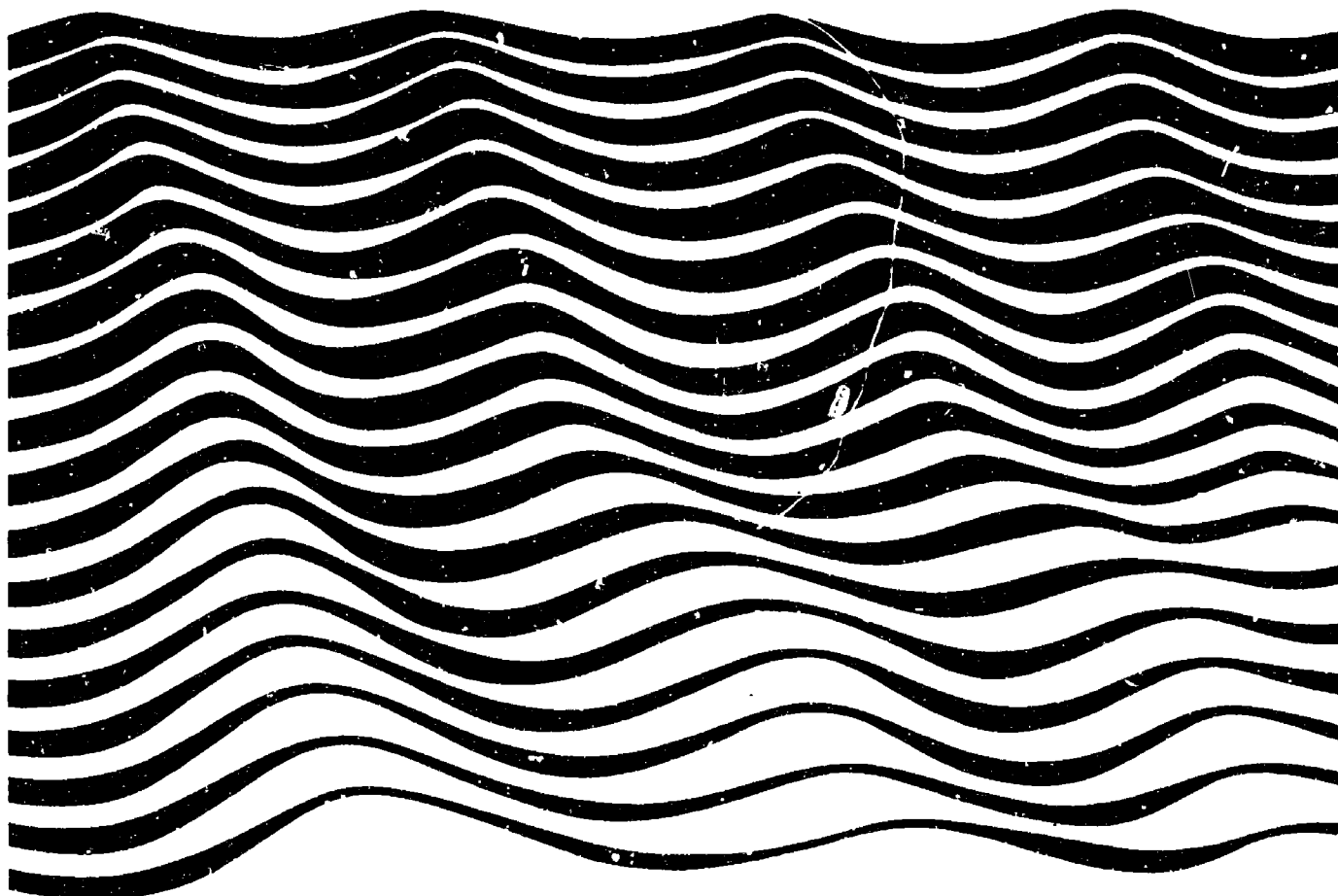


Unesco technical papers
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Ninth report of the joint panel on oceanographic tables and standards

Unesco, Paris
11-13 September 1978

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19	Marine Science Teaching at the University Level. Report of the Unesco Workshop on University Curricula - <i>Available in French, Spanish and Arabic</i>	1974	—
20	Ichthyoplankton. Report of the CICAR Ichthyoplankton Workshop <i>Also published in Spanish</i>	1975	—
21	An intercomparison of open sea tidal pressure sensors. Report of SCOR Working Group 27: "Tides of the open sea"	1975	WG 27
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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
25	Marine science programme for the Red Sea: Recommendations of the workshop held in Bremerhaven, FRG, 22-23 October 1974; sponsored by the Deutsche Forschungsgemeinschaft and Unesco	1976	—
26	Marine sciences in the Gulf area - Report of a consultative meeting, Paris, 11-14 November 1975	1976	—
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 janvier 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 developments in oceanographic research and marine science affairs.

