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Thermodynamics of the carbon dioxide system in seawater

Report by the carbon dioxide
sub-panel of the joint panel
on oceanographic tables and standards

Unesco 1987

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22	European sub-regional co-operation in oceanography. Report of Working Group sponsored by the Unesco Scientific Co-operation Bureau for Europe and the Division of Marine Sciences	1975	—
23	An intercomparison of some currents meters, III. Report on an experiment carried out from the Research Vessel Atlantis II. August-September 1972, by the Working Group on Continuous Velocity Measurements: sponsored by SCOR, IAPSO and Unesco	1975	WG 21
24	Seventh report of the joint panel on oceanographic tables and standards, Grenoble, 2-5 September 1975; sponsored by Unesco, ICES, SCOR, IAPSO	1976	WG 10
27	Collected reports of the joint panel on oceanographic tables and standards, 1964-1969	1976	WG 10
28	Eighth report of the joint panel on oceanographic tables and standards, Woods Hole, U.S.A., sponsored by Unesco, ICES, SCOR, IAPSO	1978	WG 10
29	Committee for the preparation of CLOFETA-Report of the first meeting, Paris, 16-18 January 1978	1979	—
30	Ninth report of the joint panel on oceanographic tables and standards, Unesco, Paris, 11-13 September 1978	1979	—

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PREFACE

This series, the Unesco Technical Papers in Marine Science, is produced by the Unesco Division of Marine Sciences as a means of informing the scientific community of recent advances in oceanographic research and on recommended research programmes and methods.

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Abstract

This report contains the results of the deliberations of the Sub-Panel on Carbon Dioxide of the Joint Panel on Oceanographic Tables and Standards.

Recommendations are presented for pH scales in seawater. Particular emphasis is given to a new set of standards that can be used in seawater or seawater-like solutions.

Best fit equations are suggested for the first and second dissociation constants of carbonic acid and the dissociation constant of boric acid as functions of temperature, salinity, and pressure. In addition recommendations are presented for the solubility products of calcite and aragonite in seawater as functions of temperature, salinity, and pressure.

Recommendations are presented with respect to future work that will lead to the refinement of the thermodynamic data base on the carbonic acid system in seawater.

RESUME

Ce rapport contient les conclusions des délibérations du Sous-Groupe sur le dioxyde de carbone du Groupe mixte d'experts sur les tables et les normes océanographiques.

Des recommandations y sont présentées en ce qui concerne les échelles du pH dans l'eau de mer. Un accent particulier est placé sur un nouvel ensemble de normes qui peuvent être utilisées dans l'eau de mer ou dans des solutions comparables à l'eau de mer.

Il propose des équations donnant les meilleurs résultats en ce qui concerne les première et deuxième constantes de dissociation de l'acide carbonique et la constante de dissociation de l'acide borique en fonction de la température, de la salinité et de la pression. Des recommandations sont en outre présentées en ce qui concerne les produits de la dissolution de la calcite et de l'aragonite dans l'eau de mer en fonction de la température, de la salinité et de la pression.

Il contient par ailleurs des recommandations concernant des activités futures qui déboucheront sur le perfectionnement de la base de données thermodynamiques relatives au système de l'acide carbonique dans l'eau de mer.

Resumen

En este informe se exponen los resultados de los debates del Subgrupo sobre Dióxido de Carbono del Grupo Mixto de Expertos en Tablas y Normas Oceanográficas.

Se formulan recomendaciones relativas a las escalas de pH en el agua de mar. Se hace especial hincapié en un nuevo conjunto de normas que pueden utilizarse en el agua de mar y en las soluciones similares al agua de mar.

Se sugieren ecuaciones más adecuadas para la primera y segunda constante de disociación del ácido carbónico y la constante de disociación del ácido bórico en función de la temperatura, la salinidad y la presión. Asimismo, se presentan recomendaciones relativas a los productos de solubilidad de la calcita y el aragonito en el agua de mar en función de la temperatura, la salinidad y la presión.

Se formulan recomendaciones con respecto a las tareas que se realizarán en el futuro para lograr el perfeccionamiento de la base de datos termodinámicos sobre el sistema del ácido carbónico en el agua de mar.

Резюме

Данный доклад содержит результаты работы подгруппы по двуокиси углерода Объединенной группы по океанографическим таблицам и стандартам.

Рекомендации представлены для шкал pH в морской воде. Особое внимание уделяется новому набору стандартов, которые можно использовать в морской воде и в сходных с морской водой растворах.

Предлагаются наиболее приемлемые уравнения для первой и второй константы диссоциации углекислоты и константы диссоциации борной кислоты как функций температуры, солености и давления. Кроме того, представлены рекомендации, касающиеся продуктов растворимости кальцитов и арагонитов в морской воде как функций температуры, солености и давления.

Даны рекомендации в отношении будущей работы, которая позволит заново определить базу термодинамических данных о системе углекислоты в морской воде.

ملخص

يتضمن هذا التقرير نتائج مداولات اللجنة الفرعية المعنية بثانى أكسيد الكربون والتابعة للجنة المشتركة الخاصة بالجداول والمعايير الأقيانوغرافية .

وتقدم فى التقرير توصيات بشأن موازين الرقم الهيدروجينى فى مياه البحار ، مع التركيز بوجه خاص على مجموعة جديدة من المعايير التى يمكن استخدامها فى مياه البحار أو فى المحاليل المشابهة لها .

وتقترح أيضا أنسب المعادلات للثابت الأول والثابت الثانى لتفكك حامض الكربونيك ولثابت تفكك حامض البوريك بفعل الحرارة والملوحة والضغط . وتقدم فضلا عن ذلك توصيات بشأن نواتج انحلال الكالسيت والأراغونيت فى مياه البحر بفعل الحرارة والملوحة والضغط .

