(OH)_4} \Phi_v[MB(OH)_4] \end{aligned} \quad (24)$$

It should be pointed out that by determining the Φ_v by this method, one essentially eliminates excess cation-anion interactions (due to ion pair formation).

By dividing the Φ_v of sea salts into an infinite dilution term (Φ_{v°) and a concentration term (S_{V*}) it is possible to simplify the use of Equation (22)

$$\Phi_{v^\circ} = \sum E_M E_X \Phi_{v^\circ}(MX) + E_B \Phi_{v^\circ}(B) \quad (25)$$

and

$$S_V^* = \sum E_M E_X S_V^*(MX) + E_B S_V^*(B) \quad (26)$$

Since the infinite dilution volume properties are always additive [$\Phi_v^\circ(MX) = \Phi_v^\circ(M^+) + \Phi_v^\circ(X^-)$], the Φ_v° can be estimated from data on soluble salts. Since reliable S_V^* data are not available for all the sea salts, the additivity method must be used. For example, the S_V^* for CaSO_4 can be estimated from

$$S_V^*(\text{CaSO}_4) = S_V^*(\text{CaCl}_2) + S_V^*(\text{MgSO}_4) - S_V^*(\text{MgCl}_2) \quad (27)$$

Similar arguments can be made for any apparent molal quantity (Φ)

$$\Phi = \frac{(P - P^\circ)}{n_T} \quad (28)$$

where P and P° are, respectively, a physical property for sea water and water. By combining equation (28) with the general form of equations (24), (25), and (26), any physical property can be attributed to

$$P = P^\circ + \sum \text{ion-water interactions} + \sum \text{ion-ion interactions} \quad (29)$$

The second term is related to the weighted ion-water interactions of the major sea salts [$\Phi^\circ = E_M E_X \Phi^\circ(MX) + E_B \Phi^\circ(B)$] and the third term is due to the weighted ion-ion interactions of the major sea salts [$S_V^* = E_M E_X S_V^*(MX) + E_B S_V^*(B)$].

This general approach of examining the physical properties of seawater serves two purposes: 1) it provides the theoretical concentration dependence and 2) it emphasizes the importance of ion-water and ion-ion interactions of the major components of seawater.

By using binary solution data and the PVT properties of water, these general methods can be used to estimate the volume properties of seawater. A sample calculation of Φ_v and S_V^* for seawater is given in Table I. A comparison of the calculated and measured Φ_v 's for 35‰ salinity seawater are given in Table II.

The estimated Φ_v 's are in good agreement with the measured values over a wide pressure and temperature range. A comparison of the specific volumes determined from the estimated Φ_v 's are shown in Figure 9. Over the oceanographic range of pressure and temperature the estimated specific volumes agree with the measured values to

Table I
Calculation of Φ_v° and S_v^* for Sea Salt
from Equation 36 at 0°C and 1 ATM

SALT	$E_M E_X$	$\Phi_v^\circ (MX)$	$S_v^* (MX)$	$E_M E_X \Phi_v (MX)$	$E_M E_X S_v^* (MX)$
NaCl	0.696033	12.36	3.323	8.6030	2.3129
1/2Na ₂ SO ₄	0.072003	0.40	5.095	0.0288	0.3669
NaHCO ₃	0.002460	16.80	5.770	0.0413	0.0142
NaBr	0.001070	18.95	2.976	0.0203	0.0032
1/2Na ₂ CO ₃	0.000517	-8.58	4.928	-0.0044	0.0025
NaB(OH) ₄	0.000110	10.51	9.580	0.0012	0.0011
NaF	0.000086	-6.00	8.051	-0.0005	0.0007
1/2MgCl ₂	0.158297	5.23	2.200	0.8279	0.3483
1/2MgSO ₄	0.016376	-6.73	4.915	-0.1102	0.0805
1/2Mg(HCO ₃) ₂	0.000560	16.13	8.248	0.0090	0.0046
1/2MgBr ₂	0.000243	11.82	1.960	0.0029	0.0005
1/2MgCO ₃	0.000118	-15.71	4.884	-0.0018	0.0006
1/2Mg[B(OH) ₄] ₂	0.000025	3.38	8.428	0.0001	0.0002
1/2MgF ₂	0.000020	-13.13	6.899	-0.0003	0.0001
1/2CaCl ₂	0.030532	6.43	2.123	0.1963	0.0648
1/2CaSO ₄	0.003158	-5.53	4.824	-0.0175	0.0512
1/2Ca(HCO ₃) ₂	0.000108	17.33	8.200	0.0019	0.0009
1/2CaBr ₂	0.000047	13.03	1.960	0.0006	0.0001
1/2CaCO ₃	0.000023	-14.51	4.839	-0.0003	0.0001
1/2Ca[B(OH) ₄] ₂	0.000005	4.58	8.383	0.0000	0.0000
1/2CaF ₂	0.000004	-11.93	6.851	-0.0000	0.0000
KCl	0.015173	22.98	3.291	0.3487	0.0499
1/2K ₂ SO ₄	0.001570	11.02	4.933	0.0173	0.0077
KHCO ₃	0.000054	33.88	9.640	0.0018	0.0005
KBr	0.000023	29.57	3.219	0.0007	0.0001
1/2K ₂ CO ₃	0.000011	2.04	6.004	0.0000	0.0001
KB(OH) ₄	0.000002	21.13	9.548	0.0000	0.0000
KF	0.000002	4.62	9.041	0.0000	0.0000
1/2SrCl ₂	0.000272	5.80	2.409	0.0016	0.0007
1/2SrSO ₄	0.000028	-6.16	5.110	-0.0002	0.0001
1/2Sr(HCO ₃) ₂	0.000001	16.70	8.486	0.0000	0.0000
1/2SrBr ₂	0.000000	12.39	2.286	0.0000	0.0000
1/2SrCO ₃	0.000000	-15.14	5.186	-0.0000	0.0000
1/2Sr[B(OH) ₄] ₂	0.000000	3.95	8.730	0.0000	0.0000
1/2SrF ₂	0.000000	-12.56	7.137	-0.0000	0.0000
B(OH) ₃	0.000541 ^a	36.56	3.191	0.0198	0.0017
TOTAL				$\Phi_v^\circ = 9.9880$	$S_v^* = 3.2782$

