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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

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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 بشانى أكسيد الكربون والتابعة للجنة المشتركة الخاعة 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 الديناميكية 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).

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [SiO(OH)_3^-] \tag{3.8b}$$

$$+ [HPO_4^{2-}] + 2[PO_4^{3-}] - [H^+] - [H_3PO_4] + \cdots$$

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

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

where K_B is the dissociation constant of boric acid, and

$$H_2O \overset{K_w}{=} H^+ + OH^- \tag{3.10}$$

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:

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

and

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

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 5×10^{-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)

$$\begin{aligned} &(H^+)^3 A + (H^+)^2 (K_1(A-1) + K_B(A-B)) \\ &+ (H^+)(K_1 K_B(A-B-1) + K_1 K_2(A-2)) + K_1 K_2 K_B(A-B-2) = 0 \end{aligned} \tag{4.7}$$

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:

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

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).

$$\ln K_o = A_1 + A_2(100/T) + A_3 \ln(T/100) + S[B_1 + B_2(T/100) + B_3(T/100)^2] \qquad (5.1)$$

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)

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

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·H$^+$ or Bis·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,

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

$$= pm_H - \Delta$$

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

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*$s = (RSS/(m-p))^{1/2}$: 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^*(±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^* (±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.

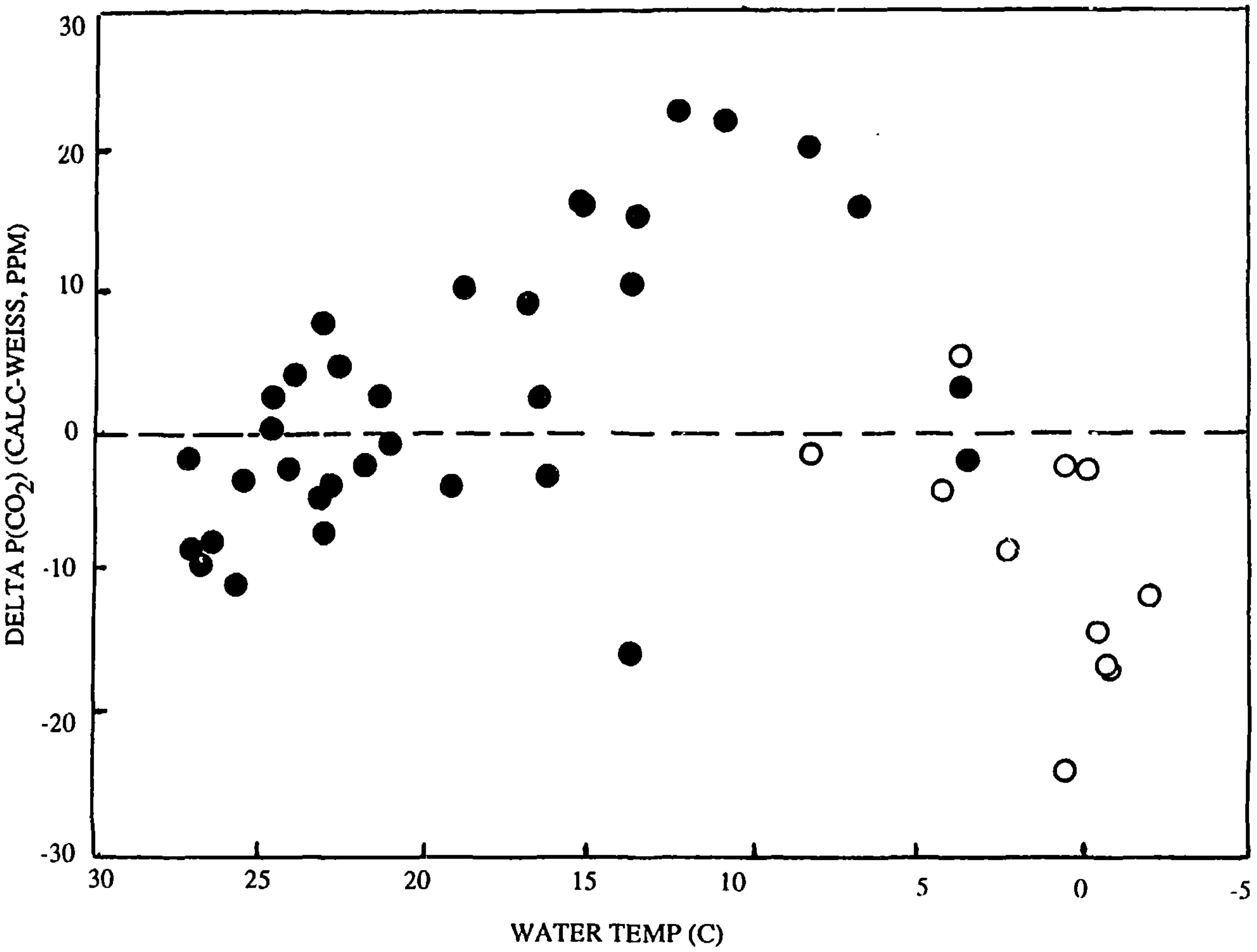

Figure 1. Plot of the deviations between calculated and measured P(CO$_2$) for samples from the North Atlantic and Hudson Bay as a function of temperature. The TA were measured by the PACODF (Physical and Chemical Oceanographic Data Facility of Scripps Institution of Oceanography) (●), and by E.P. Jones 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:

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

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^{2}kg^{-2}x10^7)	K_{sp}(arag) (mol^{2}kg^{-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:

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

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

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

$$\log (K^{o}_{sp}(\mathrm{arag})/K^{o}_{sp}(\mathrm{calc})) = 0.0385 + 63.974/T \qquad (10.3.3)$$

and for aragonite

$$\log K^{o}_{sp}(\mathrm{arag}) = -171.945 - 0.077993T + 2903.293/T + 71.595 \log T \qquad (10.3.4)$$

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

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

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)

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

where for calcite

$$-\Delta V_c = 48.76 - 0.5304t \tag{10.3.6a}$$

$$-10^3\Delta K_c = 11.76 - 0.3692t \tag{10.3.6b}$$

For aragonite one must assume that ΔV_A ~$2.8 cm^3 mol^{-1}$ lower than ΔV_C, and that $\Delta K_A \sim \Delta K_C$. 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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ANNEX 1

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pH scales and proton-transfer reactions in saline media such as sea water

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Abstract—The three approaches to defining pH scales for use in sea water: the N.B.S. scale, the pH(SWS) or 'total' hydrogen ion concentration scale and the 'free' hydrogen ion concentration scale are described, and it is shown how these arise as a direct consequence of alternative experimental procedures for determining practical acidity constants. The advantages of conceptual simplicity and of experimental precision inherent in the use of concentration products to describe proton-transfer reactions in saline media are emphasised. In addition, the problems of theoretical interpretation and of reproducibility which result from the conventional nature of the N.B.S. pH scale are described, and the effect on the corresponding 'apparent' constants outlined. Insofar as it is concentration products rather than 'apparent' constants that are amenable to prediction using models for activity coefficients, the deliberate use of a 'free' hydrogen ion concentration scale should be applicable to many areas of aqueous geochemistry in addition to marine chemistry.

INTRODUCTION

THE FIELD of pH scales and the study of proton-transfer reactions in sea water is one of the more confused areas of marine chemistry. At the moment there are three alternative approaches to defining pH scales for use in sea water: the N.B.S. scale, the pH(SWS) or 'total' hydrogen ion concentration scale and the 'free' hydrogen ion concentration scale. There are also three corresponding definitions of 'constants' to describe proton-transfer reactions in sea water. The reasons for this are primarily historical. They reflect the gradual refinement of the experimentally convenient potentiometric determination of acidity in order that the numbers obtained might be usefully interpreted as a property of hydrogen ion in solution.

Why are pH measurements important? As GUGGENHEIM (1930) forcefully pointed out, it is rarely the hydrogen ion content of a solution that is of itself important. Rather, the hydrogen ion content is indicative of the state of the various proton-transfer equilibria occurring in solution. The case of reaction rates is no exception if we take into account the quasi-equilibrium between the reactants and the critical complex (transition state). It is thus misleading to separate the discussion of pH scales from a consideration of the theoretical and practical aspects of determining the corresponding acidity constants.

In this article, I should like to show how the various pH scales mentioned above arise naturally from alternative approaches to determining practical acidity constants for use in ionic media. I shall review how the conventional nature of the N.B.S. pH scale gives rise to problems both of theoretical interpretation and of reproducibility, and shall discuss the implications of this to the ultimate usefulness of the so-called 'apparent' acidity constants for describing proton-transfer processes in sea water. I shall therefore reiterate the experimental and conceptual advantages inherent in the use of the 'free' hydrogen ion concentration scale, and would like to point out that such an approach should be generally useful in many areas of aqueous geochemistry apart from marine chemistry. In particular, the 'free' hydrogen ion concentration scale is directly compatible with the various phenomenological models for describing and predicting activity coefficients in electrolyte solutions. In future, it should be possible to discuss proton-transfer reactions in a wide variety of geochemical systems on a common basis.

Although this paper does not discuss the practical determination of pH, the reader is referred to the publications by BATES (1973), CULBERSON (1981), and GRASSHOFF (1983) for a thorough discussion of the pitfalls involved.

PROTON-TRANSFER REACTIONS IN AQUEOUS SOLUTIONS

Introduction

It is safe to say that free protons do not exist in any significant amount in aqueous solutions. Rather the proton is bonded to a water molecule thus forming an H_3O^+ ion; this in turn is hydrogen bonded to three other water molecules to form an $H_9O_4^+$ ion (see CONWAY, 1981—chap. 17). This solvation structure has important consequences for the mechanism and kinetics of a wide range of reactions in aqueous solution (for a detailed discussion see EIGEN, 1964). Nevertheless, it is convenient (and thermodynamically correct) to use the term "hydrogen ion" and the symbol "H^+" as a shorthand for the various hydrates: this is the sense in which I shall employ it.

If HA and A denote an acid and its conjugate base, while HB and B denote another conjugate pair, then the chemical reaction

$$HA + B = A + HB$$

is typical of a proton-transfer reaction. It is convenient in the treatment of aqueous solutions to discuss and tabulate the standard acidity constant K_A^0 for the formal dissociation process:

$$HB = B + H^+$$

$$K_A^0 = (m_B m_H / m_{HB})(\gamma_B \gamma_H / \gamma_{HB}).$$

Water itself can also be considered to dissociate:

$$H_2O = OH^- + H^+$$

$$K_W^0 = (m_{OH} m_H)(\gamma_{OH} \gamma_H / a_{H_2O}).$$

The particular acidity constant K_W^0 is known as the ionic product of water. The equilibrium constant for any other proton-transfer reaction can then be obtained from such constants by multiplication and division.

Practical acidity constants

The property of interest in any discussion of acid-base processes is usually dependent on the ratio

$$\frac{m_{HB}}{m_B} = m_H \cdot \frac{\gamma_H \gamma_B}{\gamma_{HB}} \cdot (K_A^0)^{-1}.$$

Although K_A^0 is known for a wide variety of acids, it has often not been possible to estimate the activity coefficient product $\gamma_H \gamma_B / \gamma_{HB}$ in complex mixtures such as sea water. As a result a number of workers have defined various "practical acidity constants" for use in sea water. Each of these reflects an alternative experimental approach to expressing the ratio m_{HB}/m_B as the product of a term related to hydrogen ion concentration (which can be obtained potentiometrically—see next section), and a supposedly constant term.

The successful application of such constants rests on a principle set forth by BRÖNSTED (1927). According to this principle, the activity coefficients of substances present in small amounts in a mixture of electrolytes are virtually independent of the quantities of these substances and are determined solely by the salt present in large amounts. The previous equation can thus be written as

$$\frac{m_{HB}}{m_B} = m_H / K_A,$$

where K_A is the classical mass-action product for the acid dissociation reaction. In essence, this is equivalent to using the so-called ionic medium standard state (see SILLÉN, 1967; DICKSON and WHITFIELD, in prep.).

In 1924, SØRENSEN and LINDERSTRØM-LANG proposed a potentiometric method which they felt measured hydrogen ion activity directly in solution. As a result, it became common practice to define a hybrid acidity constant K'_A (see BRÖNSTED, 1928):

$$\frac{m_{HB}}{m_B} = a_H / K'_A,$$

or in logarithmic notation

$$\log(m_{HB}/m_B) = pK'_A - pH.$$

Such hybrid or 'apparent' constants were soon employed in both biochemistry (HASTINGS and SENDROY, 1925) and in oceanography (BUCH, 1930).

It was quickly appreciated that measurements of pH could *not* yield a value of a_H, but rather a more nebulous quantity $m_H \gamma_?$, where $\gamma_?$ is a complicated function which depends on the transport numbers of all the ions present at all parts of the cell (GUGGENHEIM, 1930). An expression for m_{HB}/m_B can however be written in the more general form

$$\frac{m_{HB}}{m_B} = 10^{-pH}/K'_A$$

$$= (m_H \gamma_?)/(K_A \gamma_?).$$

It is therefore apparent that the presence of an arbitrary multiplicative constant in no way vitiates the practical value of this approach. The ratio m_{HB}/m_B is still well-defined, and such hybrid or 'apparent' constants have proved extremely useful in a variety of studies, both in oceanography and in biochemistry (PYTKOWICZ, 1969).

In the main discipline of solution chemistry however, such hybrid constants are only rarely employed. Rather, those workers studying solution equilibria prefer to use the classical mass-action product (K_A) to describe proton-transfer reactions in ionic media (see *e.g.* SILLÉN, 1971). Such an approach has two major advantages: (i) it allows a rigorous mass balance expression to be written for hydrogen ion, and (ii) it is possible to achieve a higher degree of experimental reproducibility than one can with hybrid constants. Both these points will be discussed in more detail in the following sections.