Many of the texts published within the series result from research activities of the Scientific Committee on Oceanic Research (SCOR) and are submitted to Unesco for printing following final approval by SCOR of the relevant working group report.

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I. INTRODUCTION

The meeting was opened by the Chairman, N. Fofonoff, in the Miollis Building of Unesco. Dr. D. Krause, Chief of the Division of Marine Sciences, welcomed the Panel members to Unesco.

The following members of the Panel attended the meeting:

Dr. N. P. Fofonoff (Chairman)	Woods Hole Oceanographic Institution Woods Hole MA 02543, USA	IAPSO
Dr. F. Culkin	Institute of Oceanographic Sciences Wormley, Godalming Surrey GU8 5UB, U. K.	ICES
Dr. J. Gieskes	Scripps Institution of Oceanography Mail Code A-015 La Jolla CA 92093, USA	SCOR
Prof. Dr. K. Grasshoff	Institut für Meereskunde Düsternbrooker Weg 20 D-2300 Kiel F.R.G.	SCOR
Prof. Dr. W. Kroebe	Institut für Angewandte Physik Olshausenstrasse 40-60 D-2300 Kiel F.R.G.	IAPSO
Dr. E. L. Lewis	Frozen Sea Research Group Institute of Ocean Sciences P. O. Box 6000 9860 W. Saanich Road Sidney, B. C. V8L 3B2, Canada	SCOR
Mr. M. Menaché	Institut Océanographique 195, rue Saint Jacques 75005 Paris, France	Unesco
Prof. F. Millero	Rosenstiel School of Marine and Atmospheric Sciences University of Miami 4600 Rickenbacker Causeway Miami FL 33149, USA	Unesco
Dr. A. Poisson	Laboratoire d'Océanographie Physique Université P. et M. Curie Tour 24, 4 place Jussieu 75230 Paris, Cedex 05, France	ICES

Mr. C. K. Ross

Atlantic Oceanographic Laboratory
Bedford Institute of Oceanography
P. O. Box 1006
Dartmouth, N. S. B2Y 4A2, Canada ICES

The following experts and/or representatives were also present during the meeting:

Dr. T. M. Dauphinee
National Research Council
Montreal Road
Ottawa 7, Ontario K1A 0R6, Canada

Dr. G. Girard
Bureau International des Poids et Mesures
Pavillon de Breteuil
F-92310 Sèvres, France

Panel members G. N. Ivanov-Frânzkevich and O. Mamayev were unable to attend.

The following agenda was adopted:

1. Opening of the meeting
2. Adoption of the agenda
3. The definition of the Practical Salinity Scale (1978)
 - a) the relationship between salinity of standard seawater and R_{15}
 - b) the temperature dependence of conductivity ratios R_T, R_p
 - c) the potassium chloride conductivity standard for seawater
 - d) the salinity-conductivity tables
4. The new equation of state for seawater
5. The carbon dioxide system in seawater
6. The specific heat and freezing point and sound speed measurements in seawater
7. Use of SI units in physical oceanography
8. Future activities of W.G. 10
9. Election of a new Chairman

II. REPORT BY AGENDA ITEM

1. The definition of a Practical Salinity Scale (1978)

a) The relationship between Salinity of Standard Seawater and R_{15}

Dr. E. L. Lewis reported on the work of the subgroup on the Practical Salinity Scale (1978) formed at the 9th meeting of the Panel held in Woods Hole (May 1977).

The measurements of conductivity ratio R_{15} at 15°C ($R_{15} = C(S,15,0)/C(35,15,0)$, where $C(S,T,P)$ is electrical conductivity at salinity S , temperature T and pressure P) on samples of weight diluted and evaporated Standard Seawater made independently by Dauphinee and Poisson were fitted by a polynomial of fifth order in $\sqrt{R_{15}}$ with a standard deviation from the experimental data of 0.0005 ‰ (see Annex 1, recommendation 1/1978). A criterion used in the choice of the form of the equation was to minimize the number of terms needed in the fit. Polynomial expansions in R_{15} require at least 10 terms to provide a fit of equal precision. Fofonoff pointed out that an alternative fit to the experimental data could be made using an expansion in $(R_{15} - 1)$ that took into account the constraint that a salinity of 35 ‰ corresponds to R_{15} equal to unity. He conceded that the resulting formula was not simpler in form because high-order powers (> 12) of $(R_{15} - 1)$ are necessary to simulate the behaviour for low values of R_{15} . Although the introduction of $\sqrt{R_{15}}$ represents additional computation, its use is compatible with most pocket calculators and presents no difficulties for larger computers. It should be stressed that use of $\sqrt{R_{15}}$ has no physical implications. Almost all of Dauphinee's data and Poisson's data fit the equation to ± 0.001 ‰. The combined data sets are fitted very well except at higher salinities ($S > 35$ ‰) where slightly larger deviations (± 0.0015 ‰) occur.