ويتضمن التقرير توصيات بشأن الأنشطة المقبلة التى ستؤدى الى تحسين قاعدة البيانات الدينامية الحرارية المتعلقة بدورة حامض الكربونيك فى مياه البحار .

摘　　要

本报告载有海洋学图表及标准联合研究组二氧化碳分组的讨论结果。

文中对海水中PH（氢离子浓度负对数值）的比度划分提出了建议，特别重点分析了可用于海水或类似海水的分解的一套新的标准。

文中提出了一些把碳酸的第一和第二离解常数及硼酸的离解常数作为温度含盐度及压力函数的最高合适的方程式。此外，也提出了一些把方解石及霰文石在海水中的溶度积作为温度含盐度及压力函数的建议。

还有一些有关今后工作的建议，这些建议将有助于改进海水碳酸法方面的热力数据库。

Table of Contents

1. Introduction

During the 9th meeting in Paris (11-13 September, 1978) the Joint Panel on Oceanographic Tables and Standards, upon suggestions by its sponsoring agencies, decided that, especially because of the increased importance of precise evaluations of carbon dioxide speciation in seawater, a sub-group of the panel should be formed to consider the information available on the thermodynamics of the CO_2 system in seawater. Several meetings have been held on this subject: in Miami, Florida on September 21-23, 1981; in Kiel, Germany on August 26 and 27, 1983; in La Jolla, December 11 and 12, 1984. A preliminary report on the deliberations of the sub-panel has been published (UNESCO, 1983). In this report we present a detailed report on recommendations by the sub-panel addressing several topics of importance to this problem:

(1) An introduction to the thermodynamics of the CO_2 system;

(2) A section on the performance of calculations using the thermodynamic information;

(3) A section on pH scales;

(4) A section on thermodynamic information on solubility of CO_2 and on dissociation constants of carbonic acid and boric acid;

(5) A section on the information available on the solubilities of various carbonate phases.

The carbon dioxide system in seawater, although of long-standing interest in marine chemistry, has been a major problem for solution chemists. Until recently thermodynamic information on carbon dioxide gas solubility and on the dissociation constants of carbonic acid and boric acid have, to a large extent, been based on relatively meagre information. Before 1940 two groups of investigators paid attention to this problem: Moberg and co-workers at Scripps Institution of oceanography (Moberg et al., 1934; Lyman, 1957) and Buch and co-workers, under the sponsorship of the International Council for the Exploration of The Sea (Buch, 1933, 1938, 1951; Buch et al., 1932). Investigations of the pressure dependence of the dissociation constants were only carried out in the late 1960's (Distèche and Distèche, 1967; Culberson, 1968; Culberson and Pytkowicz, 1968; Culberson et al., 1967).

Solubility product constants for calcite and aragonite polymorphs of calcium carbonate were first investigated by Wattenberg (1933), and later by MacIntyre (1965), with pressure effects being investigated by Pytkowicz and coworkers (e.g., Pytkowicz and Connors, 1964; Pytkowicz and Fowler, 1967; Hawley and Pytkowicz, 1969).

Edmond and Gieskes (1970) summarized much of the thermodynamic information available in the late 1960's. Since then, however, much more extensive work on the determination of the dissociation constants has been carried out, particularly by Pytkowicz and co-workers and Dyrssen and co-workers. The new information has yielded more precise data and much of the work reported here is based on an evaluation of these recent data. The purpose of this report is to present a critical evaluation of this newly available information so that it can be used in a uniform manner in research on the CO_2 system in seawater.

2. Membership of CO_2 Sub-Panel

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3. Thermodynamics of the CO_2 system

The carbon dioxide system in seawater is governed by the following equilibria:

$$CO_2(g) \overset{K_o}{=} CO_2(aq) \tag{3.1}$$

where K_o is the solubility coefficient of carbon dioxide in seawater. Subsequently, the dissolved gas becomes hydrated

$$CO_2(aq) + H_2O \overset{K_H}{=} H_2CO_3 \tag{3.2}$$

where $K_H \sim 10^{-3}$, so that most undissociated dissolved CO_2 gas is in the CO_2 (aq) form. In determinations of dissociation constants one does not differentiate between CO_2 (aq) and H_2CO_3 and the sum of their concentrations is used. This sum is denoted by CO_2.

The partial pressure of dissolved CO_2 is defined by the relationship

$$P(CO_2) = \frac{[CO_2]}{K_o} \tag{3.3}$$

where the quantity in brackets represents the concentration in solution.
Furthermore upon dissociation

$$CO_2 + H_2O \overset{K_1}{=} H^+ + HCO_3^- \tag{3.4}$$

where K_1 is the *first* dissociation constant of carbonic acid.

$$K_1 = \frac{(H^+)[HCO_3^-]}{[CO_2]} \tag{3.5}$$

defining the activity of water to be equal to one.

$$HCO_3^- \overset{K_2}{=} H^+ + CO_3^{2-} \tag{3.6}$$

where K_2 is the *second* dissociation constant of carbonic acid

$$K_2 = \frac{(H^+)[CO_3^{2-}]}{[HCO_3^-]} \tag{3.7}$$

All quantities in square brackets are stoichiometric concentrations; the ``activity´´ of hydrogen (H^+) is determined by the pH scale used.

In seawater, estimates of carbon dioxide speciation often rely on estimates of the titration alkalinity (TA)

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] \tag{3.8a}$$

Here $[OH^-]$ includes OH^- bound to magnesium, and $[H^+]$ includes H^+ bound to sulphate and fluoride. Titration alkalinity also includes minor concentrations of other bases (Dickson, 1981; Johansson and Wedborg, 1982).