Determination of acidity constants

In order to clarify the various possible definitions of practical acidity constants for use in sea water, it will be useful to review briefly the equations underlying the potentiometric determination of such constants. To measure the equilibrium constant of a reaction, all one needs in principle is a method of determining the concentration (or some quantity related to it) of one of the participants: the concentrations of the others can be calculated from their total stoichiometric concentrations and the stoichiometry of the reaction. In order to illustrate this, I shall discuss in brief the determination of the dissociation constant for a monoprotic acid HB. (The algebra for a more complex system is similar in principle, although necessarily more involved.) The basic equations which determine the equilibrium relationships fall into two classes:

(a) The mass-action equations: these define the stoichiometry of the various equilibria and the corresponding concentration constants:

$$K_W = m_H m_{OH}$$

$$K_A = m_H m_B / m_{HB}.$$

(b) The mass-balance equations: these relate the concentrations of the various species to the analytical (total stoichiometric) composition of the solution:

$$H_T = m_H - m_B - m_{OH}$$

$$B_T = m_{HB} + m_B.$$

The mass-balance equation for hydrogen ion is calculated relative to a *defined* equivalence point or zero level of protons. This is known as a proton condition (BUTLER, 1964; STUMM and MORGAN, 1981). The zero level chosen here corresponds to H_2O and HB.

These four equations thus uniquely define the four concentrations m_H, m_{OH}, m_{HB} and m_B.

In the potentiometric determination of acidity constants, it is convenient to use the cell

Reference half-cell	Solution in which equilibria take place	Electrode reversible to hydrogen ion

whose e.m.f. is given by

$$E = E^0 + (RT/F) \ln h,$$

where h is proportional to m_H (*i.e.* $h = m_H k$, see next section). The determining equations can therefore be rewritten as a single expression which combines the independently measurable parameters $E(h)$, B_T and H_T:

$$H_T = h/k - B_T/(1 + h/K'_A) - K'_W/h$$

(where $K'_A = K_A k$ and $K'_W = K_W k$). This equation is the basis for all determinations of acidity constants.

In order to obtain values for h, it is necessary to specify a value for E^0. The alternative approaches to defining pH scales, and hence the corresponding acidity constants, each represent alternative procedures for defining or estimating E^0. Once such a procedure has been defined, then the corresponding value of K'_A can be estimated from a set of e.m.f. data as a function of composition.

THE POTENTIOMETRIC DETERMINATION OF ACIDITY

Introduction

The special influence of the hydrogen ion concentration on a variety of processes in aqueous solution was first recognised and described by SØRENSEN (1909), who proposed a potentiometric procedure for the determination of hydrogen ion concentrations which he expressed as the "hydrogen ion exponent":

$$P_H = -\log c_H.$$

Development of the modern formulation of the concepts of thermodynamics, and of the newer theories of electrolyte solutions, showed that the e.m.f. of galvanic cells is related more directly to activity than to concentration; thus SØRENSEN and LINDERSTRØM-LANG (1924) proposed a new acidity unit:

$$pa_H = -\log a_H.$$

It is now well recognised that the activity of a single ion plays no real part in the e.m.f. of a galvanic cell, whether or not the cell is of the type with liquid junction (GUGGENHEIM, 1930). There is nevertheless a need for a reproducible pH scale based on the experimentally convenient potentiometric determination of acidity (MACINNES, 1948), and this has led to a wide acceptance of an *operational* definition of the measurement of pH.

The operational definition of pH

The pH of a solution is defined in terms of measurements on the particular cell

Reference electrode	Concentrated KCl sol.	Test sol.	Electrode reversible to hydrogen ion

The reference electrode is usually reversible to chloride ion, and the e.m.f. of this cell can be formally written as (after BATES, 1973)

$$E = \{E^0 + (RT/F) \ln a_{Cl(KCl)} + E_j\} + (RT/F) \ln a_H$$

$$= E^{0'} + (RT/F) \ln a_H,$$

where E_j is the (formal) liquid junction potential between the two half cells. This formula is actually a conventional definition of $E^{0'}$ and a_H, the value of each depending on the value assigned to the other. In the operational definition of pH (see BATES, 1973; IUPAC, 1979), the pH of solution X is related to the pH of standard S:

$$\mathrm{pH(X)} = \mathrm{pH(S)} + \frac{E_S - E_X}{(RT \ln 10/F)}.$$

Therefore

$$\frac{E_S - E_X}{(RT \ln 10/F)} = \frac{E_S^{0'} - E_X^{0'}}{(RT \ln 10/F)} - \log a_H(\mathrm{X}) + \log a_H(\mathrm{S}).$$

It is clear that pH(X) can only be identified with the conventional activity term if two conditions are met: (a) The term $E_S^{0'} - E_X^{0'}$ is *assumed* to be zero. (b) pH(S) is defined as $-\log a_H(\mathrm{S})$, where $a_H(\mathrm{S})$ has been *conventionally* assigned.

Although it has been widely recognised that $E_S^{0'} - E_X^{0'}$ is rarely equal to zero, its finite value is usually ascribed to differences in the liquid junction potential (see *e.g.* CULBERSON, 1981; BREZINSKI, 1983). It is thus only possible to measure this term accurately in other solutions for which the conventional value of a_H is known, *i.e.* other solutions with assigned pH(S) values (see *e.g.* BATES *et al.*, 1950; COVINGTON *et al.*, 1983).

The *definitive* method for pH measurement in dilute aqueous solutions is based on measuring the e.m.f. (E) of the cell

$$\text{Ag(s)}\left|\text{AgCl(s)}\right|\begin{array}{c}\text{Dilute aq. sol.}\\ \text{with added NaCl}\end{array}\left|\text{H}_2\text{(g, 1atm)}\right|\text{Pt(s)}.$$

The calculated function is

$$\text{pH} = \lim_{m_{\text{NaCl}}\to 0}\left\{\frac{E^0 - E}{(RT\ln 10/F)} + \log m_{\text{Cl}} + \log \gamma_{\text{Cl}}\right\}.$$

E^0 is the standard potential of the Ag/AgCl half cell. The present convention (Bates and Guggenheim, 1960) is based on the assumption that the molal activity coefficient of chloride ion in dilute aqueous solution ($I_m \leq 0.1$ mol kg^{-1}) can be estimated by means of the equation

$$\log \gamma_{\text{Cl}} = -AI_m/(1 + 1.5I_m),$$

where A is the usual temperature dependent Debye-Hückel constant. This is essentially the procedure that has been used to determine the pH in a series of primary aqueous calibration solutions, the so-called N.B.S. buffers (Bates, 1973). It is also the approach taken by Covington *et al.* (1983) in order to assess the magnitude of the error in pH measurements in low ionic strength media such as lake water.

The measurement of hydrogen ion concentration

In ionic media (*i.e.* where the activity coefficients of the various reacting species are dominated by the presence of the bulk electrolyte—the ionic medium), it is possible to measure hydrogen ion concentration directly using the cell

$$\begin{array}{c|c|c}\text{Reference} & \text{Solution in which} & \text{Electrode reversible}\\ \text{half-cell} & \text{equilibria take place} & \text{to hydrogen ion}\end{array}$$

A number of reference half-cells have been used. The best systems (stablest, most reproducible e.m.f.) use an electrode which responds to one of the non-reacting ions of the ionic medium, *e.g.* a sodium glass electrode (see Biedermann *et al.*, 1974):

$$E = E^0 + (RT/F)\ln(a_{\text{H}}/a_{\text{Na}}),$$

or a silver-silver chloride electrode (*e.g.* Bates *et al.*, 1943; Thurmond and Millero, 1982):

$$E = E^0 + (RT/F)\ln(a_{\text{H}}a_{\text{Cl}}).$$

Other experimenters have used cells with liquid junctions (*e.g.* Hansson, 1972, 1973a,b,c,d; Dickson and Riley, 1979a,b). In these cases the e.m.f. of this cell is given by the formal expression

$$E = E^0 + (RT/F)\ln a_{\text{H}} + E_J,$$

(see discussion by Guggenheim, 1936; Dickson and Whitfield, in prep.).

In every one of these cases, the e.m.f. can be expressed by the classical Nernst equation:

$$E = E^0 + (RT/F)\ln m_{\text{H}}.$$

A comparison of this with the previous equations shows that, in the case of cells without liquid junction, the constancy of E^0 depends on the constancy of the activity coefficients despite any compositional variations which might occur during the course of an experiment (usually a titration). In the case of cells with liquid junction, there is the additional possibility that the liquid junction e.m.f. might vary. To a first approximation, this is the result of the highly mobile proton and $\Delta E_J \approx j_{\text{H}}m_{\text{H}}$ (see Biedermann and Sillén, 1953; Rossotti and Rossotti, 1961). The value of j_{H} in sea water media is approximately 30 mV mol^{-1} kg (Dickson and Riley, 1979a), and thus the variation in liquid junction e.m.f. can often be neglected. Bates and Macaskill (1975) also imply that this is the case.

APPLICATION TO SALINE MEDIA SUCH AS SEA WATER

Introduction

The discussion so far has implicitly assumed that *none of the various reacting species were complexed* by the medium. In a solution which can complex these species, *e.g.* sea water, it is possible to get side-reactions such as

$$\text{H}^+ + \text{SO}_4^{2-} = \text{HSO}_4^-$$

$$\text{Mg}^{2+} + \text{OH}^- = \text{MgOH}^+$$

etc. The formal simplicity of the mass-action, mass-balance and Nernst equations can however be retained by defining them in terms of total concentrations:

$${}^{\text{T}}m_{\text{H}} = m_{\text{H}} + \sum \textit{complexes with medium ions}$$

$${}^{\text{T}}m_{\text{OH}} = m_{\text{OH}} + \sum \textit{complexes with medium ions}$$

etc. The utility of this approach clearly depends on the assumption that the ratio ${}^{\text{T}}m_{\text{X}}/m_{\text{X}}$ is constant over the range of conditions considered. This is certainly true for acids and bases present in sea water at low concentrations (see for example the discussions by Pytkowicz *et al.*, 1974; Dickson and Whitfield, in prep.): it is implicit in the original proposal of Buch (1930) that the equilibria involving carbonic acid in sea water might be successfully treated using apparent constants. For example, in a medium containing sulphate (but no other protophilic ligands)

$$\begin{aligned}{}^{\text{T}}m_{\text{H}} &= m_{\text{H}} + m_{\text{HSO}_4}\\ &= m_{\text{H}}(1 + \beta(\text{HSO}_4)m_{\text{SO}_4});\end{aligned}$$

thus

$${}^{\text{T}}m_{\text{H}}/m_{\text{H}} = 1 + \beta(\text{HSO}_4)m_{\text{SO}_4},$$

and will remain essentially constant as long as $m_{HSO_4} \ll m_{SO_4}$ (*i.e.* at low m_H values). A similar reasoning applies also to the other reacting species.

The mass-balance equation for hydrogen ion is therefore

$$H_T = {}^Tm_H - {}^Tm_B - {}^Tm_{OH},$$

and similarily

$$B_T = {}^Tm_{HB} + {}^Tm_B.$$

(In the remainder of the text ${}^Tm_{HB}$ and ${}^Tm_B$ should strictly be used in place of m_{HB} and m_B to signify that complexes with medium ions are included. However no real ambiguity is introduced by omitting the T superscript.)

The three alternative approaches to defining pH scales (and thus acidity constants) for use in sea water (see *e.g.* Bates, 1982) reflect alternative approaches to interpreting the potentiometric determination of acidity

$$E = E^0 + (RT/F) \ln h.$$

The N.B.S. pH scale and 'apparent' constants

In this approach, $-\log h$ is defined as equal to pH(N.B.S.), *i.e.* using the operational definition of pH. Then

$$E^0 = E_S + (RT \ln 10/F) \cdot \text{pH(S)}$$

and the apparent constant

$$K'_A = 10^{-\text{pH}} m_B/m_{HB}.$$

Then

$$H_T = 10^{-\text{pH}}/k^* - B_T/(1 + 10^{-\text{pH}}/K'_A) - K'_w/10^{-\text{pH}},$$

and therefore in order to describe the system over a wide range of pH it is necessary to measure both k^* and K'_w in addition to K'_A.

This approach has been taken by a number of recent workers who have used the N.B.S. pH scale in order to determine acidity constants (see *e.g.* Culberson and Pytkowicz, 1973; Mehrbach *et al.*, 1973; Atlas *et al.*, 1976; Sass and Ben-Yaakov, 1977) who have each determined

$$k^* = 10^{-\text{pH}}/{}^Tm_H$$

in their various media. The authors cited use symbols such as f_H or even γ_{H^+} to denote this parameter which they think of as an 'apparent activity coefficient' for hydrogen ion (see Discussion).

pH(SWS) and 'stoichiometric' acidity constants

This approach was first suggested for use in sea water by Lars Gunnar Sillén (Sillén, 1967; Dyrssen and Sillén, 1967). The key feature of this approach is that h is defined as equal to ${}^Tm_H$, and the stoichiometric constant

$$K_A^* = {}^Tm_H m_B/m_{HB}.$$

The mass balance equation for hydrogen is thus

$$H_T = {}^Tm_H - B_T/(1 + {}^Tm_H/K_A^*) - K_W^*/{}^Tm_H.$$

The essence of this approach therefore, is that the electrode system is calibrated simultaneously with the determination of the constants. Usually this is achieved by some least squares minimisation procedure which treats both E^0 and K_A^* as adjustable parameters. It is usually sound practice to determine K_W^* from a separate experiment in which $B_T = 0$. A wide variety of computer programs have been written for such problems (see Leggett, 1983). A number of workers in the past have calibrated glass electrodes as a hydrogen ion probe, and then transferred them to the test cell (see *e.g.* Rossotti and Rossotti, 1961): this is not now considered the optimal technique (Rossotti, 1974), as it has been shown that there are small changes in E^0 resulting from the transfer of glass electrodes from one solution to another (Pehrsson *et al.*, 1976).

Values of K_A^* (*i.e.* using a 'total' hydrogen ion concentration scale) have been determined for a wide range of proton-transfer reactions in sea water media: the ionic product of water (Hansson, 1972, 1973b; Dickson and Riley, 1979a), carbonic acid (Hansson, 1973b,c), boric acid (Hansson, 1973a,c), hydrogen sulphide (Almgren *et al.*, 1976), phosphoric acid (Dickson and Riley, 1979b; Johansson and Wedborg, 1979), ammonia (Johansson and Wedborg, 1980).