The empirical formula is restricted to salinities > 1 ‰ because the equation does not reduce to zero and contains a singularity in the derivatives at $R_{15} = 0$. Although measurements were made at salinities less than 1 ‰, the behaviour was not considered by Dauphinee to be sufficiently well explored to give a definitive relationship. Furthermore, a more precise fit at very low salinities to the present data would unnecessarily complicate the relationship for $S > 1$ ‰.

Fofonoff brought to the attention of the Panel a recent manuscript by Brewer (1978) estimating the effect of dissolved CO_2 on conductivity. The accumulated effect of fossil fuel usage is estimated to change salinity at a marginally detectable level (~ 0.001 ‰ increase) and will continue as a slight trend in salinity values based on conductivity.

b) A remarkable simplification has been achieved in representing the temperature dependence of S by separation of the temperature variation as a multiplicative factor from the dependence on R_T ($R_T = C(S,T,0)/C(35,T,0)$) (Annex 1, recommendation 1/1978)). This separation is considered fortuitous and not expected from physical chemistry. The resultant fit to the recent data sets (unpublished) provided by Dauphinee and Poisson yields a standard deviation of 0.0007 ‰. The agreement with the independent measurements of temperature dependence of R_T by Bradshaw and Schleicher (unpublished) is within 0.001 ‰. Thus, the close agreement among the three data sets obtained on three different types of apparatus provides a solid basis for the formula recommended in Annex 1, recommendation 1/1978.

c) Temperature dependence of the conductivity of Standard Seawater, r_T

Following the published work of Dauphinee and Klein (1977) on $r_T = C(35,T,0)/C(35,15,0)$, further measurements (unpublished) have been made independently by Dauphinee and Klein and by Bradshaw and Schleicher respectively which are in extremely good agreement. All their points have been fitted to equation (3) (Annex 1, recommendation 1/1978) with a standard deviation of 8.27×10^{-6} (~ 0.0005 ‰ salinity) with a maximum deviation of about 2 standard deviations. This relationship is essential for the reduction of in situ CTD data.

Fofonoff raised the question of an inverse formula to compute conductivity ratios R_{15} and R_T given salinity and temperature. Dauphinee stated that the inverse relationship presented difficulties. They were able to obtain a representation of the inverse relationship using a rational function regression (a quotient of polynomials). A simple inverse formula was not found. After further discussion, the Panel concluded that numerical inversion using simple iterative methods should be used. This procedure would avoid introducing two formulae that could not be made exact inverses of one another.

Fofonoff reported that Bradshaw and Schleicher have finished work on the experimental setup for measurements of effects of pressure on the electrical conductivity of seawater and that the experimental work on determining R_P has started ($R_P = C(S,T,P)/C(S,T,0)$) (unpublished). Runs will be made on standard seawater samples for salinities of 35, 22, 14 and 2 ‰ at approximately 5°C intervals from freezing point to 30°C and pressures near atmospheric to 1 000 bars at 200 bar intervals and back to low pressure to check for drift. Lewis pointed out that their previous measurements (Bradshaw and Schleicher, 1965) for salinities above 31 ‰ were of high quality based on comparisons with in situ measurements. The proposed run at 35 ‰ salinity is planned to check the new experiment against their previous results. The Panel stressed that the new formula for the pressure dependence must not have salinity variable but be an explicit function of in situ conductivity ratio, pressure and temperature.

The pressure dependence of the conductivity ratio R_p can be introduced as a multiplicative factor with a value of unity at atmospheric pressure. Its determination is thus separated from the 1 atmosphere equation and can be treated independently. A different scheme for factoring the conductivity ratios reviewed by Fofonoff at the 9th meeting in Woods Hole is not necessary because the new formula does not require explicit values of R_{15} to calculate salinity.