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [SiO(OH)_3^-] \qquad (3.8b)$$
$$+ [HPO_4^{2-}] + 2[PO_4^{3-}] - [H^+] - [H_3PO_4] + \cdots$$

In the speciation calculations only the carbon dioxide contributions to TA, i.e., carbonate alkalinity ($CA = [HCO_3^-] + 2[CO_3^{2-}]$), are considered so that correction must be made for the contributions of $[B(OH)_4^-]$, $[OH^-]$ and $[H^+]$ to TA. For this one needs to consider the equilibria

$$B(OH)_3 + H_2O \overset{K_B}{=} B(OH)_4^- + H^+ \qquad (3.9)$$

where K_B is the dissociation constant of boric acid, and

$$H_2O \overset{K_w}{=} H^+ + OH^- \qquad (3.10)$$

where K_w is the dissociation constant for water.

Finally, in seawater the solubility of calcium carbonate, in either of its polymorphic forms aragonite and calcite, is often considered. These solubilities are governed by the following equilibria:

$$CaCO_3 \overset{K_{sp}(arag)}{=} Ca^{2+} + CO_3^{2-} \qquad (3.11)$$

and

$$CaCO_3 \overset{K_{sp}(calc)}{=} Ca^{2+} + CO_3^{2-} \qquad (3.12)$$

where $K_{sp}(i)$ is the solubility product of aragonite or calcite.

All acid/base concentrations are expressed as stoichiometric concentrations, i.e., disregarding any speciation or interaction with other ionic constituents. For these reasons it is necessary to specify the constants not only as a function of temperature and pressure, but also of salinity and the pH scale used in the determination of the dissociation constants.

4. Calculations of constituent concentrations

Among the primary objectives for the detailed study of the thermodynamics of the CO_2 system in seawater are the estimation of the partial pressure of carbon dioxide, and of the carbonate ion concentration. The former is of importance in studies of CO_2 exchange between the atmosphere and the oceans, and the latter in studies of the state of saturation of seawater with respect to calcium carbonate.

Among the commonly measured quantities which are necessary for the above calculations are pH, titration alkalinity, total dissolved carbon dioxide, and partial pressure of carbon dioxide, or a combination of at least 2 of these, together with the various constants (Park, 1969; Skirrow, 1965, 1975). For

most of the calculations it is convenient to evaluate the values of the *in situ* pH and the *in situ* carbonate alkalinity ($CA = [HCO_3^-] + 2[CO_3^{2-}]$).

The total borate concentration

$$TB = [B(OH)_4^-] + [B(OH)_3] \tag{4.1}$$

is conservative in seawater, i.e., proportional to salinity (Culkin, 1965). Thus, combining (3.8a) and (4.1) yields

$$CA = TA - TB/(1 + (H^+)/K_B) - [OH^-] + [H^+] \tag{4.2a}$$

in which the terms for $[OH^-]$ and $[H^+]$ are often ignored, especially if the imprecision in TA is greater than $5x10^{-6}$ mol/kg, thus yielding

$$CA = TA - TB/(1+(H^+)/K_B) \tag{4.2b}$$

Of course

$$TCO_2 = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \tag{4.3}$$

and TA and TCO_2 are independent of temperature and pressure if expressed in concentration units of moles per kilogram of seawater (Dyrssen and Sillèn, 1967).

From the thermodynamic relationships described in this section and the previous section one derives (c.f., Skirrow, 1965)

$$[CO_3^{2-}] = CA/(2 + (H^+)/K_2) \tag{4.4}$$

and

$$[HCO_3^-] = CA/(1 + 2\,K_2/(H^+)) \tag{4.5}$$

and thus

$$CA = TCO_2 \cdot (1 + 2K_2/(H^+)) / (1 + (H^+)/K_1 + K_2/(H^+)) \tag{4.6}$$

and combining with (4.2b), c.f., Edmond and Gieskes (1970)

$$(H^+)^3A + (H^+)^2(K_1(A-1) + K_B(A-B)) \tag{4.7}$$

$$+ (H^+)(K_1K_B(A-B-1) + K_1K_2(A-2)) + K_1K_2K_B(A-B-2) = 0$$

where $A = TA/TCO_2 \sim 1.5$ and $B = TB/TCO_2 \sim 0.18$.

If greater accuracies are warranted by the data, a combination of equations (4.2a) and (4.6) will yield an equation containing the fifth power of (H^+) and K_w.

Equation (4.7) can be solved for the *in situ* value of (H^+) using values of K_1,K_2,K_B at the appropriate *in situ* temperature, pressure, and salinity. Hence, CA, $[CO_3^{2-}]$, and $[HCO_3^-]$ can be calculated for *in situ* conditions.

Classically a combination of pH and TA has been measured at a specified temperature and pressure (Harvey, 1955), from which, of course TCO_2 can be computed, and thus equation (4.7) can be applied subsequently. Other workers have used measurements of $P(CO_2)$ and TCO_2. With this information the pH can be evaluated as well as TA. The various combinations of measuring parameters and their subsequent use in carbon dioxide system calculation have been discussed by Park (1969). We advocate the determination of TA and TCO_2 independently, especially because each quantity is of intrinsic interest in chemical oceanography.

Keir (1979) also suggested a more direct method for the evaluation of the carbonate ion concentration from TA and TCO_2, but this method also ignores the species OH^- and H^+.

Calculations of the degree of saturation of calcium carbonate are based on the evaluation of the *in situ* concentration of the product of Ca^{2+} and CO_3^{2-} concentrations, and the *in situ* value of the solubility product:

$$\Omega = [Ca^{2+}][CO_3^{2-}]/K_{sp}(i) \tag{4.8}$$

The calcium concentration is approximately conservative (Culkin, 1965).