At high acidity, ${}^Tm_H$ is no longer directly proportional to m_H. It is therefore preferable to allow explicitly for the formation of species such as HSO_4^- and HF (see *e.g.* Hansson and Jagner, 1973; Dickson and Riley, 1979a). If desired, the final data can be presented on a "sea water scale" of hydrogen ion concentration:

$$m_H(\text{SWS}) = m_H(1 + \beta(HSO_4)^Tm_{SO_4} + \beta(HF)^Tm_F)$$

$$\approx {}^Tm_H.$$

This form of presentation achieves a measure of independence from systematic errors resulting from the use of inaccurate values for $\beta(HSO_4)$ and $\beta(HF)$ (Dickson, 1977; Dickson and Riley, 1979a).

There has been no agreement as to whether to include HF in the definition of a 'total' hydrogen ion concentration scale. It was included implicitly by Mehrbach *et al.* (1970), who used natural sea water for their experiments: it was included explicitly by Dickson in his work in synthetic seawater media. Other workers who have used a synthetic sea water without fluoride have of course not included the effect of fluoride in a definition of ${}^Tm_H$ (see *e.g.* Hansson's work).

The 'free' hydrogen ion concentration scale

Although the 'total' hydrogen ion scale is thermodynamically rigorous and well suited to the determination of acidity constants by titration techniques, it is however much clearer to use a 'free' hydrogen ion concentration scale, and to write the full equation explicitly incorporating the formation of bisulphate and hydrogen fluoride. In 1975, at the Dahlem Conference on "The Nature of Seawater," a working group on conventions for sea water equilibria proposed that it would be worth considering a 'free' hydrogen ion concentration scale, thus allowing a clear description of proton-transfer processes in sea water (HANSSON *et al.*, 1975). Professor Roger G. Bates, together with a variety of co-workers at the University of Florida, has therefore pursued this goal.

The basis of this approach has been to use the highly reproducible hydrogen/silver—silver chloride cell in a synthetic sea water whose chloride concentration is known. Then

$$E = E^0 + (RT/F)\ln(m_\text{H}m_\text{Cl}) + (2RT/F)\ln\gamma_{\pm}(\text{HCl}),$$

or, at trace hydrogen ion concentrations

$$E = \{E^0 + (RT/F)\ln m_\text{Cl} + (2RT/F)\ln {}^{\text{tr}}\gamma_{\pm}(\text{HCl})\} + (RT/F)\ln m_\text{H}$$

$$= E^{0\prime} + (RT/F)\ln m_\text{H}.$$

If ${}^{\text{tr}}\gamma_{\pm}(\text{HCl})$ is known in the synthetic sea water, it is then possible to measure m_H directly in solution. Two approaches have been used to determine ${}^{\text{tr}}\gamma_{\pm}(\text{HCl})$:

(i) Values have been measured in a chloride mixture which is thought to approximate the synthetic sea water (see KHOO *et al.*, 1977a).

(ii) Values of ${}^{\text{tr}}\gamma_{\pm}(\text{HCl})$ and $\beta(\text{HSO}_4)$ are obtained simultaneously from a minimisation procedure using data for various concentrations of HCl in synthetic sea water (see *e.g.* BATES and CULBERSON, 1977).

This latter approach has been applied by DICKSON *et al.* (in prep.), in order to obtain a self-consistent suite of values over a wide range of temperature and ionic strength. Once the value of ${}^{\text{tr}}\gamma_{\pm}(\text{HCl})$ is known, it is possible to estimate accurate values of acidity constants defined as

$$K_\text{A} = m_\text{H}m_\text{B}/m_\text{HB}.$$

This is best achieved by extrapolating e.m.f. data obtained using buffer mixtures of known composition to zero buffer concentration (*i.e.* the ionic medium standard state):

$$\ln K_\text{A} = \lim_{\text{B}_\text{T}\to 0}\left\{\frac{E - E^0}{(RT/F)} + \ln(m_\text{B}/m_\text{HB})\right\}.$$

This can be done with high precision (see *e.g.* KHOO *et al.*, 1977b).

Although no-one has yet used a 'free' hydrogen scale for evaluating titration data in a sea-water medium in order to determine acidity constants, there is no reason in principle why this should not be done provided that an accurate value of $\beta(\text{HSO}_4)$ is known for the medium. The mass balance equation for hydrogen ion could then be written as

$$\text{H}_\text{T} = m_\text{H} + {}^\text{T}m_{\text{SO}_4}/(1 + (1/\beta(\text{HSO}_4)m_\text{H})) - \text{B}_\text{T}/(1 + m_\text{H}/K_\text{A}) - K_\text{W}/m_\text{H},$$

and E^0 and K_A evaluated simultaneously as has been done for the 'total' hydrogen ion scale.

Sea water buffers

The idea of using buffers made up in a synthetic sea water background was first proposed by SMITH and HOOD (1964) who suggested that there were experimental advantages to doing so. These authors suggested that such buffers should have the position of secondary standards, and that they should be calibrated with respect to the N.B.S. pH scale. More recently, in an attempt to use the experimentally convenient potentiometric determination of pH to estimate hydrogen ion concentration in sea water, some workers (*e.g.* HANSSON, 1973d; RAMETTE *et al.*, 1977) have proposed values of pH(S) for buffer solutions made up in a background of synthetic sea water. The key to the successful application of this approach lies in the matching of the buffer composition with that of the sample. This is apparent from the following equations.

The e.m.f. of the pH cell in sea water can be written as

$$E = E^0 + (RT/F)\ln m_\text{H}$$

(see last section), therefore

$$\frac{E_\text{S} - E_\text{X}}{(RT\ln 10/F)} = \frac{E^0_\text{S} - E^0_\text{X}}{(RT\ln 10/F)} - \log m_\text{H}(\text{X}) + \log m_\text{H}(\text{S}).$$

Again this is only useful if $E^0_\text{S} - E^0_\text{X}$ is zero, and if $m_\text{H}(\text{S})$ is accurately known, otherwise pH(X) is strictly only an operational value. The calibration of the buffers is no different in principle from measuring an acidity constant and is achieved in much the same manner. Thus HANSSON (1973d) titrated his buffer with HCl in order to calibrate his electrode system and thus assign a value of ${}^\text{T}m_\text{H}(\text{S})$. Bates's group (RAMETTE *et al.*, 1977) use the value of ${}^{\text{tr}}\gamma_{\pm}(\text{HCl})$ to estimate E^0 and thus assign $m_\text{H}(\text{S})$.

The use of buffers based on a sea water background has not yet found any following within the oceanographic community. The reasons for this are various (see the excellent discussion by CULBERSON, 1981), but predominantly reflect the feeling that the considerable effort required to prepare such buffers is not repaid by commensurate gains in precision. In a regime where it is not possible to match the background composition of the buffer with that of the sample (*e.g.* estuaries or brines) the use of such buffers is impractical.

DISCUSSION

It has been claimed by a number of authors (PYTKOWICZ, 1969; BEN-YAAKOV and SASS, 1978;

CULBERSON, 1981) that the pH-apparent constant approach is equivalent to the use of stoichiometric acidity constants to describe proton-transfer reactions in ionic media. This claim, although correct in principle, is misleading. It is apparent from the discussion of the previous section, that

$$10^{-\mathrm{pH}} = m_{\mathrm{H}}\gamma_{?} \approx {}^{\mathrm{T}}m_{\mathrm{H}}k^{*},$$

(see also the discussions by HAWLEY and PYTKOWICZ, 1973; CULBERSON, 1981). In addition the 'apparent' dissociation constant

$$K'_{\mathrm{A}} = K_{\mathrm{A}}\gamma_{?} = K^{*}_{\mathrm{A}}k^{*}$$

incorporates the same constant term and thus the ratio

$${}^{\mathrm{T}}m_{\mathrm{HB}}/{}^{\mathrm{T}}m_{\mathrm{B}} = 10^{-\mathrm{pH}}/K'_{\mathrm{A}}$$

will be unambiguously defined if k^{*} is a constant. Unfortunately, it is not.

A number of workers have measured k^{*} (or f_{H} as it is often termed) in sea water media and it is apparent that considerable systematic differences exist (see Fig. 1). The value of $\gamma_{?}$ (and hence of k^{*}) is dependent on the physical design of the liquid-liquid junction in the pH cell—see the discussion of reference electrodes by CULBERSON (1981). As a result, for each well-defined value of a stoichiometric acidity constant, there will exist a multitude of possible 'apparent' constants, each corresponding to a particular reference half-cell. This problem has been acknowledged by some workers using apparent constants (see *e.g.* MEHRBACH *et al.*, 1973; ATLAS *et al.*, 1976) who are careful to specify the exact reference electrode used, and the particular reference buffer employed. Even this is not always sufficient; both MEHRBACH *et al.* (1973) and myself (DICKSON, 1977) have compared data for supposedly identical reference electrodes, and have obtained systematic differences equivalent to more than 0.01 pH units.

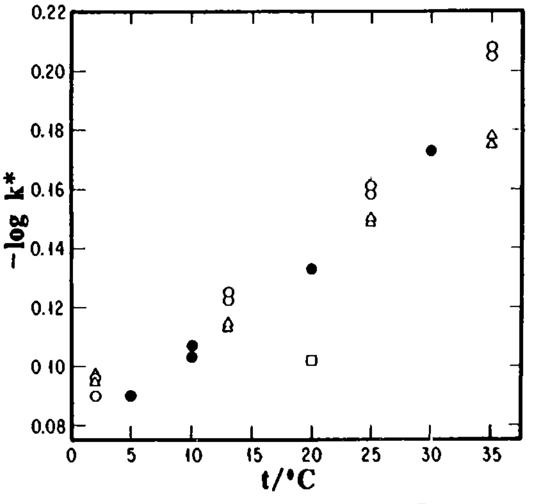

FIG. 1. Values of $-\log k^{*} = \mathrm{pH(NBS)} + \log {}^{\mathrm{T}}m_{\mathrm{H}}$ for sea water of $S \simeq 35$. Δ, CULBERSON and PYTKOWICZ (1973), O, MEHRBACH *et al.* (1973), □, ATLAS *et al.* (1976), ●, DICKSON (1977).

This problem has further ramifications. It is common practice in the field of geochemistry to assume that the N.B.S pH scale gives activities for the proton. As has been pointed out in the preceding discussion, this is not the case. As a result the magnitude of any 'single ion activities' calculated using this assumption will be dependent on the liquid junction potential, and thus do not even represent a useful *conventional* scale.

Culberson suggests that this problem would be overcome by the development of a reproducible liquid-liquid junction (and presumably the use of such a junction to determine K'_{A}). This systematic error is however not the only problem in obtaining apparent acidity constants. The definition of apparent constants, *i.e.* using the pH cell, automatically precludes the use of cells without liquid junction for the measurement of acidity constants. This is unfortunate, as the cell without liquid junction effectively eliminates problems resulting from possible variation of the liquid junction during a titration. A further technique used to improve the quality of hydrogen ion concentration data obtained using glass electrodes is to design the experiment so that the electrode pair can be calibrated directly in the test solution, if possible before the introduction of the reacting system of interest (see ROSSOTTI, 1974; DICKSON and RILEY, 1979b). This approach obviates the shift in E^{0} that has sometimes been observed when an electrode pair is shifted from one solution to another. Again, this avenue is of necessity closed to those wishing to determine apparent constants.

Although I have cited a number of disadvantages above, I do not feel that they represent the *major* drawback to the use of apparent constants. Rather, as WHITFIELD (1975) points out:

> "If we are to explain rather than describe the chemistry of protolytic species in sea water it is important that pH scales should be available that are defined on some thermodynamically acceptable scale rather than specified in terms of particular procedures."

The concentration constant K_{A} is unambiguously related to the standard acidity constant:

$$K^{0}_{\mathrm{A}} = K_{\mathrm{A}}\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{B}}}{\gamma_{\mathrm{HB}}}.$$

This allows a number of possibilities which are not easily available to the assiduous user of apparent constants:

(1) Measured values of $K^{0}_{\mathrm{A}}/K_{\mathrm{A}}$ can be used to assess the performance of models of interactions in electrolyte solutions (which attempt to predict the magnitude of the activity coefficient term). If K_{A} is measured in simple ionic solutions, this information can even be used to obtain parameters for such models (see *e.g.* THURMOND and MILLERO, 1982).

(2) Models of electrolyte solutions could be used to estimate values for K_{A} from a knowledge of K^{0}_{A}

and the composition of the solution. This would be invaluable for the study of brines and other geologically important solutions where it will be an impossible task to measure acidity constants for every composition of interest.

(3) Models of electrolyte solutions can be used in order to assess the effect of compositional changes on the values of K_A (see *e.g.* BEN-YAAKOV and GOLDHABER, 1973). This will probably be the most accurate method for treating the compositional changes that occur in marine pore waters during early diagenesis.

Although at the moment such models are at an early stage of development (see WHITFIELD, 1979), they hold promise for the future as a framework for linking together a variety of measurements in solutions of different compositions (see *e.g.* HARVIE, 1981; HARVIE *et al.*, 1984). A knowledge of analytical parameters such as the equilibrium partial pressure of CO_2—$P(CO_2)$—and the total inorganic carbon—C_T—will allow the calculation of hydrogen ion concentration, without recourse to the measurement of pH. This in turn will allow the calculation of m_{HB}/m_B for any other acid-base system. The accurate measurement of parameters such as $P(CO_2)$ or C_T requires however fairly sophisticated instrumentation; there will thus always be a call for a method of determining hydrogen ion concentration which has the convenience and simplicity of the pH measurement.