The practical salinity scale is defined by formulas in Annex 1, recommendation 1/1978 and is made consistent with the previous definition and with historical data by fixing the scale at 35 ‰ to coincide with the previous scale introduced in 1969 (Wooster et al. 1969).

Conversion formulae between the new scale and the previous scales need to be developed.

d) Potassium Chloride (KCl) standard

The new practical salinity scale is fixed at 35 ‰ salinity by reference to conductivity at 15°C of a potassium chloride solution containing a mass of 32.435 7 grams of KCl in a mass of 1 kilogram of solution. The value of 32.435 7 grams of KCl is based on independent measurements of Dauphinee and Poisson relative to standard seawater (batch P79) at 35 ‰.

Smith and Culkin (unpublished data) have made measurements of absolute conductivity on both standard seawater and KCl solutions. Their value for the KCl standard (32.433 grams per kg solution) differs significantly from those of Dauphinee and Poisson (unpublished data). Culkin reported that the Wormley equipment showed an electrode effect on switching from KCl solution to seawater and vice versa but stable and very reproducible results were obtained when the electrodes had been in contact with the appropriate solution for several days. In discussion of the different results it was concluded that a possible cause could be a small frequency dependence of the Wormley equipment. Dauphinee's measurements were made at zero frequency by exciting the bridge with a square wave signal, and those of Poisson were made at several frequencies (2 000, 2 500, 3 000 and 4 000 Hz) and extrapolated the resistance versus the inverse of frequency to zero, suggesting that frequency effects are not present in either set of results. The Wormley measurements were made at only one frequency (1 500 Hz) and it was decided that the frequency dependence of the Wormley equipment should be checked in an effort to resolve the discrepancy.

In further discussion, it was noted by Dauphinee that different batches of KCl contain varying amounts of water but yield the same conductivity after drying. The three investigators used KCl from the same manufacturer's batch for the determinations. Lewis pointed out that the procedure for preparing the standard KCl solution must be presented together with recommendation 1/1978 in Annex 1. Dauphinee, Culkin and

Poisson agreed to provide a description of the procedure (Annex 2). In addition to the concentration of KCl solution having the same conductivity at 15°C as Standard Seawater of chlorinity 19.374 0 ‰ (or salinity 35.000 0 ‰), a formula giving variations of conductivity ratio with KCl concentration in the neighborhood of this point is necessary for interpolation.

Subsequent to the meeting, Dauphinee submitted the following formulae for the dependence of conductivity ratio on concentration and temperature of the KCl solution to Standard Seawater at 35 ‰ salinity:

$$S_{KCl} = 32.4357 + 33.648 \Delta x_{15} + 0.397 \Delta x_{15}^2$$

$$X_{15} = \frac{C_{KCl}(S_{KCl}, 15, 0)}{C_{SW}(35, 15, 0)} - 1.0000$$

$$\text{range: } |\Delta x_{15}| < 0.03$$

where

S_{KCl} is grams KCl per kilogram solution;

C_{KCl} is the electrical conductivity of KCl solution at concentration

S_{KCl} at 15°C temperature atmospheric pressure;

C_{SW} the electrical conductivity of Standard Seawater at 35 ‰

salinity, 15°C temperature and atmospheric pressure;

and

$$\frac{C_{KCl}(32.4357, T, 0)}{C_{SW}(35, T, 0)} = 1 - 1.4640 \times 10^{-3}(T - 15) + 0.8969 \times 10^{-5}(T - 15)^2$$

$$\text{range: } 14-30^\circ\text{C}$$

$$\text{error: } \sim 0.2 \times 10^{-6}$$

The temperature variation of the ratio is based on measurements at six temperatures (15, 19, 21, 24, 27 and 30°C).

The Panel discussed procedures for communicating to oceanographers the results of investigations leading to the recommendations for a new practical salinity scale. In order to provide a wide distribution as well as a comprehensive description, three types of publication are needed: 1) a short notice announcing the practical salinity scale (1978) with references to the present Panel report and relevant papers in the literature to be published in several oceanographic journals; 2) detailed

descriptions of the methods used, the measurements obtained, the analysis procedures and results to be published, for example, as a Unesco technical report; and 3) papers in refereed journals summarizing the methods and results.

It is highly desirable that the Panel report and the notice to oceanographers be published about the same time so that reactions and comments can be obtained based on the more detailed descriptions of the recommendations contained in this report.

e) Salinity-conductivity ratio tables

After considerable discussion the Panel concluded that tables of salinity versus R_{15} should be prepared with the same resolution as the present Unesco tables together with tables of $\Delta_{15}(R_T, T) = R_{15} - R_T$ at coarser resolution to allow conversion from temperatures differing from 15°C.