5. Solubility of Carbon Dioxide

The ad-hoc group discussed the data available on the solubility of carbon dioxide in seawater. It was decided that the formula provided by Weiss (1974) gives the best representation of CO_2 gas solubility as a function of temperature and salinity as measured by Murray and Riley (1971) and Weiss (1974).

$$\ln K_o = A_1 + A_2(100/T) + A_3 \ln(T/100) \tag{5.1}$$

$$+ S[B_1 + B_2(T/100) + B_3(T/100)^2]$$

where K_o may be expressed either in mol dm^{-3} atm^{-1} (referred to a dm^3 of solution at the temperature of measurement and one atmosphere fugacity in the gas phase) or in mol kg^{-1} atm^{-1} (referring to one kilogram of solution). T is the thermodynamic temperature (K) and S the salinity. A_i and B_i are constants and are given in the following table:

	mol dm^{-3} atm^{-1}	mol kg^{-1}(seawater) atm^{-1}
A_1	-58.093 1	-60.240 9
A_2	90.506 9	93.451 7
A_3	22.294 0	23.358 5
B_1	0.027 766	0.023 517
B_2	-0.025 888	-0.023 656
B_3	0.005 057 8	0.004 703 6

6. Symbols for pH and related quantities

In the description of weak acid equilibria various types of pH scales and various definitions of equilibrium constants have been used. These various approaches have been reviewed recently by Dickson (1984), whose contribution is attached to this report as Annex 1.

Below we propose four sets of symbols depending on the standard state chosen for hydrogen ions, and on the concentration units used. Current usage has been maintained as far as is consistent with an unambiguous set of symbols.

				Ref.
The N.B.S.[1] pH scale.	a_H(NBS)	pH(NBS)	pK′	(2)
The 'free' hydrogen ion concentration scale (mol/kg-H_2O).	m_H	pm_H	pK_m	(3)
The 'total' hydrogen ion concentration scale (mol/kg-H_2O).	$m_H(SWS) \approx {}^T m_H$	$pm_H(SWS)$	pK_m^*	
The 'total' hydrogen ion concentration scale (mol/kg-soln).	$[H]_{SWS} \approx {}^T[H]$	pH(SWS)	pK^*	(4)

(1) National Bureau of Standards

(2) Mehrbach *et al.* (1973)

(3) Bates and Culberson (1977)

(4) Hansson (1973a)

Notes:

(a) The symbol p in pm_H, pK etc. retains its usual meaning of -lg X, where X is the appropriate dimensionless quantity. In pm_H, strictly the quantity is the ratio $m_H/m°$, where m° is assigned the value of 1 mol/kg-H_2O.

(b) $m_H(SWS)$ is a quantity proportional to m_H and is defined by the equation

$$m_H(SWS) = m_H(1 + \beta_{HSO_4}\,{}^T m_{SO_4} + \beta_{HF}\,{}^T m_F)\ ,$$

whereas the total analytical concentration of hydrogen ion is given by

$${}^T m_H = m_H + m_{HSO_4} + m_{HF} + \cdots$$

(A similar distinction exists between $[H]_{SWS}$ and ${}^T[H]$.)

(c) If it is desired to indicate the acid or base to which a dissociation constant refers, it should be done thus: $pK_m^*(HCO_3^-)$.

(d) It is not necessary to include all of the modifiers for a particular symbol in those circumstances where there is no possibility of ambiguity.

6.1 *Standard reference solutions for pH*

The titration measurements of Hansson (1973a) have determined values of pH(SWS) for the buffer Tris (0.005 mol/kg-soln), Tris·HCl (0.005 mol/kg-soln) in fluoride-free synthetic seawater at salinities from 10 to 40 in the temperature range of 5-30°C. His results lead to the equation (Almgren *et al.*, 1975)

$$pH(SWS) = \frac{4.5S+2559.7}{T} - 0.01391S - 0.5523 \qquad (6.1.1)$$

where T is the thermodynamic temperature (K). The pH(SWS) scale, together with Equation (6.1.1) is also useful for pH measurements in estuarine waters between S = 20 to 35 (Butler *et al.*, 1985; Whitfield *et al.*, 1985). pH scales at lower salinities are discussed by Millero (1986).

Standard values of pm_H for two useful buffer solutions in synthetic seawater without fluoride have been determined as a function of salinity and temperature (Ramette *et al.*, 1977; Bates and Calais, 1981). Compositions in moles per 1000 g of synthetic seawater for Hansson's pH(SWS) standard and for the two pm_H standards are as follows:

pH (SWS) Standard:

0.005 moles (0.606g) ''Tris''

0.005 moles (0.788g) Tris·HCl

pm_H Standard A:

0.02 moles (2.423g) ''Tris''

0.02 moles (3.152g) Tris·HCl

pm_H Standard B:

0.02 moles (2.103g) ''Bis''

0.02 moles (2.832g) Bis·HCl

NOTE: Tris = Tris(hydroxymethyl)aminomethane (2-amino-2-(hydroxymethyl)-1,3-propanediol).
Bis = Bis(hydroxymethyl)methylaminomethane (2-amino-2-methyl-1,3-propanediol).

Tris, Tris·HCl, and Bis are obtainable commercially (for example, from Sigma Chemical Co., St. Louis, MO 63178). Bis·HCl can be crystallized from a concentrated solution of Bis that has been neutralized with purified hydrochloric acid.

The pm_H values for both standard solutions are nearly the same as pK_m for the corresponding protonated amines, $Tris{\cdot}H^+$ or $Bis{\cdot}H^+$. Furthermore, the pH is relatively insensitive to changes in the molality of the buffer components, provided equivalence of the two buffer species (e.g., Tris and Tris-HCl) is

maintained. Thus, the pH values of the 0.005 mol/kg-H_2O and 0.02 mol/kg-H_2O Tris buffers are nearly identical (see also Millero, 1986). The reference values of pm_H listed in Tables 6.1.I and 6.1.II have estimated uncertainties of ±0.004 unit.