One such approach which would be of widespread applicability, is to calibrate ones own pH cell to measure hydrogen ion concentration. The technique would be to determine experimentally an estimate of the factor k^* as a function of composition. This could be achieved using either synthetic (CULBERSON and PYTKOWICZ, 1973; DICKSON, 1977) or natural samples (MEHRBACH *et al.*, 1973). This approach would be particularly appropriate to estuarine studies where matched buffers for hydrogen ion concentration are clearly impractical. The resulting pH data could then be reported as hydrogen ion concentrations. As I have pointed out above, such a value constitutes an *empirical* correction for a particular electrode system, and it would be most unwise to use a value that had been obtained for another reference electrode.

Such a pragmatic empirical approach is not entirely satisfactory, and it may be better in the future to consider the possibility of using cells without liquid junction. A promising candidate would be the combination of a hydrogen glass electrode and a sodium glass electrode. If the composition of the test solution is known, it should be possible to obtain thermodynamic information which could be unambiguously related to m_H. This suggestion is originally credited to George Scatchard (see HITCHCOCK, 1936), although it has been considered more recently by WILDE and ROGERS (1970).

It is apparent therefore that useful quantitative information about the concentration of hydrogen ion can be obtained only in systems whose composition is known. This is what one should expect. pH can thus retain its utility as a semi-quantitative measure of acidity in those systems where the detailed acid-base chemistry is not known (MACINNES, 1948). The question then arises as to which is the more useful, 'free' or 'total' hydrogen ion concentration. This is by no means a clear cut choice. The use of the 'free' hydrogen ion scale is certainly conceptually clearer in that the species HSO_4^- is well established, and ignoring its existence (although thermodynamically permissible) is inherently confusing. In order to use the 'free' hydrogen ion scale it is necessary to know a value for $\beta(HSO_4^-)$. This however is quite a weak association, and thus it is not a simple matter to determine an accurate value for the association constant. Any error in this value will result in a systematic error in the estimated 'free' hydrogen ion concentration. In those circumstances where an investigator believes that the value of $\beta(HSO_4^-)$ appropriate to his system is poorly known, it is probably better (although potentially more confusing) to employ a 'total' hydrogen ion concentration scale.

CONCLUSIONS

CULBERSON (1981) has recently reviewed the current status of pH measurements in sea water. In his discussion (pp. 202–204), he states that:

> "The major problem with the NBS pH scale for equilibrium measurements in sea water is the unreproducibility of its liquid junction potential, not its lack of theoretical meaning. . . . hydrogen ion concentration scales have no practical advantages for pH measurements in low (estuaries) or high (brines) salinity environments. . . . Adoption of one of the hydrogen ion concentration scales will still require the use of the NBS pH scale for measurements in estuaries and brines, and will mean that oceanographers use a pH scale different from that used by geochemists and biochemists."

Culberson then concludes that it would be more profitable to design a reproducible liquid junction than to adopt the 'free' or 'total' hydrogen ion pH scales.

Although I concur fully with the need for a reproducible liquid junction, and would refer the interested reader to the results of BIEDERMANN and DOUHÉRET (1980a,b,c) in this regard, I do not agree with Culberson's other comments.

In the preceding sections I hope to have brought out the advantages of experimental precision and conceptual simplicity that are inherent in using concentration constants rather than 'apparent' constants for the study of proton-transfer reactions in saline media, whether in the laboratory or in the field. These advantages are briefly summarised here.

(1) Constants based on hydrogen ion concentration scales (*i.e.* ionic medium standard states) are clear and unambiguous. In addition, they allow where desired the optimal precision in their determination.

(2) As a result of this, the relationship between such constants and the so-called "infinite dilution" values is readily apparent. This can be used either to test models of activity coefficients, or to predict

values of the stoichiometric constants for use in solutions where they have not been measured.

(3) If one is prepared to take the trouble, an estimation of hydrogen ion concentration is probably possible in any solution *whose composition is known.*

The measurement of pH *per se* (even if the problems of the reproducibility of the liquid junction are overcome) should only be a method of last resort. Its utility as a quantitative indication of the state of acid-base equilibria is tenuous at best, and is particularly so in solutions where the composition is not well known. Even in physiological media (~0.16 M NaCl), where the liquid junction problems are not as acute as they are for geochemical brines, there is no clear consensus as to the desirability of N.B.S. pH measurements compared to a hydrogen ion concentration scale (Bates, 1973; Anon., 1976).

Although the operational pH (NBS) scale is widely used by those geochemists studying lakes, streams, ground water etc., the same problems exist. In waters at a low ionic strength, it may be possible to utilize specially developed low ionic strength buffers together with a flowing cell (Covington *et al.*, 1983). Such pH measurements would be expected to lie on the conventional hydrogen ion activity scale and could be used together with other thermodynamic data for modelling acid base processes in low ionic strength systems. In ground waters, or brines where the ionic strength is somewhat higher (>0.1*m*), it is not possible to ascertain to what extent such pH measurements are bedevilled by liquid junction problems. In these systems, the investigator will have to decide what accuracy is required for their investigation in order to ascertain whether conventional pH measurements are adequate, or whether an alternative approach is justified.

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ANNEX 2

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The pH of estuarine waters

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Abstract

The emf measurements for the TRIS buffer in seawater have been used to define buffer solutions that can be used to determine the pH on a free or total proton scale for estuarine waters. The pH is related to the stoichiometric dissociation constant (K^*) of $TRISH^+$, the concentration of buffer (m_{TRIS}) and salinity (S) by

$$pH = pK^* + (aS + bS^2)m_{TRIS}$$

where $a = -9.73 \times 10^{-5}$ and $b = 6.988 \times 10^{-5}$. The values of pK^* were fit to equations of the form

$$pK^* = A/T + B + C \log T$$

where A, B, and C are functions of salinity and T is the absolute temperature.

An electrode system with liquid junction was used to measure these buffers to compare the various pH scales.

The pH of natural waters provides a master variable for describing the status of acid-base equilibria, the speciation of metals, and biological and kinetic processes. The demands of making pH measurements vary considerably. For characterizing the carbonate system, values of ±0.01 pH units are necessary, while for water quality purposes ±0.1 pH units are sufficient. Three methods are now in use to define the pH scales used for marine waters (Dickson 1984). In dilute solutions such as rivers, lakes, or groundwaters, dilute NBS buffers (Covington et al. 1983; Bates 1973, 1975) have found wide use. The pH on the NBS scale is defined by

$$pH_{NBS} = -\log a_H. \quad (1)$$

In constant ionic media like seawater (Culberson 1981; Dickson 1984), attempts have been made to define appropriate pH scales. Recent work has also defined scales and calibration procedures for estuarine waters (Whitfield et al. 1985). The work in seawater has resulted in the formulation of the pH_T scale, based on the total proton concentration (Hansson 1973)

$$pH_T = -\log[H^+]_T \quad (2)$$

where the value of $[H]_T$ is given by

$$[H^+]_T = [H^+]_F + [HSO_4^-]. \quad (3)$$

Bates and coworkers (Bates 1975; Bates and Macaskill 1975; Khoo et al. 1977) have formulated the pH_F scale for seawater based on the free proton concentration

$$pH_F = -\log[H^+]_F. \quad (4)$$

Although these later scales were introduced >10 years ago, most workers still use the NBS scales. One can debate which scale is better (Culberson 1981; Dickson 1984), but considerable variability has been found when using commercial reference electrodes (Pytkowicz et al. 1966; Johnson et al. 1977; Whitfield et al. 1986) and the NBS scale. This is due to the variations in the liquid junction of various reference electrodes. To avoid these problems, which can cause unknown variations between different studies, it is better to use the pH_T or pH_F scales with buffers in the ionic media of interest (Dickson 1984; Whitfield et al. 1986). When combined with the NBS scale, these buffers can at least provide a calibration of the electrode system used in a given study, so that adjustments can be made among various workers.

Practical pH scales for seawater solutions based on the concentration of the total

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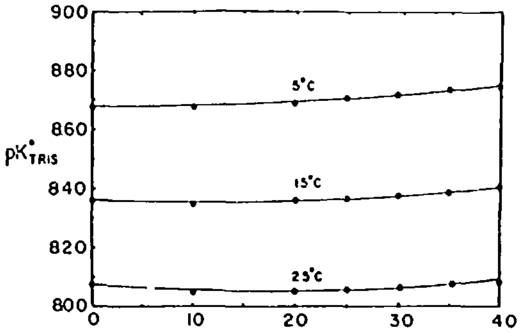

Fig. 1. Values of pK^*_{TRIS} for the ionization of $TRISH^+$ in seawater at t = 5°, 15°, and 25°C as a function of salinity (S).

(Hansson 1973) and free (Bates 1975) proton have been developed with buffer solutions of TRIS, tris-(hydroxymethyl)aminomethane. Smith and Hood (1964) were the first to suggest the use of TRIS buffers in seawater. They, however, did not provide an independent estimation of the pK* for the dissociation of $TRISH^+$,

$$TRISH^+ \rightarrow H^+ + TRIS, \qquad (5)$$

in seawater needed to develop a reliable scale. Hansson (1973) determined values of pH_T for $m = 0.005$ TRIS buffers in seawater from $S = 20$–40 and t = 5°–25°C from potentiometric titrations. Ramette et al. (1977) determined values of pH_F for $m = 0.01$ to 0.06 TRIS buffers in seawater from $S = 30$–40 and t = 5°–40°C. Although Hansson and Ramette et al. did not make measurements below $S = 20$, it is possible to derive a reasonable extrapolation to lower salinities because the pK* for the ionization of $TRISH^+$ is almost a linear function of salinity (Fig. 1). This near-linear behavior arises because the activity coefficient ratio of $TRISH^+$ and H^+ varies only slowly with ionic strength, and the activity coefficient of the nonelectrolyte TRIS can be represented by a Setchenow type equation

$$\log \gamma_{TRIS} = aS. \qquad (6)$$

At a given salinity, the pH (total or free) is a linear function of the concentration of buffer (m_{TRIS}); thus (Ramette et al. 1977),

$$pH = pK^* + a m_{TRIS}. \qquad (7)$$

The slope a is independent of temperature and its salinity dependence can be approximated by

$$a = -9.73 \times 10^{-5} S + 6.988 \times 10^{-5} S^2. \qquad (8)$$

By fitting the values of pK* on a given pH scale to a function of temperature and salinity, one can define the pH of TRIS buffers for estuarine waters.

To accomplish this, I first determined the values of pK* extrapolated to zero concentration of buffer. These values of pK* were then fitted to functions of temperature and salinity with methods developed earlier to examine the carbonate system (Millero 1979). To demonstrate the use for these buffers, I have determined the emf of TRIS buffers from $S = 2.5$ to 40 using an electrode system with liquid junction at 25°C.

Comparison of the pH_T and pH_F scales for seawater

The free and total pH scales are related by

$$pH_T = pH_F - \log(1 + \beta_{HSO_4}[SO_4^{2-}]) \qquad (9)$$

where β_{HSO_4} is the association constant

$$\beta_{HSO_4} = [HSO_4^-]/[H^+][SO_4^{2-}] \qquad (10)$$

for the formation of HSO_4^-. Although several workers (Culberson et al. 1970; Dyrssen and Hansson 1973; Millero 1983) have determined β_{HSO_4} for seawater at 25°C, the most extensive estimates have been made using the emf data of Khoo et al. (1977). A comparison of the values of pK* for the ionization of $TRISH^+$ on the pH_T scale of Hansson (1973) and the adjusted results of Ramette et al. (1977) is given in Table 1 (molal units). The differences of ~0.01 obtained with the values of β_{HSO_4} from Khoo et al. (1977) are larger than expected (~0.004). The differences become smaller (within 0.008) when one uses the values of β_{HSO_4} from Bates and Calais (1981). Since the β values from these studies were both determined from the same emf data of Khoo et al. (1977) for seawater with SO_4^-, the differences are related to the method used to evaluate the data.

The values of pH_i (i = F or T) can be determined from the emf (E) measurements using the equation (Ramette et al. 1977)

$$pH_i = (E - E^*_i)k + \log[Cl^-] \qquad (11)$$

Table 1. Comparison of values of pK^* for the dissociation of $TRISH^+$ in seawater on the pH_T scale. ΔpK^* (Hansson 1973 − Ramette et al. 1977). Values of β_{HSO_4} from (a) Khoo et al. 1977, (b) Bates and Calais 1981, and (c) Eq. 14.

Temp (°C)	$S = 30$			$S = 35$			$S = 40$		
	a	b	c	a	b	c	a	b	c
5	0.013	0.006	0.008	0.009	0.002	0.003	0.014	0.008	0.006
15	0.015	0.008	0.007	0.012	0.005	0.003	0.013	0.007	0.002
25	0.008	0.002	0.001	0.008	0.002	0.001	0.012	0.008	0.004

where E^*_i is the standard potential (mV) at infinite dilution in the ionic media on the free or total scale, $k = RT \ln 10/F = 0.198412T$ (E in mV), and $[Cl^-]$ is the molal concentration of Cl^- ion. The values of E^*_i are determined from emf measurements in media with small amounts of added HCl so that the Cl^- concentration and ionic strength are unchanged (Khoo et al. 1977). The values of E^*_i are defined by (Bates and Culberson 1977)

$$E^*_i = E_i + k\log[H^+]_i + k\log[Cl^-] + 2\log\gamma^*_\pm(HCl) \qquad (12)$$

where $\gamma^*_\pm(HCl)$ is the mean ion activity coefficient in the media. Since $\gamma^*_\pm(HCl)$ approaches 1.0 when $[H^+]_i \rightarrow 0$, the values of E^*_i can be obtained by extrapolating $E_i - 2\log\gamma^*_\pm(HCl)$ to $[H^+] = 0$. Khoo et al. (1977) determined values of E^*_F from measurements in seawater without SO_4^{2-} and $[H^+] = 0.01m$. Ramette et al. (1977) used these values at the ionic strength of seawater (corrected for ion-pairing) to determine value of pH_F for TRIS buffers using Eq. 11. The values of E^*_F and E^*_T are related by (Khoo et al. 1977)

$$E^*_T = E^*_F + k\log(1 + \beta_{HSO_4}[SO_4^{2-}]). \qquad (13)$$

Khoo et al. (1977) evaluated values of β_{HSO_4} from emf measurements of HCl from 0.01 to $0.06m$ in seawater with SO_4^{2-} using Eq. 13 by an iteration technique and assuming E^*_F was equal to the values in seawater without SO_4^{2-} at the same ionic strength (corrected for ion-pairing). Two possible problems with this technique are selecting the proper ionic strength to use and that model calculations indicate that the replacement of Cl^- with SO_4^{2-} in seawater can cause changes in $\gamma_\pm(HCl)$ not related to the formation of HSO_4^- (Millero 1983). The use of an effective ionic strength corrected for ion-pairing rather than the formal ionic strength is a function of the ion-pairing model used and causes differences that may or may not be valid. Fortunately, the effect is not large, $\Delta pH = 0.001$, 0.002, and 0.004 at $S = 30$, 35, and 40.