Recommendations for preparation of the tables and their format are included in Annex 1, recommendation 4/1978.

Millero pointed out that all salinometers will have a linear offset when run at 24°C from the new equation and should be calibrated at least at two salinities. Lewis pointed out that this fact was noted in Lewis and Sudar (1972). Culkin commented that the Standard Seawater Service were still unable to provide low salinity standards for salinometer calibrations because all the ampoules supplied by the manufacturer were required for the 35 ‰ standard. Judging by the small number of enquiries received in recent years, however, there appears to be little demand for extra standards. Grasshoff suggested that a procedure be described for preparation of diluted standard samples so that these calibrations can be carried out more readily.

2. The new equation of state for seawater

At the Woods Hole meeting of the Panel in May 1977, five data sets were selected to construct the equations of state for seawater. These were the direct measurements of relative density by Millero, Gonzalez and Ward (1976) consisting of 115 points from 0.5 to 40 ‰ salinity and 0 to 40°C temperature; the high pressure specific volume values of Chen and Millero (1976) obtained with a magnetic float densitometer consisting of 486 points from 5 to 40 ‰ salinity, 0 to 40°C temperature and 100 to 1 000 bars pressure; the high pressure compression measurements by Bradshaw and Schleicher (1976) consisting of 72 points at 10°C from 0 to 40 ‰ salinity and 100 to 1 000 bars pressure; the high pressure thermal expansion data of Bradshaw and Schleicher (1970 and unpublished data) consisting of 612 points from 0 to 40 ‰ salinity, -4 to 30°C temperature and 8 to 1 000 bars pressure; and the specific volumes from sound speed from water by Chen, Fine and Millero (1977) and for seawater by Chen and Millero (1978) consisting of 810 points from 0 to 40°C temperature, 0 to 40 ‰ salinity and

0 to 1 000 bars pressure. The total of 2 023 data points were used by Millero to construct an equation of state in the secant bulk modulus form,

$$K = pv^0 / (v^0 - v^p)$$

where K is the bulk modulus. Solving for v^p ,

$$v^p = v^0 (1 - p/K)$$

where v^p and v^0 are specific volumes at applied pressure p and atmospheric pressure ($p = 0$) respectively.

Millero developed the formula in four parts. At atmospheric pressure the Biggs (1967) formula was adjusted to Miami distilled water used to dilute the seawater samples. The Millero, Gonzalez and Ward (1976) formula for the difference of seawater and pure water relative density at atmospheric density was converted to absolute density difference by multiplying the coefficient by $0.999\,974\text{ g cm}^{-3}$.

The pressure dependence of the secant bulk modulus K_w for pure water was obtained from the sound speed estimates of Chen, Fine and Millero (1976) and Bradshaw and Schleicher (1976). The data set of Bradshaw and Schleicher for seawater at high pressure was normalized by subtracting pure water specific volumes using a formula developed from their data for pure water compression and thermal expansion and by subtracting the corresponding difference at one atmosphere. The differences agreed with those obtained from the Chen and Millero high pressure data within $8 \times 10^{-6}\text{ cm}^3\text{ g}^{-1}$.

The standard deviation for the complete equation was $4.3 \times 10^{-6}\text{ cm}^3\text{ g}^{-1}$ for the pure water data and $9.0 \times 10^{-6}\text{ cm}^3\text{ g}^{-1}$ for the seawater data. This is within the range of precision established at the Grenoble meeting of the Panel in 1975.

By constructing the formula in four parts, adjustments to future measurements can be made on each part separately.

Millero has examined various orders of the coefficient polynomials in an effort to reduce the number of terms (19 for the 1 atmosphere equation and 26 for pressure dependence for a total of 45 terms). It does not seem likely that a significant reduction can be made for a full range equation without decreasing the precision of the formula.

The Panel considers Millero's work on the equation of state to be fundamental to oceanography and requests that the analysis as well as the data sets be published as a Unesco technical report.

Poisson reported a set of density measurements at 1 atmosphere recently completed on Standard Seawater using a Picker densitometer and a suspension balance system.