a) E_B

Table II
Comparison of the Measured and Calculated
 Φ_V for 35‰ Salinity Sea Water

	0°C		25°C	
P	$\Phi_V(\text{Meas})$	$\Delta\Phi_V^a$	$\Phi_V(\text{Meas})$	$\Delta\Phi_V^a$
0	12.724	-0.009	15.699	-0.37
200	13.937	0.029	16.483	0.031
400	15.046	0.060	17.202	0.083
600	16.063	0.096	17.881	0.142
800	16.958	0.116	18.482	0.166
1000	17.735	0.096	19.012	-0.191

a) $\Phi_V(\text{Meas}) - \Phi_V(\text{Calc})$

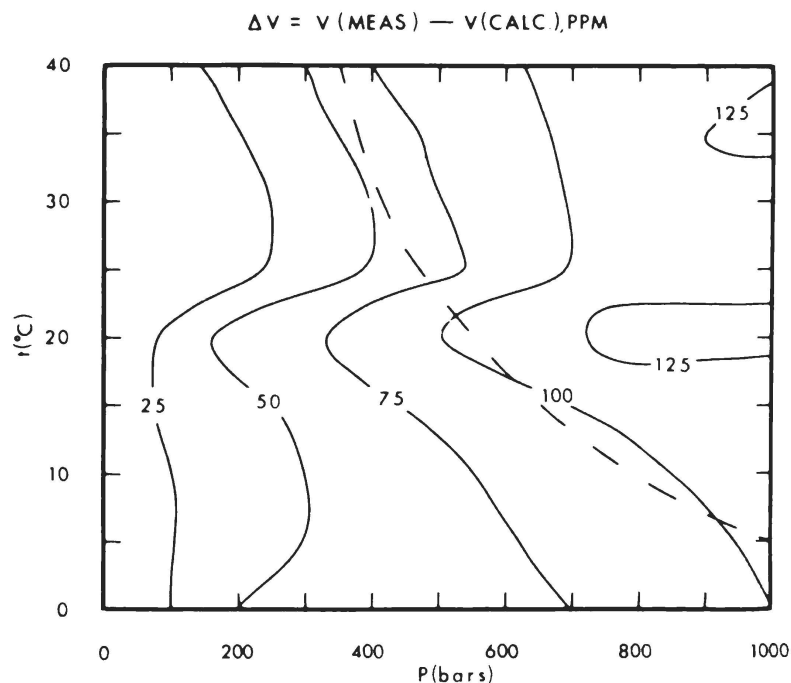


Figure 9 – Contour diagram of the differences in the directly measured specific volumes and those calculated from the additivity rule from 0 to 40°C and 0 to 1000 bars. The broken line indicates the oceanographic range.

within ± 70 ppm which is reasonable considering the scarcity of high pressure binary solution data.

Summary

Reliable PVT properties of seawater can be determined by making precise specific volume or sound speed measurements. By using recent developments on treating the properties of multicomponent electrolyte solutions it is possible to interpret the PVT properties of seawater in terms of the weighted ion-water and ion-ion interactions of the major components.

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By using recent developments on treating the properties of multicomponent electrolyte solutions it is possible to interpret the PVT (pressure-volume-temperature) properties of seawater in terms of the weighted ion-water, and ion-ion interactions of the major components.

Cover Caption

Sample collection in the ocean for chemical analyses in the shipboard laboratory for nutrients, trace elements and dissolved gases.

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