The question of whether seawater without SO_4^{2-} (replaced with Cl^-) is the best medium to use to evaluate E^*_F cannot be answered with certainty. Model calculations using Pitzer's (1973) equations give exact calculations of $\gamma_\pm(HCl)$ in seawater without SO_4^{2-} (Millero 1983). If the same equations are used for seawater with SO_4^{2-}, the media $\gamma_\pm(HCl)$ values without correction for β_{HSO_4} do not agree with the values in seawater without SO_4^{2-}. The differences are small, but lead to lower values of β_{HSO_4} (Millero 1983). Ideally the values of E^*_F and E^*_T should be determined from the same emf data on seawater with SO_4^{2-} as a function of added HCl (Khoo et al. 1977). Bates and Culberson (1977) have evaluated values of E^*_F at 25°C from the values of $E^*_T - 2\log\gamma^*_\pm(HCl)$ with the emf measurements of

Table 2. Comparison of the values of β_{HSO_4} in seawater ($S = 35$) obtained by various workers.

Temp (°C)	HSO_4	Reference
5	8.0	This study
	7.8	Bates and Calais 1981
	7.1	Khoo et al. 1977
15	10.3	This study
	9.8	Bates and Calais 1981
	9.0	Khoo et al. 1977
25	12.8	This study
	12.5	Bates and Calais 1981
	11.9	Khoo et al. 1977
	12.1	Culberson et al. 1970
	11.3	Dyrssen and Hansson 1973
	10.4	Harvie et al. 1984
	9.9	Millero 1983

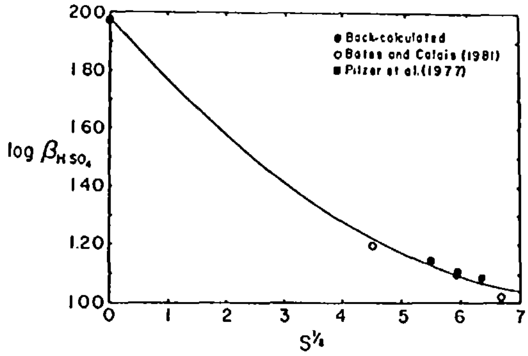

Fig. 2. Values of $\log \beta_{HSO_4}$ for the association of HSO_4^- in seawater at t = 25°C as a function of the square root of salinity ($S^{1/2}$).

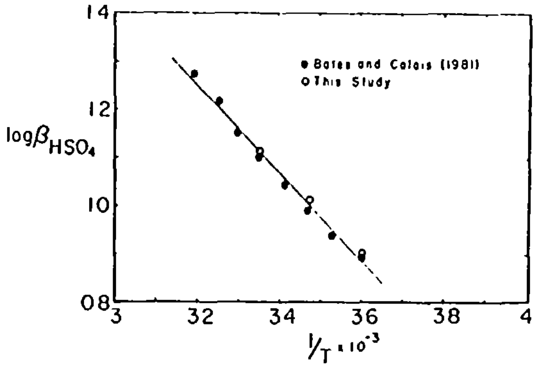

Fig. 3. Values of $\log \beta_{HSO_4}$ in seawater at S = 35 as a function of the reciprocal of absolute temperature ($1/T$).

Khoo et al. (1977) by an iterative adjustment of β_{HSO_4}. Unlike the iteration of Khoo et al. (1977) they adjusted β_{HSO_4} until $E^*_T - 2 \log \gamma^*_\pm(HCl)$ became independent of m_{HCl} and equaled the value to E^*_F. Similar calculations (Bates and Calais 1981) have been made over the entire salinity and temperature range of the measurements of Khoo et al. (1977). The resultant values of β_{HSO_4} have been fit to an equation of the form (Bates and Calais 1981)

$$\log \beta_{HSO_4} = A/T + B + C \ln T \quad (14a)$$

where A, B, and C are functions of salinity. As shown in Table 1 these values of β_{HSO_4} yield differences between the two pH scales that are in reasonable agreement. The small differences that remain using the two pH scales are undoubtedly related to experimental errors in the measurements (0.005), to the assumptions made concerning the ionic strength, and to neglecting the concentration dependence of $\gamma^*_\pm(HCl)$ when determining β_{HSO_4}. To improve the estimations of β_{HSO_4}, one needs new emf measurements in seawater with SO_4^{2-} below $m_{HCl} = 0.01$ and at low salinities. Until this is done, I believe that the differences between pH_T and pH_F (which may or may not be related exactly to β_{HSO_4}) should be treated as operational parameters relating the two scales.

If one assumes that the two scales are correct as given, one can derive operational values of β_{HSO_4} from the experimental measurements of Hansson (1973) and Ramette et al. (1977) from 5°–25°C and S = 30–40. These operational values are given in Table 2 along with the values obtained by others. The effects of salinity and temperature on the values of $\log \beta_{HSO_4}$ are shown in Figs. 2 and 3. The pure water values are taken from Pitzer et al. (1977). By combining the back-calculated values with those of Bates and Calais (1981) and Pitzer et al. (1977) I obtain the following coefficients for Eq. 14a:

$$A = -1{,}226.966 + 65.6S^{1/2} \quad (14b)$$

$$B = 6.09405 - 0.4502S^{1/2} + 1.3525 \times 10^{-2}S \quad (14c)$$

$$C = 0 \quad (14d)$$

(SE = 0.03). This equation reproduces the differences between the two pH scales on the average to ±0.004 with a maximum error of 0.008 (*see Table 1*). It represents what I think are the best operational values of β_{HSO_4} relating the two pH scales.

Evaluation of pK for the ionization of TRISH⁺*

The values of pK^*_F on the free proton pH_F scale have been evaluated at $m_{TRIS} = 0$ in seawater from the pH_F results of Ramette et al. (1977) with Eq. 7 and 8. the values of pK^*_T on the total proton pH_T scale have been determined from the direct measurements of Hansson (1973) and Ramette et al. (1977), corrected to the pH_T scale with Eq. 9 and 14. These values of pK^*_F and pK^*_T were fit to equations of the form (Millero 1979)

Table 3. Values of pK^*_F for $TRISH^+$ in estuarine waters.

S	pK^*_F (molal)							
	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
40	8.826	8.662	8.506	8.356	8.212	8.073	7.940	7.812
35	8.810	8.647	8.491	8.341	8.197	8.059	7.926	7.798
30	8.794	8.632	8.476	8.326	8.182	8.044	7.911	7.784
25	8.777	8.615	8.459	8.309	8.166	8.028	7.895	7.768
20	8.759	8.597	8.442	8.292	8.149	8.011	7.879	7.751
15	8.741	8.579	8.423	8.274	8.131	7.993	7.861	7.734
10	8.721	8.559	8.404	8.255	8.112	7.975	7.843	7.716
5	8.701	8.539	8.384	8.235	8.092	7.955	7.823	7.696
2.5	8.690	8.528	8.374	8.225	8.082	7.945	7.813	7.687
1.2	8.684	8.523	8.368	8.219	8.077	7.940	7.808	7.681

$$pK^*_i - pK = A_i + B/T. \qquad (15a)$$

The pK values for the ionization of $TRISH^+$ at infinite dilution in water (Bates and Hetzer 1961) from 0° to 50°C were fit to the equation

$$pK = -22.5575 + 3477.5496/T + 3.32867 \ln T \qquad (15b)$$

where SE = 0.0017. The salinity-dependent terms A_i and B_i determined by the method of least-squares are given by

$$A_F = 2.065 \times 10^{-3}S - 1.770 \times 10^{-4}S^2, \qquad (15c)$$

$$B_F = 0.64S, \qquad (15d)$$

$$A_T = -2.3755 \times 10^{-2}S + 6.165 \times 10^{-5}S^2, \qquad (16a)$$

and

$$B_T = 6.313S, \qquad (16b)$$

with $SE_F = 0.0012$ and $SE_T = 0.003$ in pK^*_i. These equations combined with Eq. 7 and 8 can be used to define pH scales for the TRIS buffer in estuarine water $S = 0–40$, $t = 5°–40°C$, and $m_{TRIS} = 0.005–0.06$ molal. Values of pK_T and pK_F at $m_{TRIS} = 0$ for estuarine waters are given in Tables 3 and 4. Values of pH_i at various molalities of TRIS can be obtained by adding the terms $am_{TRIS} = pH_i - pK^*_i$ given in Table 5.

Preparation of pH buffers

The composition of $S = 35$ artificial seawater used by Ramette et al. (1977) is given in Table 6. Since the values of pH_F and pH_T are known as a function of $m_{TRIS} = m_{TRISH^+}$, a convenient way to make up the buffers for estuarine waters is to make a stock $S = 35$ salinity buffer with $m_{TRIS} = m_{TRISHCl} = 0.06$ m. This stock solution can then be diluted with pure water to make up a series of buffers with sufficient buffer in dilute solutions. A dilution of $S = 2.5$ will still have 0.004 moles of TRIS. To keep the Cl^- concentration constant in the media I reduced the NaCl concentration by the amount of

Table 4. Values of pK^*_T for $TRISH^+$ in estuarine waters.

S	pK^*_T (molal)							
	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
40	8.736	8.558	8.388	8.224	8.067	7.916	7.771	7.631
35	8.718	8.542	8.374	8.212	8.057	7.908	7.764	7.626
30	8.703	8.529	8.363	8.203	8.050	7.902	7.760	7.624
25	8.691	8.520	8.355	8.197	8.046	7.900	7.760	7.625
20	8.683	8.513	8.351	8.195	8.045	7.901	7.762	7.629
15	8.677	8.510	8.349	8.195	8.047	7.905	7.768	7.636
10	8.675	8.509	8.351	8.198	8.052	7.912	7.776	7.647
5	8.675	8.512	8.355	8.205	8.060	7.922	7.788	7.660
2.5	8.677	8.514	8.359	8.209	8.066	7.928	7.795	7.668
1.2	8.678	8.516	8.361	8.212	8.069	7.931	7.799	7.672

Table 5. The effect of various concentrations of TRIS on the pH_t scales for estuarine waters.

	$pH_t - pK^*_t$ (m_{TRIS})						
S	0.06	0.05	0.04	0.03	0.02	0.01	0.005
40	0.007	0.006	0.004	0.003	0.002	0.001	0.001
35	0.005	0.004	0.003	0.003	0.002	0.001	—
30	0.004	0.003	0.003	0.002	0.001	0.001	—
25	0.003	0.002	0.002	0.001	0.001	—	—
20	0.002	0.001	0.001	0.001	0.001	—	—
15	0.002	0.001	0.001	—	—	—	—
10	—	—	—	—	—	—	—
5	—	—	—	—	—	—	—
2.5	—	—	—	—	—	—	—

S	S = 35 diluted buffer	
	m_{TRIS}	$pH_t - pK^*_t$
35	0.060	0.005
30	0.051	0.005
25	0.041	0.003
20	0.031	0.002
15	0.025	0.001
10	0.017	—
5	0.008	—
2.5	0.004	—
1.25	0.002	—

TRISHCl added. The composition of this buffer (m = 0.06) is also given in Table 6. The concentration of TRIS in diluted samples of this stock S = 35 and m_{TRIS} = 0.06 buffer are given in Table 5 along with values of $pH_t - pK^*_t$.

Since it is easier to make up the solutions by volume, I have also given the values in grams per liter of solution at 25°C. The density of the artificial seawater solution at 25°C was 1.023422 g cm^{-3} by direct measurement, which is in reasonable agreement with real seawater (1.023343 g cm^{-3}) at S = 35 and t = 25°C (Millero and Poisson 1982). Measurements of the density of 0.06 m TRIS (S = 35) buffer were also made (ρ = 1.025960 g cm^{-3}). The differences with seawater are related to TRIS and TRISHCl added to the solution and the decrease in Na^+. The densities for the 0.06 buffer between 20° and 25°C (typical laboratory temperatures) can be estimated from

$$\rho = 1.033060 - 2.846 \times 10^{-4} t \quad (17)$$

where the temperature coefficient has been estimated from the equation of state for seawater (Millero and Poisson 1982).

For more accurate work with buffers at a fixed molality at a given salinity (S), the values of m_i (mol kg^{-1}) and g_i (g kg^{-1}) can be determined from

$$m_i \text{ (mol kg}^{-1}) = (m_{35} X_{H_2O})(S/35) \quad (18)$$

$$g_i \text{ (g kg}^{-1}) = (m_{35} M_i X_{H_2O})(S/35) \quad (19)$$

where M_i is the molecular weight of salt i and m_{35} is the molality at S = 35. The fraction of water in the molal solutions is given by

$$X_{H_2O} = 1{,}000/(1{,}000 + \Sigma\, m_i M_i). \quad (20)$$

For solutions of different molality of TRIS (m_{TRIS}) the moles and grams of NaCl are given by

$$m_{NaCl} \text{ (mol kg}^{-1}) = (0.42664 - m_{TRIS}) X_{H_2O} \quad (21)$$

and

$$g_{NaCl} \text{ (g kg}^{-1}) = (0.42664 - m_{TRIS}) 58.443\, X_{H_2O} \quad (22)$$

where

$$X_{H_2O} = 1{,}000/[1{,}011.3938 + (0.42664 - m_{TRIS}) 58.443 + 278.74 m_{TRIS}]. \quad (23)$$

The densities at salinities other than S = 35

Table 6. Composition of TRIS buffer for $S = 35$ seawater.