6.2 *Relationship between pm_H and pm_H(SWS)*

The interconversion of pm_H and pm_H(SWS) is readily carried out when values of the formation constants β_i of the species HSO_4^- and HF are known. Thus,

$$pm_H(SWS) = pm_H - \log(1 + \beta_{HSO_4}\,{}^Tm_{SO_4} + \beta_{HF}({}^Tm_F) \qquad (6.2.1)$$

$$= pm_H - \Delta$$

where Δ is a function of temperature and salinity. From the measurements of Khoo *et al.* (1977) in fluoride-free synthetic seawaters, it has been shown (Bates, 1985) that $\log \beta_{HSO_4}$ for salinities from 20 to 45 and temperatures from 5 to 40°C is given by

$$\log \beta_{HSO_4} = 1121.1/T - 45.2167 \qquad (6.2.2)$$

$$+ 7.484 \ln T + 0.0011984S - 1.2613\times10^{-4}S^2$$

where T is the thermodynamic temperature. The standard deviation of fit is 0.0068 in $\log \beta_{HSO_4}$. Combination of Equations (6.2.1) and (6.2.2) shows that the difference (Δ) between pm_H(SWS) and pm_H at a salinity of 35 has the following values in the range to 5 to 40°C:

t/°C:	5	10	15	20	25	30	35	40
Δ:	0.077	0.088	0.100	0.114	0.129	0.146	0.164	0.185

Millero (1986) has reevaluated this problem and provides information over the range of S = 1-40 and t = 5-40°C (see also Annex 2).

6.3 *Experimental measurement of pm_H and pm_H(SWS)*

Values of pm_H(SWS) and pm_H can be obtained experimentally from measurements of the emf (E) of the pH cell

Reference electrode | KCl(3.5M or saturated) | | Seawater (X) | glass electrode (6.3.1)

standardized with a standard buffer (S) prepared in a synthetic seawater without fluoride, of a composition close to that of the ''unknown'' seawater (X). The operational pH formula then applies:

$$pH(X) = pH(S) - \frac{(E_X - E_S)F}{RT \ln 10} \qquad (6.3.2)$$

In this equation, F, R, and T are respectively the Faraday constant, the gas constant, and the thermodynamic temperature. Matching of the salinity of the standard S with that of seawater X assures that the residual liquid-junction error is nullified (Bates and Macaskill, 1975).

The synthetic seawater can be prepared from NaCl, KCl, $CaCl_2$, $MgCl_2$, and Na_2SO_4 according to recipes given elsewhere (for example, Khoo *et al.*, 1977; Bates and Calais, 1981). Recrystallization of the NaCl used in preparing the synthetic seawaters is advisable, in order to eliminate traces of acidic and basic contaminants that might alter the standard values of pm_H or pm_H(SWS).

TABLE 6.1.I

pm_H(S) values for Standard A (Tris buffer)

Salinity	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°
30	8.798	8.635	8.479	8.330	8.187	8.050	7.917	7.789
35	8.812	8.649	8.493	8.343	8.200	8.062	7.929	7.801
40	8.826	8.663	8.507	8.357	8.214	8.076	7.943	7.815

TABLE 6.1.II

pm_H(S) values for Standard B (Bis buffer)

Salinity	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
30	9.509	9.341	9.178	9.022	8.873	8.729	8.588	8.453
35	9.574	9.404	9.241	9.084	8.934	8.788	8.647	8.512
45	9.599	9.430	9.267	9.110	8.960	8.814	8.673	8.538

Millero (1986) provides a wider range of standard values for S = 10-40 and t = 5-40°C. These values can be derived from his Tables 3, 4 and 5 for the Tris buffer (Annex 2).

7. The dissociation constants of boric acid

There are presently only two sets of data on the dissociation constant of boric acid in seawater media — the data of Lyman (1957) and those of Hansson (1972, 1973b). The Hansson data, although very limited, are by far the most reliable. Recent independent measurements (Dickson, upublished work) agree with Hansson's data at S = 35 to within ~0.015 in pK_B. We, therefore, propose that the equation of Millero (1979) should be used to calculate the borate contribution to the alkalinity. This equation is fitted to the data of Hansson, and allows a smooth extrapolation to the infinite dilution data of Owen (1934):

$$\ln K_B^* - \ln K_B^\circ = (0.5998 - 75.25/T)S^{1/2} - 0.01767\ S \qquad (7.1a)$$

where

$$\ln K_B^o = 148.0248 - 8966.90/T - 24.4344 \ln T \qquad (7.1b)$$

8. The dissociation constants of carbonic acid

In this section we present an analysis of the data sets available for K_1 and K_2 of carbonic acid, as well as an error estimate based on the discrepancy between these data sets.

8.1 *Comparison of dissociation constants*

Measurements of apparent (K_1') or stoichiometric (K_1^*) ionization constants for carbonic acid have been made by a number of workers (Buch *et al.*, 1932; Buch, 1951; Lyman, 1957; Mehrbach *et al.*, 1973; Hansson, 1972, 1973b). The more recent work of Mehrbach *et al.* and of Hansson is more reliable than earlier studies. We therefore consider only these data here. This comparison is based on a recent paper by Dickson and Millero (1987). In order to compare the two studies, both data sets were adjusted to a common pH scale. The details of this adjustment are given in Annex 3.

It was impossible to assess which set of data is "better". Both of the corrected sets of data have approximately the same precision. (The raw data of Mehrbach *et al.* for pK_1' appear to have a higher precision than the corrected data.) In addition, it is apparent that the systematic difference between the two sets of data is approximately equal to the precision (~2s).* Even the precision of the final pooled data set is of a similar magnitude to that of the independent sets of data (see Annex 3).