Polynomial formulae fitted separately to this set and the corresponding data set of Millero, Gonzalez and Ward exhibit significant differences in the oceanic range of salinity and temperature. A fit to the combined data set showed significant differences from the 1 atmosphere formula proposed by Millero at 35 ‰ salinity for higher temperatures. Although the Panel specifically recommended that other data sets need not be considered in developing the equation of state for seawater, the possibility of significant discrepancies in the seawater range, particularly at atmospheric pressure where greater precision is expected, could not be ignored. Poisson and Millero agreed to analyze the data sets further to determine if the differences could be attributed to the different weighting and fitting procedure used. If the differences persist, Millero suggested that a few additional measurements at the high temperature range at 35 ‰ salinity be made to resolve the discrepancies. If the measurements prove to be necessary, six months should be allowed for completion. Thus, the 1 atmosphere portion of the equation for seawater could not be accepted by the Panel at the present time. The remaining parts of the equation of state were adopted by the Panel and recommended in Annex 1, recommendation 2/1978.

3. The carbon dioxide system in seawater

A report (Annex 3) on the carbon dioxide system in seawater was presented by Gieskes to the Panel as requested at the Woods Hole Meeting. A discussion followed on the need to establish a subgroup of experts to examine the CO₂ system and to develop recommendations for future action, and brief mention of the present status and needs for future work was added to Annex 3.

4. The specific heat and freezing point of seawater

Millero noted that three sets of measurements of specific heat of seawater agree within 0.001 J g⁻¹ K⁻¹ which is sufficient for estimating adiabatic lapse rates but not for defining the enthalpy of seawater. There are no measurements of specific heat of seawater at high pressures to provide an independent check on the thermodynamic relationship

$$\frac{\partial C_p}{\partial P} = -T \frac{\partial^2 V}{\partial T^2}.$$
 However, measurements made on pure water do show good agree-

ment with the thermodynamic relationship. Millero felt that it was premature to make any recommendations concerning specific heat until more measurements were available.

Two studies of freezing point of seawater (Fujino, Lewis, Perkin 1974; Doherty and Kester 1974) agree within 0.002°C over the oceanographic range of salinities. Millero and Leung (1976) fitted an equation of the Debye-Hückel limiting law type to their free energy data determined from

the freezing point measurements. The equation is given in the 8th report of the Joint Panel (1978). The Panel agreed with Millero's recommendation that the formula given in Annex 6 of the 8th report be adopted for general use. The formula for freezing point, which includes the pressure term, should be used in preference to earlier versions which have lower precision, particularly that of Miyake (1939).

A report on sound speed measurements in seawater is included in Annex 4.

5. Use of SI units in oceanography

The development of SI units for use in oceanography was reviewed by Menaché who recalled that the Panel, at its last meeting, had requested that he provide additional explanation to propositions contained in SUN WG Paper No. 1, presented on behalf of the IAPSO working group on Symbols, Units and Nomenclature in physical oceanography of which he is chairman. As this explanation had been circulated to all Panel members, he hoped he could have the benefit of individual and group expertise on the proposed changes.

As all Panel members were not prepared to give detailed critique at the time, it was agreed that Menaché would provide an outline of relevant comments already received from many colleagues who had received SUN WG Paper No. 1 as well as certain proposed amendments. Interested Panel members would then forward their critique to Menaché in time for consideration at the final draft stage (January 1979).

The Panel did agree that the introduction and adoption of SI units and nomenclature was agreeable in principle and, indeed, perhaps inevitable, although the Panel did not feel that they could take a position at this stage as to endorsing the proposed SI units. A number of specific objections were noted to the proposed changes, and unanimous opinion was voiced that the definition of salinity must agree with the recommendations of the Panel. It was recommended (recommendation 4/1978) that future oceanographic tables issued by Unesco follow ISO guidelines regarding the grouping of digits about the decimal sign.

6. Future activities of WG 10

Considerable work remains to be carried out on physical and chemical properties of seawater. The major task of developing an acceptable and precise salinity scale and a new equation of state has occupied the attention of the Panel for many years. This task is nearing completion and the effort can be directed to other properties for review and standardization.

The Panel and activities of its members have encouraged a number of studies on seawater properties that may have not been done otherwise. The members felt that the Panel should continue to exist but that membership be reviewed by sponsoring organizations.

7. Election of the Chairman

J. Gieskes was elected chairman.

III. ANNEXES

Annex 1

Recommendation 1/1978

Practical Salinity Scale (1978) for seawater

We recommend that:

(1) Absolute salinity, symbol S_A , be defined as the ratio of mass of dissolved material in seawater to the mass of solution. In practice this quantity cannot be measured directly and a practical salinity, symbol S , shall be defined for reporting oceanographic observations.