Solute	m	mol kg^{-1}	g kg^{-1}	g dm^{-3} (25°C)*
		Artificial seawater		
NaCl	0.42664	0.41168	24.061	24.625
Na_2SO_4	0.02926	0.02823	4.011	4.105
KCl	0.01058	0.01021	0.761	0.779
$CaCl_2$	0.01077	0.01039	1.153	1.180
$MgCl_2$	0.05518	0.05325	5.069	5.188
		g salt	35.055	
		g H_2O	964.945	
		m = 0.06 TRIS buffer		
NaCl	0.36664	0.34933	20.416	20.946†
Na_2SO_4	0.02926	0.02788	3.960	4.063
KCl	0.01058	0.01008	0.752	0.772
$CaCl_2$	0.01077	0.01026	1.139	1.169
$MgCl_2$	0.05518	0.05258	5.006	5.136
TRIS	0.06	0.05717	6.926	7.106
TRISHCl	0.06	0.05717	9.010	9.244
		g salt	47.209	
		g H_2O	952.791	

* On the basis of an experimental measurement of $\rho = 1.023422\ g\ cm^{-3}$ at 25°C, values at other temperatures can be estimated from $\rho = \rho sw + 2.26 \times 10^{-4} t$, where ρ_{sw} is the density of seawater at a given perature (Millero and Poisson 1982).

† On the basis of an experimental measurement of $\rho = 1.025960\ g\ cm^{-3}$, values at other temperatures can be estimated from Eq. 24.

needed to make up the solutions by volume can be estimated from the equation of state of seawater (Millero and Poisson 1982) with a correction for the amount of TRIS.

$$\rho = \rho_{sw} + 0.0583 m_{TRIS}. \qquad (24)$$

The buffer can be added by using a neutralized stock solution of TRIS or by adding TRIS and TRISHCl separately by weight.

Table 8. Comparisons of the measured and calculated values of f_H for $S = 35$ and $t = 25°C$.

f_H	Δ	Reference
0.70	–	This study
0.699	0.00_2	Merhbach et al. 1973
0.696	0.01	Culberson and Pytkowicz 1973
0.726	−0.03	Culberson et al. 1970
0.731	−0.03	Bates and Culberson 1977
0.688	0.01	Millero and Schreiber 1982
0.693	0.01	Hansson 1973

The $MgCl_2$ and $CaCl_2$ should be added from stock solutions of known concentrations. The molalities of the stock solutions can be determined by $AgNO_3$ titration or by measuring densities using the equations of state for the salts (Millero 1979). Almgren et al. (1975) have suggested that the salts $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 2H_2O$ can be used directly without changes in composition sufficient to seriously affect the pH. For accurate work this practice should be avoided.

Use of the pH buffers for estuarine waters

To examine the use of the pH scales given here, I have measured the emf of a series of buffers ($m_{TRIS} = 0.005$) with a glass electrode (Corning) and a calomel double-junction reference electrode (Orion—sleeve-type). The results are given in Table 7 along with those for a pH = 7.413 NBS buffer (phosphate). The values of pH_{NBS} have been calculated from the measured emf values (E) using

Table 7. Calibration of pH electrode with TRIS buffer ($m_{TRIS} = 0.005$) in estuarine waters at 25°C.

S	E (mV)	pH_{NBS}*	pH_F†	Δ1‡	pH_T§	Δ2‡	f_H‖
40.0	−74.5	8.209	8.212	−0.003	8.068	0.141	0.72
35.0	−74.6	8.211	8.198	0.013	8.057	0.154	0.70
30.0	−74.1	8.202	8.182	0.020	8.050	0.152	0.71
25.0	−73.7	8.196	8.166	0.030	8.046	0.150	0.71
20.0	−73.6	8.194	8.149	0.045	8.045	0.149	0.71
15.0	−73.3	8.189	8.131	0.058	8.047	0.142	0.72
10.0	−73.2	8.187	8.112	0.075	8.052	0.135	0.73
5.0	−73.6	8.194	8.092	0.102	8.060	0.134	0.74
2.5	−71.6	8.160	8.082	0.078	8.066	0.094	0.81
0	−69.5	8.125	8.072	0.053	8.072	0.053	0.89

* $pH_{NBS} = 7.413 + (E_s - E)/59.16$, where $E_s = -27.4$ mV.

† Assigned value from Eq. 7, 8, and 15a–d.

‡ $\Delta 1 = pH_{NBS} - pH_F$; $\Delta 2 = pH_{NBS} - pH$.

§ Assigned value from Eq. 7, 8, 15a, b, and 16 a, b.

‖ $f_H = a_H/[H^+]_T = 10](pH_T - pH_{NBS})$.

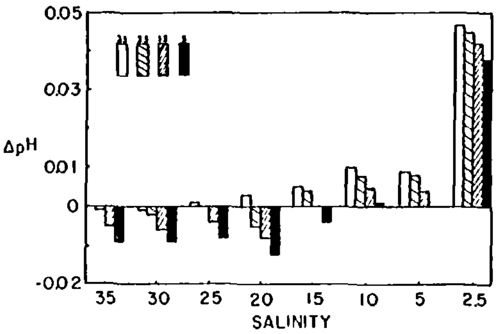

Fig. 4. Errors in pH in estuarine waters caused by using a fixed salinity buffer.

$$pH_{NBS} = 7.413 + (E_S - E)/59.16 \qquad (25)$$

where E_S is the emf in the standard buffer (−27.4 mV). The differences between the pH_F and pH_{NBS} are small, as found by others (Bates and Culberson 1977). This is fortuitous, presumably due to a compensation of the liquid junction potential by changes in activity coefficients (Bates and Culberson 1977). The differences between pH_T and pH_{NBS} can be attributed to the apparent activity coefficient (f_H) of H^+ (this includes effects of liquid junction, the definition of the NBS scale, and γ_H: Dickson 1984).

$$a_H = f_H[H^+]_T. \qquad (26)$$

At $S = 35$ the values obtained for $\Delta = pH_{NBS} - pH_T$ and f_H are in reasonable agreement (Table 8) with literature values. As demonstrated by Whitfield et al. (1986) this agreement may be fortuitous since different reference electrodes give different values of f_H. It does point out the need to use a seawater or estuarine buffer to compare values of pH between various workers.

The results in Table 7 can also be used to examine the use of a buffer at a fixed salinity to study an entire estuarine system (Whitfield et al. 1986). The errors in pH_T calculated by using a fixed buffer at $S = 35$, 25, 15, and 5 are shown in Fig. 4. Differences of 0.01 pH units, at most, occur when the $S = 35$ buffer is used over the salinity range of $S = 40$–5. At salinities between 0 and 2.5 the errors are as large as 0.09 in pH. Even when the $S = 5$ buffer is used, the errors are 0.08 pH units. These results indicate that for salinities between 40 and 5 any buffer at a fixed salinity can be used (the best being $S = 15$). This is in general agreement with the findings of Whitfield et al. (1986). At salinities below 5.0 one should use a series of dilute buffers for accurate work to account for the large changes due to variations in activity coefficients and liquid junctions.

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ANNEX 3

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A COMPARISON OF THE EQUILIBRIUM CONSTANTS FOR THE DISSOCIATION OF CARBONIC ACID IN SEA WATER MEDIA.

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Abstract — The published experimental data of HANSSON and of MEHRBACH *et al.* have been critically compared after adjustment to a common pH scale based upon total hydrogen ion concentration. No significant systematic differences are found within the overall experimental error of the data. The results have been pooled to yield reliable equations that can be used to estimate pK_1^* and pK_2^* for sea water media at salinities from 0 to 40 and at temperatures from 2 to 35 °C.

INTRODUCTION

Early work on the dissociation constants of carbonic acid in sea water (Buch *et al.*, 1932; Lyman, 1956) has been superceded by more recent determinations at Oregon State University by Mehrbach *et al.* (1973), and at the University of Göteborg by Hansson (1972; 1973). Each of these later determinations has defined the ionisation functions K_1 and K_2 in the general form

$$K_1 = k\,[\mathrm{H}][\mathrm{HCO_3}]/[\mathrm{CO_2^*}] \quad ,$$

and

$$K_2 = k\,[\mathrm{H}][\mathrm{CO_3}]/[\mathrm{HCO_3}] \quad ,$$

where k is a multiplier relating [H] to the pH scale used:

$$k\,[\mathrm{H}] = 10^{-\mathrm{pH}} \quad .$$

The two pH scales used are the NBS pH scale (Mehrbach *et al.*) and the pH(SWS) scale (Hansson). They are related by the expression

$$10^{-\mathrm{pH(NBS)}} = f_{\mathrm{H}}[\mathrm{H}]_{\mathrm{SWS}}$$

$$= f_{\mathrm{H}}[\mathrm{H}]\,(1 + \beta(\mathrm{HSO_4})\,{}^{\mathrm{T}}[\mathrm{SO_4}] + \beta(\mathrm{HF})\,{}^{\mathrm{T}}[\mathrm{F}]) \quad ;$$

f_{H} is known as the "apparent" total hydrogen ion activity coefficient (Culberson and Pytkowicz, 1973), $\beta(\mathrm{HSO_4})$ and $\beta(\mathrm{HF})$ are formation constants for the species $\mathrm{HSO_4^-}$ and HF respectively, and the superscript T implies total concentration. Hansson in fact defined his pH scale as

$${}^{\mathrm{T}}[\mathrm{H}] = [\mathrm{H}] + [\mathrm{HSO_4}] = [\mathrm{H}]\,(1 + \beta(\mathrm{HSO_4})[\mathrm{SO_4}]) \quad .$$

However, the definition given above is more rigorous (Dickson and Riley, 1979; Dickson, 1984).

It is difficult to compare these two sets of constants directly as the major differences are due solely to the change of pH scale. An indirect comparison of the various reported constants can be made with the ratio

$$K_1/K_2 = [\mathrm{HCO_3}]^2/[\mathrm{CO_2^*}][\mathrm{CO_3}] \quad ,$$

i.e. the stoichiometric equilibrium constant (K) for the reaction:

$$\mathrm{CO_2^*} + \mathrm{H_2O} + \mathrm{CO_3^{2-}} = 2\,\mathrm{HCO_3^-} \quad .$$

Fig. 1, like the plots of Skirrow (1975), Bates and Culberson (1977), and of Millero (1979), indicates the presence of a slight systematic discrepancy with an average magnitude of about 0.03 in pK. It is necessary to take account of the difference between the two pH scales employed, so as to assess whether this discrepancy is due to errors in K_1 or in K_2.

CONVERSION TO A COMMON BASIS

The data sets of Mehrbach *et al.* and of Hansson are contained in Tables 2 and 3 respectively; each investigator used the concentration unit moles per kilogram of solution (mol/kg–soln). The following strategy was adopted to place the data on a common basis with the minimum of manipulation. The values of the constants were corrected to the pH(SWS) scale, i.e.

$$10^{-\mathrm{pH(SWS)}} = [\mathrm{H}]\,(1 + \beta(\mathrm{HSO_4})\,{}^{\mathrm{T}}[\mathrm{SO_4}] + \beta(\mathrm{HF})\,{}^{\mathrm{T}}[\mathrm{F}]) \ ,$$

where the values of ${}^{\mathrm{T}}[\mathrm{SO_4}]$ and ${}^{\mathrm{T}}[\mathrm{F}]$ are the expected values in natural sea water at a salinity of 35: 0.02824 mol/kg–soln and 0.00007 mol/kg–soln respectively. It is therefore necessary to correct the values of Mehrbach *et al.* using the appropriate values of f_{H}, and to correct the values of Hansson to take account of the fact that his medium had no fluoride and had a slightly different amount of sulphate ion compared with natural sea water. The difference in formal ionic strength between Hansson's medium and natural sea water of the same nominal salinity can be neglected.

Mehrbach *et al.* reported data for f_{H} at the same salinities and temperatures as their experimental values of K_1. We therefore corrected their K_1 data directly:

$$\mathrm{p}K_1^* = -\lg\,\{K_1(\text{experimental})\,/\,f_{\mathrm{H}}(\text{experimental})\,\} \ .$$

They also measured $\mathrm{pH_o}$, the equilibrium pH which does not change on addition of sodium bicarbonate to a sea water solution. The values of $\mathrm{pH_o}$ (and hence of the product K_1K_2 — see below) were measured at salinities which differ slightly from those corresponding to the reported values of K_1. It is therefore necessary to interpolate the values of f_{H} and K_1 to obtain corrected values of K_2. We used a quadratic function of salinity to interpolate the data separately at each temperature; this procedure preserves the maximum significance in the data. The value of K_1K_2 was calculated from the expression (Mehrbach *et al.*, 1973),

$$K_1K_2(\text{experimental}) = \{10^{-2\mathrm{pH_o}} + (1 - A)\,K_1(\text{interpolated})\,10^{-\mathrm{pH_o}}\}/2(A - 1)$$

where $A = 0.9991$ (A is a measure of the purity of the $\mathrm{NaHCO_3}$ used), and

$$\mathrm{p}K_2^* = -\lg \frac{K_1K_2(\text{experimental})}{f_{\mathrm{H}}(\text{interpolated})\,K_1(\text{interpolated})} \ .$$

The final corrected values, $\mathrm{p}K_1^*$ and $\mathrm{p}K_2^*$, are included in Table 2.

Hansson's reported data were corrected using the following expression

$$\mathrm{p}K_i^* = \mathrm{p}K_i(\text{experimental}) - \lg \frac{(1 + \beta(\mathrm{HSO_4})\,{}^{\mathrm{T}}[\mathrm{SO_4}]_{\mathrm{SW}} + \beta(\mathrm{HF})\,{}^{\mathrm{T}}[\mathrm{F}]_{\mathrm{SW}})}{(1 + \beta(\mathrm{HSO_4})\,{}^{\mathrm{T}}[\mathrm{SO_4}]_{\mathrm{IM}})} \ ,$$

where the subscripts SW and IM refer respectively to the concentration in sea water, and to the concentration in Hansson's medium of the same nominal salinity. Values for $\beta(\mathrm{HSO_4})$ and $\beta(\mathrm{HF})$, appropriate to sea water, were obtained using the following equations:

$$\ln \beta(\mathrm{HSO_4}) = 647.59/T - 6.3451 + 0.019085T - 0.5208I^{1/2}$$

(Khoo *et al.*, 1977), and

$$\ln \beta(\mathrm{HF}) = -1590.2/T + 12.641 - 1.525I^{1/2}$$

(Dickson and Riley, 1979). Final corrected values are included in Table 3.