The proposed equations were derived from the pooled data, and can be used to estimate pK_1^* and pK_2^* for seawater from S = 0 - 40 and for temperatures from 0 to 35°C:

$$pK_1^* - pK_1^\circ = (19.894 - 840.39/T - 3.0189 \ln T)S^{1/2} + 0.0068\, S \qquad (8.1.1)$$

$$pK_2^* - pK_2^\circ = (17.176 - 690.59/T - 2.6719 \ln T)S^{1/2} + 0.0217\, S\ , \qquad (8.1.2)$$

where pK° represents the value at infinite dilution (S = 0):

$$pK_1^\circ = 6320.81/T - 126.3405 + 19.568 \ln T \qquad (8.1.3)$$

$$pK_2^\circ = 5143.69/T - 90.1833 + 14.613 \ln T\ . \qquad (8.1.4)$$

The values of 2s for these equations are ±0.017 in pK_1^* and ±0.031 in pK_2^* respectively. It should be pointed out that at low salinities these equations would be expected to have larger deviations. Using an ion pairing model we estimate that in the salinity range S = 0-5, errors are ~0.03 in pK_1^*, and ~0.1 in pK_2^*. Since the composition of most estuarine water is quite variable at these salinities, this larger error is not necessarily significant. By forcing the values of pK* in seawater to extrapolate to the pure water values, one can make reasonable estimates for estuarine water. Equations limited to the salinity range S = 20-40

*$s = (RSS/(m-p))^{1/2}$: where RSS is the sum-of-squares of the residuals, m is the number of data points, and p is the number of fitting parameters.

do not provide this advantage, and can cause much larger errors in the extrapolated values below S = 20.

Thus, it is probable that the precision of the pooled data set represents a reasonable estimate for the accuracy of the dissociation constants of carbon dioxide in seawater at this time. It is, therefore, useful to assess what contribution this magnitude of errors contributes to the various derived quantities such as $P(CO_2)$ or $[CO_3^{2-}]$. This information can be estimated from the paper by Dickson and Riley (1978). The resultant error, due to errors in K_1^* and K_2^*, depends upon the particular combination of analytical parameters used, i.e., the choice from pH, $P(CO_2)$, TA and TCO_2 and to a lesser extent upon the specific conditions (i.e., S and T). Thus for the observable combination pH and CA, i.e., discounting the effect of error in K_B, the value of $[CO_2]$, and hence $P(CO_2)$, varies by 1% for each 1% error in K_1^*($\pm$0.017 in pK_1^* = 4% in K_1^*). The error in the calculation of $[CO_3^{2-}]$ is similarly dependent on the error in K_2^* ($\pm$0.031 in pK_2^* = $\pm$7.4% in K_2^*). These errors are approximately the same magnitude as the errors due to the experimental measurements (except for the very best data, when the errors in the constants would be expected to dominate).

An indication of the extent of the shortcomings of the proposed equations is given in Figure 1. In this figure $P(CO_2)$, calculated using the equations above and data for TA (by titration) and TCO_2 (by extraction and manometric determination), is compared with the values of $P(CO_2)$ measured directly (using gas chromatography). The data represent a variety of samples from the North Atlantic covering a range of temperature and it is apparent that there is a systematic discrepancy, the extent of which varies with temperature. The maximum deviation corresponds to an error of ~0.03 in $p(K_1^*/K_2^*)$, i.e., within the estimated error bounds for the equations.

It is thus apparent that the very best analytical measurements are accurate enough to make demands on the accuracy of the constants which is beyond our current knowledge of them. However, the current data on the constants are probably adequate for a variety of purposes. In the event that more reliable data for the constants become available it may be appropriate to reconsider these recommendations.

The pooled data are based on the pH(SWS) scale: it is thus necessary to employ this scale when using these constants. It would have been impossible to correct the data to the pH(NBS) scale, as this would introduce further uncertainties.