(2) The practical salinity scale be based on a Standard Seawater having a conductivity ratio of unity at 15°C to a potassium chloride (KCl) solution containing a mass of 32.4357 grams of KCl in a mass of 1 kilogram of solution. To provide continuity with previous scales the Standard water selected to give the unity ratio was from the North Atlantic and had a chlorinity of 19.374 0 ‰. This defined the 35.000 0 ‰ salinity point on the new scale. The method of preparing the standard KCl solution is described in Annex 2.

(3) The practical salinity scale be defined as a function of the conductivity ratios, measured at 15°C (R_{15}), of samples prepared from Standard Seawater of the 35 ‰ standard after having been diluted by weight with distilled water and evaporated, according to the following equation:

$$S(\text{‰}) = a_0 + a_1 R_{15}^{1/2} + a_2 R_{15} + a_3 R_{15}^{3/2} + a_4 R_{15}^2 + a_5 R_{15}^{5/2}$$

$$a_0 = 0.008 \text{ 0}$$

$$a_1 = -0.169 \text{ 2}$$

$$a_2 = 25.385 \text{ 1}$$

$$a_3 = 14.094 \text{ 1}$$

$$a_4 = -7.026 \text{ 1}$$

$$a_5 = 2.708 \text{ 1}$$

$$\sum a_i = 35.000 \text{ 0}$$

$$1 \text{ ‰} \leq S \leq 42 \text{ ‰}$$

$$R_{15} = \frac{C(S, 15, 0)}{C(35, 15, 0)}$$

(1)

All seawater samples having the same value of R_{15} will thus have the same practical salinity.

(4) Practical salinity be related to absolute salinity by an equation

$$S_A = a + bS$$

where the parameters a and b are dependent on the ionic ratios of the sample. For Standard Seawater $a = 0$ and $b = 1.0049 \pm 0.0003$, any improvement in these values shall serve to change S_A and not S . It is probable that " a " may be put equal to zero with negligible error for nearly all oceanic water masses.

(5) The following equation to convert observed values of conductivity ratios R_T at temperature T to practical salinities by measuring the variation of conductivity ratio with temperature of samples of known practical salinity with a standard deviation of 0.0007 ‰ salinity:

$$S(^{\circ}/\text{‰}) = a_0 + a_1 R_T^{1/2} + a_2 R_T + a_3 R_T^{3/2} + a_4 R_T^2 + a_5 R_T^{5/2} \\ + \frac{(T - 15)}{1 + A(T - 15)} [b_0 + b_1 R_T^{1/2} + b_2 R_T + b_3 R_T^{3/2} + b_4 R_T^2 + b_5 R_T^{5/2}]$$

$a_0 = 0.0080$	$b_0 = 0.0005$	$A = 0.0162$
$a_1 = -0.1692$	$b_1 = -0.0056$	
$a_2 = 25.3851$	$b_2 = -0.0066$	(2)
$a_3 = 14.0941$	$b_3 = -0.0375$	
$a_4 = -7.0261$	$b_4 = 0.0636$	
$a_5 = 2.7081$	$b_5 = -0.0144$	
$\Sigma a_i = 35.0000$	$\Sigma b_i = 0.0000$	

$-2^{\circ}\text{C} \leq T \leq 35^{\circ}\text{C}$ (IPTS 1968)

$$R_T = \frac{C(S, T, 0)}{C(35, T, 0)}$$

(6) Temperature effects on the conductivity of Standard Seawater which have been measured and fitted with a standard deviation of 8.27×10^{-6} , be as follows:

$$r_T = \frac{C(35, T, 0)}{C(35, 15, 0)}$$

$$= c_0 + c_1 T + c_2 T^2 + c_3 T^3 + c_4 T^4$$

$$c_0 = 6.766\ 12 \times 10^{-1}$$

$$c_1 = 2.005\ 57 \times 10^{-2}$$

$$c_2 = 1.105\ 58 \times 10^{-4}$$

$$c_3 = -7.043\ 73 \times 10^{-7}$$

$$c_4 = 1.119\ 40 \times 10^{-9}$$

$$r_T(15) - 1 \approx 2.46 \times 10^{-6}$$

$$-2^\circ \leq T \leq 35^\circ\text{C} \quad (\text{IPTS 1968})$$

(7) The effect of pressure on the conductivity ratio be expressed as a function of in situ temperature, pressure and conductivity ratio, as soon as the new experiments started by Bradshaw and Schleicher are completed. The data of Bradshaw and Schleicher (1965) for this parameter are acceptable within the ranges quoted (0 - 10 000 decibars, 0° - 25°C and 31 - 39 ‰/‰).