DISCUSSION

It is useful to fit each data set as a function of temperature and salinity, so as to assess the precision of the final corrected data. A variety of different forms of equation were tried. The final equations chosen are given in Table 4: the residuals are presented in Fig. 2. The internal precision of the data, as indicated by the calculated standard deviation of the fit ($s_f = \{\sum (y_i - y_{calc})^2/(n-k)\}^{1/2}$), is approximately the same for the two investigators. The experimental precision ($2s_f$) is approximately ±0.01 in pK_1^* and ±0.02 in pK_2^*.

The pooled data set were fitted to yield the first group of equations in Table 5. A number of other forms of equation were tried, but these forms represent the data best. Fig. 3 shows the residuals relative to these equations. It appears that there is a small systematic difference between the two data sets. Hansson's data for pK_1^* are approximately 0.01 higher than the data of Mehrbach *et al.*, whereas the pK_2^* data of Mehrbach *et al.* are approximately 0.02 higher than Hansson's. As a result, the error in pK, i.e. $pK_2^* - pK_1^*$, is about 0.03 (cf. Fig. 1). These differences, however, are of the same order of magnitude as the experimental precision, and probably are not particularily significant.

In addition, we felt it was desirable to obtain fitting equations which allowed a smooth interpolation between the values presented here for the salinity range $20 \leq S \leq 40$, and the infinite dilution data of Harned and his co-workers (HARNED and DAVIS, 1943; HARNED and SCHOLES, 1941). The differences $pK_i^* - pK_i^\circ$ (where pK_i° represents the value at infinite dilution at the same temperature) were fitted to obtain the expressions presented in Table 5. The residuals from these equations are plotted in Fig. 4. Comparison of Figs. 3 and 4 shows that either set of equations is an equivalent representation of the pooled data; however, additional terms are required to force the data to extrapolate correctly to the values at $S = 0$. It is also interesting to compare the data at the low salinity end with values estimated using an ion-pairing model such as that of MILLERO and SCHREIBER (1982): the equations presented in Table 5 represent these estimated values reasonably closely, with an error of <0.03 in pK_1^* and a larger error of ~0.1 in pK_2^*. As the parameters of the ion pairing model are not particularily accurate it is probably not worth adjusting the equation for pK_2^* to obtain better agreement.

From this analysis it is impossible to assess which set of data is "better". Each of the corrected sets of data has approximately the same precision. (The corrected data of Mehrbach *et al.* for pK_1 appear to have a better precision than the raw data. This reflects the additional uncertainty introduced by f_H). In addition, the systematic difference between the two sets of data is approximately equal to the precision ($2s_f$). Even the precision of the final pooled data set is of a similar magnitude to that of the independent sets of data (compare Figs. 2 and 4).

Thus, it is likely that the precision of the pooled data set represents a reasonable value for the accuracy of the dissociation constants of carbon dioxide in sea water. One can then assess what contribution this magnitude of error contributes to various derived quantities, such as the equilibrium partial pressure of CO_2 (P_{CO_2}), or the concentration of carbonate ion . 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}, total alkalinity (A_T) and total dissolved inorganic carbon (C_T) and to a lesser extent upon the specific conditions. Thus for the observable combination pH and alkalinity (discounting any error in K_B) the value of $[CO_2^*]$, and hence P_{CO_2}, varies by 1% for each 1% error in K_1 (±0.017 in pK_1 = ±4% in K_1). The error in calculation of $[CO_3^{2-}]$ is similarily proportional to the error in K_2 (±0.026 in pK_2 = ±6.2% 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). Both experimenters measured K_1 and K_1K_2; the errors in K_1 and K_2 would therefore be expected to show a strong negative correlation. This is borne out by the distribution of residuals (Figs. 3 and 4). The estimated precision for $\mathrm{p}(K_1/K_2)$ over the salinity range $S = 0$ to 40, is thus ±0.038 ($2s_f$). This is somewhat larger than would be expected by simply summing the errors in K_1 and K_2.

CONCLUSIONS

A recent meeting of the Carbon Dioxide sub-committee of the Joint Panel on Oceanographic Tables and Standards agreed to recommend the adoption of the equations valid for the whole salinity range $S = 0$ to 40 (Table 5). These equations successfully represent the experimental data in the salinity range $S = 20$ to 40, and also provide a reasonable extrapolation for use in estuaries.

It seems that the current data are adequate for many oceanographic purposes. If the accuracies of the various seagoing analytical methods for the carbonate system are improved appreciably, then errors in the constants will dominate the errors in the final derived parameters. A recent report on oceanic CO_2 measurements (SCOR, 1985) emphasizes the desirability of improving the accuracy of shipboard measurements of the various CO_2 parameters. If such improved methods become routine, the current inaccuracy in the values of the constants may well become significant.

It may be argued that, as there is no clear choice between the two published sets of constants, either one could be satisfactorily employed. However, pooling the data sets reasonable limits for the probable accuracy of the constants. We pooled the data on the basis of the pH(SWS) scale; this represents our opinion that this is the most appropriate scale for sea water. In the case of calculations using C_T and A_T it is the ratio (K_1/K_2) that is of interest, and thus the specific choice of pH scale is not important. It is however undesirable to try to correct the pooled data to the pH(NBS) scale. This would introduce additional uncertainties due to the irreproducibility of f_H, and thus negate any gains that had been made.

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Table 1. Interpolating equations for the equilibrium constants of HANSSON (1972) and of MEHRBACH *et al.* (1973).[†] The terms in parentheses represent the precision ($2s_f$); T is the temperature in Kelvins.

Hansson's data (JOHANSSON and WEDBORG, 1982)

$$\mathrm{p}K_1 = 841.2/T + 3.2762 - 0.010382S + 0.00010287S^2 \qquad (\pm 0.013)$$

$$\mathrm{p}K_2 = 1376.4/T + 4.8256 - 0.018232S + 0.00011839S^2 \qquad (\pm 0.022)$$

Mehrbach's data (PLATH, JOHNSON and PYTKOWICZ, 1980)

$$\mathrm{p}K_1 = 17.788 - 0.073104T - 0.0051087S + 0.00011463T^2 \qquad (\pm 0.012)$$

$$\mathrm{p}K_2 = 20.919 - 0.064209T - 0.011887S + 0.0000873137T^2 \qquad (\pm 0.022)$$

[†] Neither of the original papers contained adequate interpolating equations. However, each of these interpolating equations comes from the same laboratory as the original measurements.

Table 2. Experimental data of Mehrbach. Based on Table 3 of MEHRBACH *et al.* (1973).
The values of pK_1^* and pK_1^* are corrected to pH(SWS).

t/°C	S	$K_1 \cdot 10^6$	f_H	pH_o	pK_1^*	pK_2^*
2	26.67			7.900		9.444
				7.898		9.440
	27.01	0.602	0.770		6.107	
		0.597	0.774		6.113	
	34.66			7.812		9.335
				7.81		9.331
				7.814		9.339
				7.818		9.347
	34.78	0.664	0.802		6.082	
		0.664	0.801		6.081	
		0.667	0.813		6.086	
	41.54			7.768		9.294
	42.88	0.729	0.836		6.059	
		0.728	0.837		6.060	
		0.723	0.827		6.059	
13	26.76	0.758	0.718		5.977	
		0.760	0.731		5.983	
	26.92			7.757		9.239
				7.759		9.243
	34.76	0.839	0.750		5.951	
		0.837	0.755		5.955	
	35.2			7.689		9.165
				7.689		9.165
	42.85	0.915	0.787		5.934	
		0.915	0.788		5.935	
	42.9			7.629		9.101
25	19.16			7.716		9.148
				7.714		9.144
				7.711		9.138
				7.716		9.148
	19.19	0.802	0.677		5.927	
		0.802	0.677		5.926	
25	25.17			7.652		9.066
				7.650		9.062
				7.648		9.058
	25.25	0.873	0.674		5.888	
		0.883	0.677		5.884	
	31.22			7.594		8.989
				7.591		8.984
				7.593		8.987
	31.49	0.949	0.684		5.858	
		0.956	0.684		5.855	
	34.9			7.569		8.961
				7.569		8.961
				7.567		8.957
	35.1	1.005	0.69		5.837	
		1.009	0.695		5.838	
	35.23	1.01	0.692		5.836	
	42.21			7.511		8.884
				7.511		8.884
	42.26	1.071	0.702		5.816	
		1.078	0.695		5.809	
		1.081	0.688		5.804	
35	26.75	0.985	0.625		5.803	
	27.04			7.564		8.905
				7.564		8.905
	34.95	1.091	0.624		5.757	
		1.071	0.619		5.762	
	35.01			7.494		8.802
				7.495		8.804
	42.67	1.157	0.629		5.735	
	42.94			7.433		8.717
				7.433		8.717

Table 3. Experimental data from Chapter I, Table 4 of HANSSON (1972). The values of pK_1^* and pK_2^* are corrected to pH(SWS).

t/°C	S	pK_1	$pK_1 + pK_2$	pK_1^*	pK_2^*	t/°C	S	pK_1	$pK_1 + pK_2$	pK_1^*	pK_2^*
5	20	6.139	15.578	6.133	9.433	20	20	5.986	15.200	5.978	9.206
		6.127	15.571	6.121	9.438			5.994	15.221	5.986	9.219
		6.132	15.583	6.126	9.445		25	5.951	15.092	5.942	9.132
	25	6.101	15.492	6.094	9.384			5.951	15.096	5.942	9.136
		6.107	15.494	6.100	9.380		30	5.929	15.012	5.920	9.074
	30	6.084	15.404	6.077	9.313			5.931	15.017	5.922	9.077
		6.085	15.405	6.078	9.313		35	5.913	14.943	5.903	9.020
	35	6.069	15.323	6.061	9.246			5.911	14.947	5.901	9.026
		6.065	15.342	6.057	9.269		40	5.890	14.885	5.880	8.985
	40	6.049	15.280	6.041	9.223			5.902	14.891	5.892	8.979
		6.060	15.278	6.052	9.210						
10	20	6.082	15.449	6.075	9.360	25	20	5.933	15.066	5.924	9.124
		6.088	15.467	6.081	9.372			5.939	15.067	5.930	9.119
	25	6.057	15.355	6.050	9.291		25	5.902	14.969	5.893	9.058
		6.055	15.358	6.048	9.296			5.905	14.976	5.896	9.062
	30	6.022	15.259	6.014	9.229		30	5.883	14.883	5.873	8.990
		6.032	15.277	6.024	9.237			5.884	14.884	5.874	8.990
	35	6.012	15.208	6.004	9.188			5.885	14.891	5.875	8.996
		6.015	15.218	6.007	9.195		35	5.862	14.815	5.852	8.943
	40	6.002	15.159	5.994	9.149			5.860	14.817	5.850	8.947
		6.003	15.162	5.995	9.150			5.857	14.796	5.847	8.929
		5.999	15.162	5.990	9.155		40	5.854	14.764	5.844	8.900
		5.994	15.142	5.986	9.139			5.855	14.759	5.845	8.894
15	20	6.019	15.308	6.012	9.282	30	20	5.881	14.903	5.872	9.013
		6.012	15.295	6.005	9.276			5.877	14.904	5.868	9.018
		6.024	15.321	6.017	9.290		25	5.856	14.839	5.846	8.973
	25	5.996	15.225	5.988	9.221			5.869	14.858	5.859	8.979
		5.991	15.221	5.983	9.222		30	5.838	14.762	5.828	8.914
	30	5.970	15.135	5.961	9.156			5.834	14.757	5.824	8.913
		5.972	15.141	5.963	9.160		35	5.805	14.668	5.794	8.852
		5.973	15.144	5.964	9.162			5.807	14.667	5.796	8.849
	35	5.953	15.060	5.944	9.098		40	5.800	14.620	5.789	8.809
		5.940	15.042	5.931	9.093			5.790	14.584	5.779	8.783
		5.954	15.058	5.945	9.095						
		5.948	15.052	5.939	9.095						
	40	5.945	15.020	5.936	9.066						
		5.936	14.988	5.927	9.043						
		5.939	14.998	5.930	9.050						

Table 4. Interpolating equations† for the corrected equilibrium constants of HANSSON and of MEHRBACH *et al.* The terms in parentheses represent the precision ($2s_f$).

Hansson's data (residuals plotted in Fig. 2).

$$\mathrm{p}K_1^* = 851.4/T + 3.237 - 0.0106S + 0.000105S^2 \qquad (\pm 0.013)$$

$$\mathrm{p}K_2^* = -3885.4/T + 125.844 - 18.141 \ln T - 0.0192S + 0.000116S^2 \qquad (\pm 0.017)$$

Mehrbach's data (residuals plotted in Fig. 2).

$$\mathrm{p}K_1^* = 3670.7/T - 62.008 + 9.7944 \ln T - 0.0118S + 0.000116S^2 \qquad (\pm 0.011)$$

$$\mathrm{p}K_2^* = 1394.7/T + 4.777 - 0.0184S + 0.000118S^2 \qquad (\pm 0.020)$$

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† The form of the equation was selected from a number of possibilities using the minimum s_f as a criterion. The number of terms is justified using an F-test.

Table 5. Interpolating equations† for the combined data of HANSSON and of MEHRBACH *et al.* The terms in parentheses represent the the precision ($2s_f$).