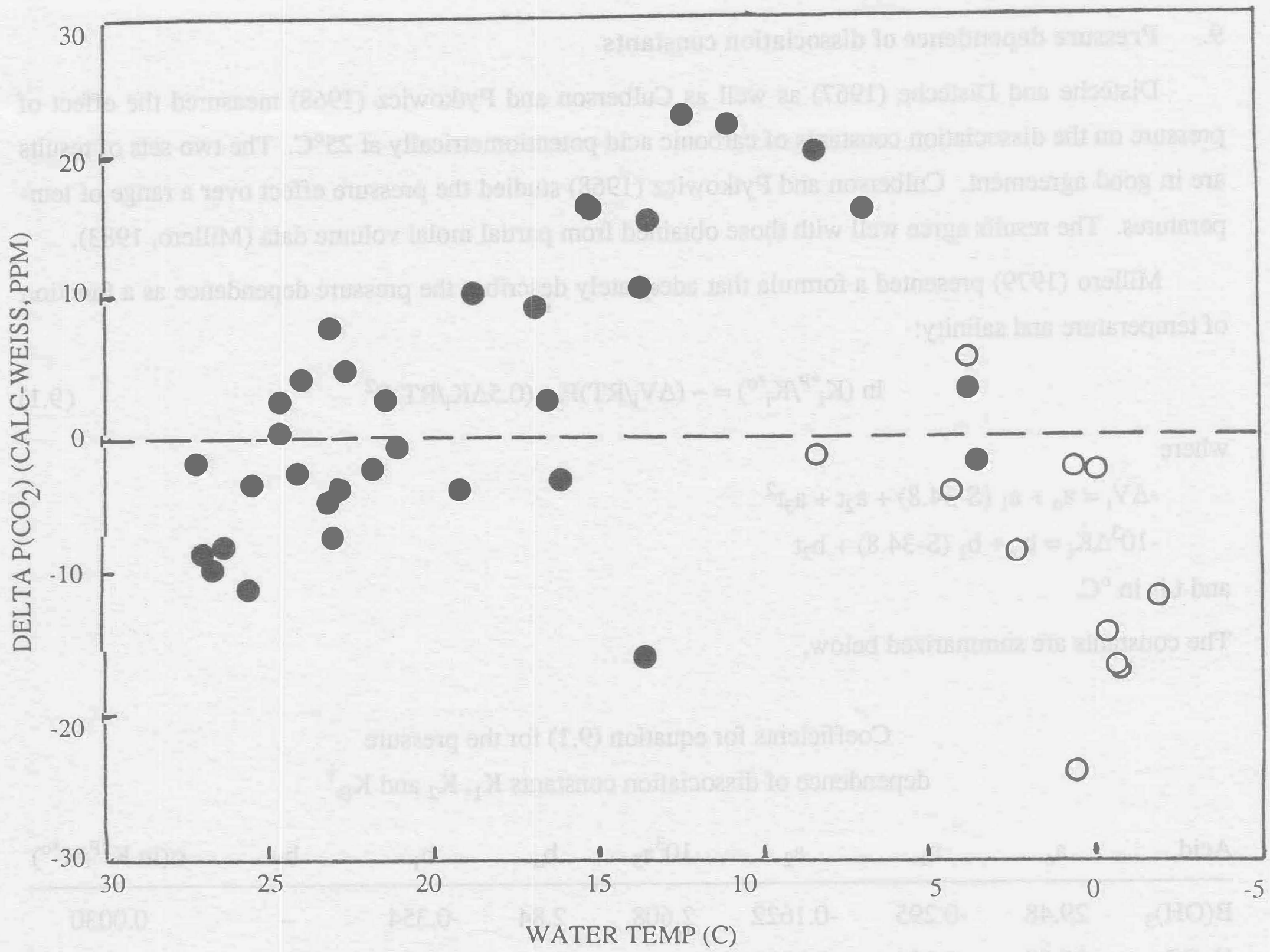

Figure 1. Plot of the deviations between calculated and measured $P(CO_2)$ for samples from the North Atlantic and Hudson Bay as a function of temperature. The TA were measured by the PACODF (Physical and Chemical Oceanographic Data Facility of Scripps Institution of Oceanography) (•), and by E.P. Jones of the Bedford Institute of Oceanography (O), the TCO_2 data by C.D. Keeling's group at S.I.O., and the $P(CO_2)$ by R.F. Weiss's group from S.I.O.

9. Pressure dependence of dissociation constants

Distèche and Distèche (1967) as well as Culberson and Pytkowicz (1968) measured the effect of pressure on the dissociation constants of carbonic acid potentiometrically at 25°C. The two sets of results are in good agreement. Culberson and Pytkowicz (1968) studied the pressure effect over a range of temperatures. The results agree well with those obtained from partial molal volume data (Millero, 1983).

Millero (1979) presented a formula that adequately describes the pressure dependence as a function of temperature and salinity:

$$\ln (K_i^{*P}/K_i^{*o}) = -(\Delta V_i/RT)P + (0.5\Delta K_i/RT)P^2 \qquad (9.1)$$

where

$$-\Delta V_i = a_o + a_1 (S-34.8) + a_2 t + a_3 t^2$$

$$-10^3 \Delta K_i = b_o + b_1 (S-34.8) + b_2 t$$

and t is in °C.

The constants are summarized below.

Coefficients for equation (9.1) for the pressure dependence of dissociation constants K_1, K_2 and K_B †

Acid	a_o	a_1	a_2	$10^3 a_3$	b_o	b_1	b_2	$\sigma(\ln K^{*P}/K^{*o})$
$B(OH)_3$	29.48	-0.295	-0.1622	2.608	2.84	-0.354	--	0.0030
H_2CO_3	25.50	0.151	-0.1271	--	3.08	0.578	-0.0877	0.0043
HCO_3^-	15.82	-0.321	0.0219	--	-1.13	0.314	0.1475	0.0042

† The appropriate range of validity is S = 20-40; t = 0-30°C, i.e., the range applicable to >99% of seawater.

10. Solubilities of calcium carbonates

The study of the solubilities of calcium carbonates is presently in a state of flux. This is due to the occurrence of metastable, kinetically controlled phases (Pytkowicz and Cole, 1979), to the presence of conventional single equilibrium states (Plummer and MacKenzie, 1974), to multistate thermodynamics (Wollast and Reinhard-Derie, 1977; Pytkowicz and Cole, 1979), and to the possible occurrence of surface coatings of compositions different from those of the bulk phases (Weyl, 1967; Möller and Parekh, 1975).

10.1 *Aragonite*

Commonly it has been assumed that solubility determinations of aragonite in seawater are relatively easy to carry out because of the lesser interference of Mg^{2+} ions. Surprisingly aragonite solubility products scatter more than those of calcite (UNESCO, 1983). This is a hitherto unexplained effect in

saturation runs which reach steady state pH and alkalinity values within a few hours at most. On the other hand, long term storage depresses the solubility. This is probably because aragonite is a metastable phase, which is converted gradually into a low magnesium calcite (Morse, 1980).

10.2 *Calcite*

The solubility product of reagent grade calcite has been reasonably well characterized by several observers (UNESCO, 1983). The solubility data at higher pressures, however, reveal discrepancies which may be due to some irreversibility of pH measurements during compression and decompression (Pytkowicz and Fowler, 1967). Ingle (1975), however, did find little hysteresis, so that pressure work deserves further attention. The partial molal volume approach of Millero (1983) can provide answers for pure phases.

The inorganic precipitation of calcite occurs only in special circumstances, such as when calcareous cements and overgrowths are formed, during evaporation of closed basins, and in interstitial waters of sediments rendered highly alkaline as a result of sulfate reduction processes.