Equations for the salinity range $20 \leq S \leq 40$ (residuals plotted in Fig. 3).

$$\mathrm{p}K_1^* = 845.0/T + 3.248 - 0.0098S + 0.000087S^2 \qquad (\pm 0.017)$$

$$\mathrm{p}K_2^* = 1377.3/T + 4.824 - 0.0185S + 0.000122S^2 \qquad (\pm 0.026)$$

Equations for the salinity range $0 \leq S \leq 40$ (residuals plotted in Fig. 4).

$$\mathrm{p}K_1^* - \mathrm{p}K_1^{\circ} = (-840.39/T + 19.894 - 3.0189 \ln T)\, S^{1/2} + 0.0068S \qquad (\pm 0.017)$$

$$\mathrm{p}K_2^* - \mathrm{p}K_2^{\circ} = (-690.59/T + 17.176 - 2.6719 \ln T)\, S^{1/2} + 0.0217S \qquad (\pm 0.032)$$

where pK_i° represents the value at $S = 0$: (MILLERO, 1979)

$$\mathrm{p}K_1^{\circ} = 6320.81/T - 126.3405 + 19.568 \ln T$$

$$\mathrm{p}K_2^{\circ} = 5143.69/T - 90.1833 + 14.613 \ln T$$

In order to allow users to confirm the values they obtain using these equations the following rounded values are presented for $T = 298.15$ K (25 °C) and $S = 35$.

For the equations for the salinity range $20 \leq S \leq 40$.

$$\mathrm{p}K_1^* = 5.8457 \;;\quad \mathrm{p}K_2^* = 8.9454$$

For the equations for the salinity range $0 \leq S \leq 40$.

$$\mathrm{p}K_1^* = 5.8477 \;;\quad \mathrm{p}K_2^* = 8.9358$$

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† The form of the equation was selected from a number of possibilities using the minimum s_f as a criterion. The number of terms is justified using an F-test.

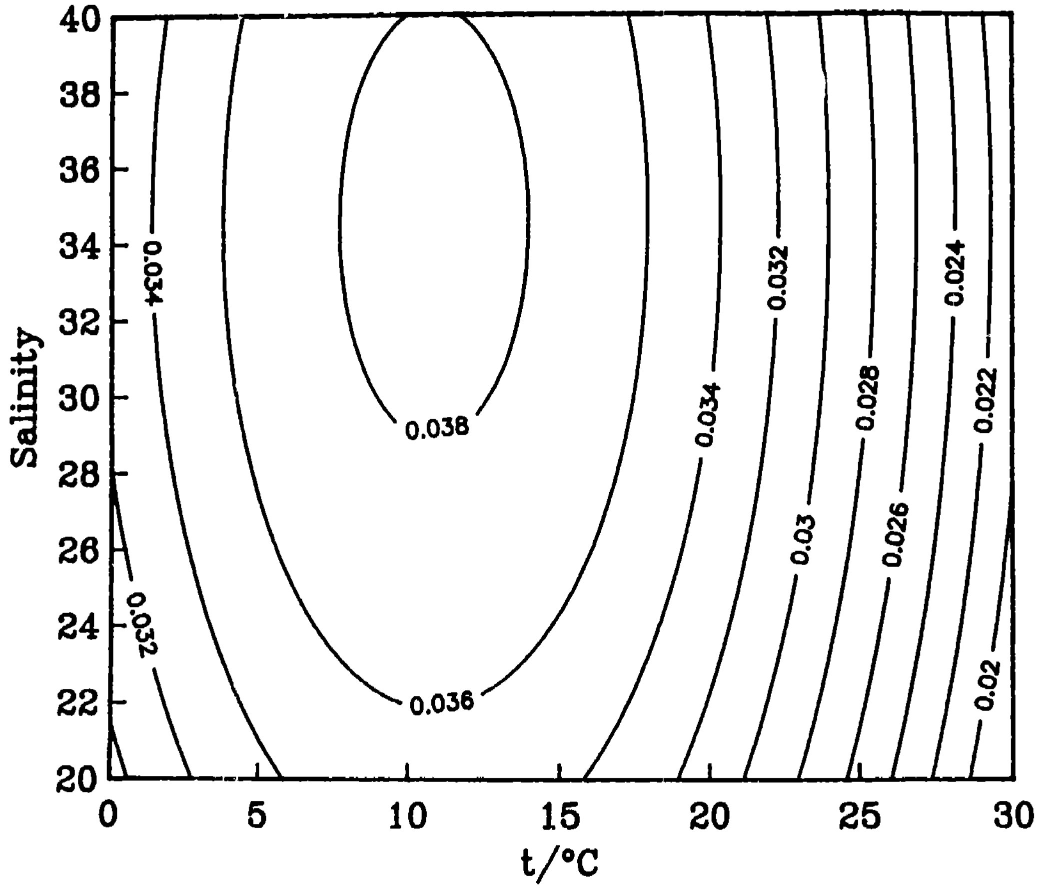

Fig. 1 Contour plot of p*K*(Hansson) – p*K*(Mehrbach *et al.*) as a function of temperature and salinity. The interpolating equations used to generate this plot are given in Table 1.

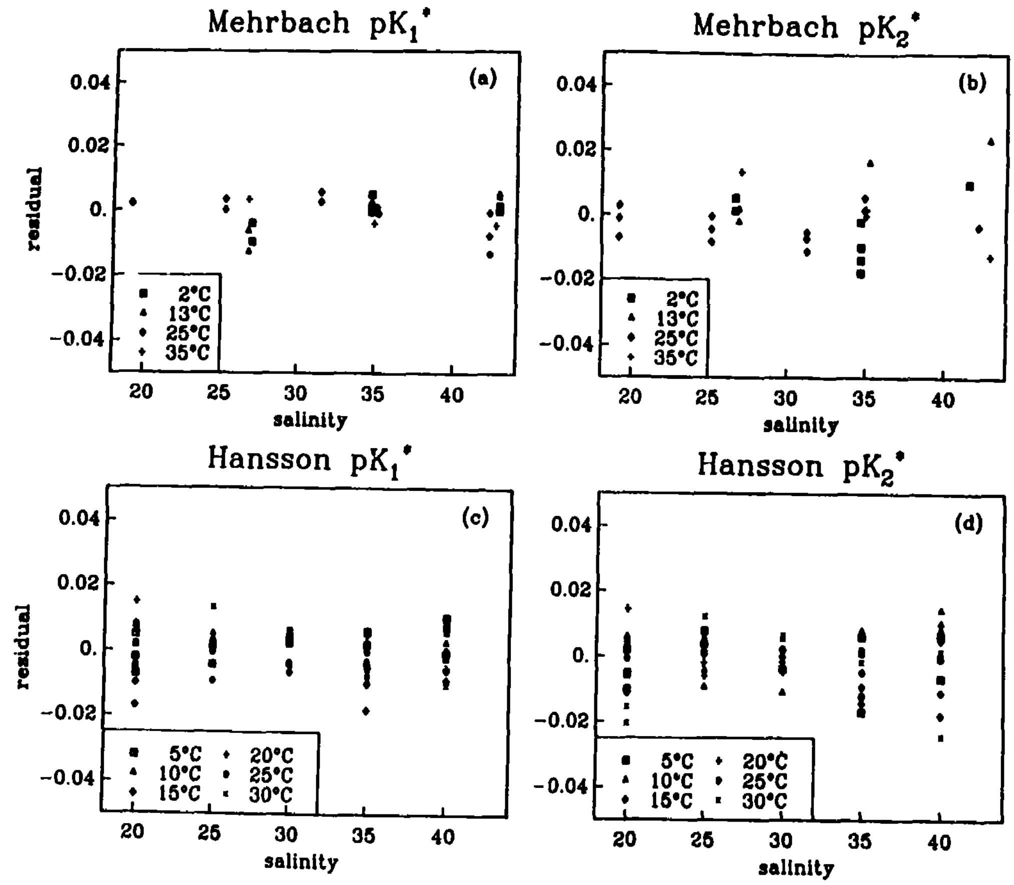

Fig. 2 Residuals resulting from fitting the corrected pK_i^* data to the equations of Table 4

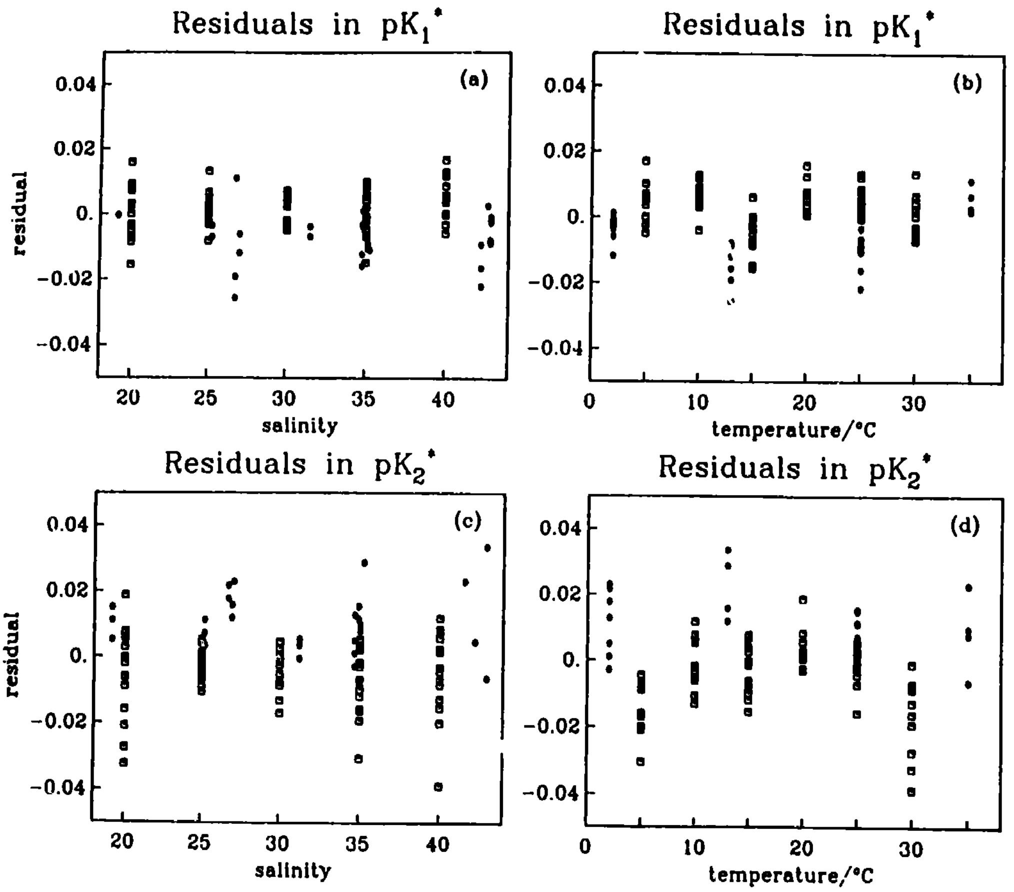

Fig. 3 Residuals resulting from fitting the pooled data set to the equations for the salinity range $20 \leq S \leq 40$ (Table 5). (•) Mehrbach's data, (▫) Hansson's data.

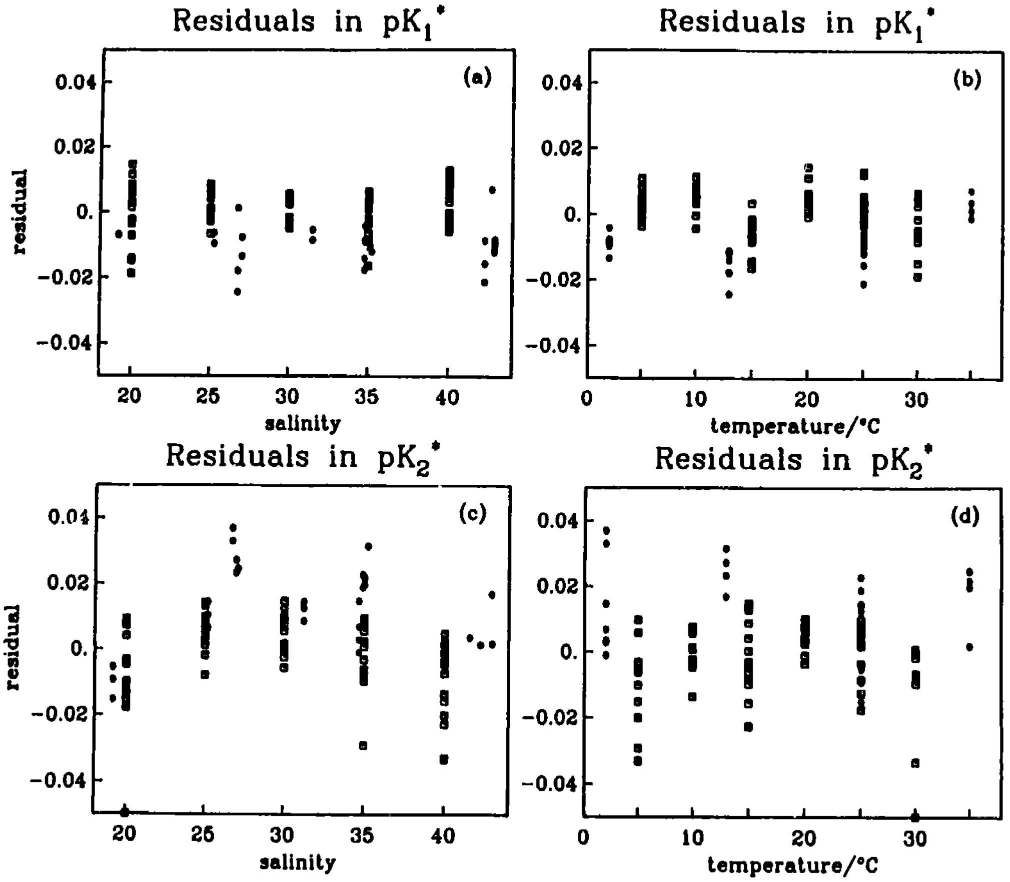

Fig. 4 Residuals resulting from fitting the values of $pK_i^* - pK_i^\circ$ so as to provide interpolating equations for the salinity range $0 \leq S \leq 40$ (Table 5). (•) Mehrbach's data, (□) Hansson's data.

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