Rapid precipitation of calcium carbonate can lead to a rate controlled metastable $Ca_xMg_{1-x}(CO_3)$ bulk phase or surface phase. The metastability of such solids can persist for long periods, especially when solid diffusion, rather than redissolution is the mechanism involved in progress to equilibrium. Laboratory experiments often lead to the formation of low Mg-calcites (with >2 mol% Mg), whereas naturally produced calcite in the ocean (i.e., calcareous skeletons of foraminifera and nano-plankton) are usually very low Mg-calcites with Mg/Ca molar ratios of $<50 \times 10^{-4}$, or <0.5 mol% Mg. The exact equilibrium Mg/Ca ratio in stable Mg-calcite in the ocean is as yet unknown, and the subject of further investigation.

10.3 *Solubility products of aragonite and calcite*

Below we summarize some of the thermodynamic information available on solubility products at 25°C and S = 35 (Morse *et al.*, 1980; UNESCO, 1983).

Summary of calcite and aragonite solubility products at 25°C and S = 35

Source	K_{sp}(calc) $mol^2kg^{-2}x10^7$)	K_{sp}(arag) ($mol^2kg^{-2}x10^7$)	K_{sp}(arag)/K_{sp}(calc)	pK_{sp}(calc)	pK_{sp}(arag)
MacIntyre (1965)	4.57(±0.27)	7.33(±0.31)	1.63(±0.17)	6.34	6.13
Ingle et al. (1973)	4.60(±0.10)		--	6.34	--
Berner (1976)		8.11(±0.23)	--	--	6.09
Plath (1979)	4.70(±0.10)	8.69(±0.49)	2.05 (±0.15)	6.33	6.04
Morse et al. (1980)	4.39(±0.20)	6.65(±0.12)	1.53(±0.10)	6.36	6.18
Plummer and Sundquist (1982)	4.60	6.66	1.45	6.34	6.18
Mucci (1983)	4.30(±0.20)	6.65(±0.12)	1.55(±0.10)	6.37	6.18

We suggest that the following values are the preferred values:

$$pK_{sp}(calc)=6.35\pm0.02 \tag{10.3.1}$$

$$pK_{sp}(arag)=6.17\pm0.02 \tag{10.3.2}$$

Mucci (1983) gives the following equation to describe the ratio of the thermodynamic solubility products of aragonite and calcite

$$\log (K^o_{sp}(arag)/K^o_{sp}(calc)) = 0.0385 + 63.974/T \tag{10.3.3}$$

and for aragonite

$$\log K^o_{sp}(arag) = -171.945 - 0.077993T + 2903.293/T + 71.595 \log T \tag{10.3.4}$$

where T = (t + 273.15) K.

Mucci (1983) selected the following equation to represent the temperature and salinity dependence of the stoichiometric solubility constants of calcite and aragonite in seawater

$$\log K^*_{sp}(i) - \log K^o_{sp}(i) = (b_o + b_1T + b_2/T)S^{0.5} + C_oS + d_oS^{1.5} \tag{10.3.5}$$

with the following values of the constants:

solid	b_o	$b_1 \cdot 10^3$	b_2	C_o	$d_o \cdot 10^3$	σ
calcite	-0.77712	2.8426	178.34	-0.07711	4.1249	0.010
aragonite	-0.068393	1.7276	88.135	-0.10018	5.9415	0.009

The pressure dependence of the solubility product can be described by the following formula (Millero, 1979)

$$\ln(K_{sp}^{*P}(i)/K_{sp}^{*o}(i)) = -(\Delta V_i/RT)P+(0.5\Delta K_i/RT)P^2 \quad (10.3.5)$$

where for calcite

$$-\Delta V_c = 48.76 - 0.5304t \quad (10.3.6a)$$

$$-10^3\Delta K_c = 11.76 - 0.3692t \quad (10.3.6b)$$

For aragonite one must assume that ΔV_A ~2.8cm^{3}mol^{-1} lower than ΔV_C, and that ΔK_A ~ΔK_C. Further measurements are needed to resolve whether this is an allowable assumption (Millero, 1979). In addition little information is available on the effect of salinity.

11. Suggestions for future work

Though for many purposes the thermodynamic information contained in this report will be sufficient, various improvements can still be made. Below we summarize some of these needs.

11.1 *pH buffers*

Though the buffer solutions described in Section 6 will help set the stage for the more convenient measurement of pH using buffers in seawater-like solutions, the values of the buffers only cover the higher range of normally measured pH in seawater (pH = 8 - 9). A search for a third standard of $pm_H(S)$ = 7 or 7.5 would be most useful. A 1:1 buffer composed of 2-aminopyridine and its hydrochloride may prove suitable for this purpose. The pm_H of this buffer in seawater of salinity 35 has been found to range from 7.3 at 5°C to 6.9 at 25°C (Erickson, 1980). More work on this proposed buffer is necessary.

11.2 *Dissociation constants*

As was pointed out in section 8, the overall precision of either the individual data sets or the pooled data sets leave room for improvement. Further work, especially over the normal seawater range of salinities (S = 30 - 40) and temperatures (t = 0 - 30°C) should be carried out. At present such efforts are underway in at least two laboratories (A. Poisson, University of Paris and A. Dickson, Scripps Institution of Oceanography). We propose adoption of the present pooled data set, with the proviso that in a few years from the publication of this report, improvements to the suggested formulae may be warranted. Meantime overdetermination of parameters, as demonstrated in Figure 6.1, will also help in any future refinement of the thermodynamic information.

11.3 *Solubility of calcium carbonate*

Much progress has been made in the measurement of the solubility products of calcite and aragonite (Mucci, 1983). However, further research is still called for, especially with respect to the pressure dependence of the solubility products.

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