(8) As soon as possible each ampoule of Standard Seawater be labelled with its value of R_{15} , as well as chlorinity. The relationship

$$S = 1.806\ 55\ C_l$$

commonly used should no longer have any definitive value. Consequently, any changes noted in the constant will not affect either salinity or chlorinity.

(9) Assuming endorsement of these proposals by the sponsoring organizations, revision of the practical salinity scale not be entertained except under most extraordinary circumstances. The equation (1) will then define the practical salinity scale and not be subject to changes in data fitting procedures or changes in the chemical properties of Standard Seawater.

(10) Following endorsement of the proposals, new oceanographic tables for use with bench salinometers be produced at the present intervals in the present format. In addition, a table covering the complete range $1\text{‰} < S < 42\text{‰}$ at intervals of R_{15} of 0.001 should be published with $\Delta_{15}(R_T, T) = R_{15} - R_T$ available as a function of temperature at 1°C intervals. It is suggested that the duplication of a computer print out be used to avoid typographical errors. A date of conversion to the practical salinity scale will need to be established by the sponsoring agencies and all national oceanographic data centers strongly encouraged to archive and use this scale.

(11) The data base for the practical salinity definition equation (1) and equation (2) be published as soon as possible by the responsible investigators, Dauphinee, Poisson and Culkin.

High Pressure Equation of State for Seawater

A Working Group on the equation of state of seawater consisting of Bradshaw, Chen, Millero and Schleicher have prepared a comprehensive paper on the data treatment of the high pressure PVT data of water and seawater (see Millero, Chen, Bradshaw and Schleicher, unpublished data).

We recommend that:

1. The form of the equation of state is:

$$K^p = pv^0 / (v^0 - v^p) = K^0 + Ap + Bp^2$$

where K^p is the secant bulk modulus at an applied pressure p in bars (10^5 Pa), K^0 is the secant bulk modulus at 1 atm ($p = 0$) and A and B are adjustable parameters. The salinity (S in parts per thousand) dependence of K^0 , A , and B are given by:

$$K^0 = K_W^0 + a S + b S^{3/2}$$

$$A = A_W + c S + d S^{3/2}$$

$$B = B_W + e S$$

The subscript W refers to pure water. The temperature dependence of the coefficients K_W^0 , A_W and B_W determined from the sound speed data of Chen and Millero (1978) and the direct measurements of water by Bradshaw and Schleicher (in preparation) are given by:

$$K_W^0 = 19\,652.21 + 148.420\,6t - 2.327\,105t^2 + 1.360\,477 \times 10^{-2} t^3 - 5.155\,288 \times 10^{-5} t^4$$

$$A_W = 3.239\,908 + 1.437\,13 \times 10^{-3} t + 1.160\,92 \times 10^{-4} t^2 - 5.779\,05 \times 10^{-7} t^3$$

$$B_W = 8.509\,35 \times 10^{-5} - 6.122\,93 \times 10^{-6} t + 5.278\,7 \times 10^{-8} t^2$$

where t is in $^{\circ}\text{C}$ (IPTS 1968) and S in the new (1978) practical salinity scale.

The standard deviation of the pure water equation of state is $4.33 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v_W^p (the specific volume of water at an applied pressure p). The coefficients a , b , c , d , and e are given by:

$$a = 54.674\,6 - 0.603\,459 t + 1.099\,87 \times 10^{-2} t - 6.167\,0 \times 10^{-5} t$$

$$b = 7.944 \times 10^{-2} + 1.6483 \times 10^{-2} t - 5.3009 \times 10^{-4} t^2$$

$$c = 2.2838 \times 10^{-3} - 1.0981 \times 10^{-5} t - 1.6078 \times 10^{-6} t^2$$

$$d = 1.91075 \times 10^{-4}$$

$$e = -9.9348 \times 10^{-7} + 2.0816 \times 10^{-8} t + 9.1697 \times 10^{-10} t^2$$

The standard deviation of the seawater equation of state is $9.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P . The standard deviation is $4.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ for Bradshaw and Schleicher's data (1970, 1976), $9.6 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ for the direct measurements by Chen and Millero (1976) and $5.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ for the sound speed data of Chen and Millero (1978).

2. After a 1 atm equation of state is adopted for v_0 and the full equation of state of seawater is endorsed by the sponsoring organizations, new tables of the PVT properties of seawater be prepared. All oceanographic centers should be encouraged to use the new equation of state.

Recommendation 3/1978

Examination of 1 atm Equation of State of Seawater

In the last report of the Panel the 1 atm (10^5 Pa) equation of state of Millero, Gonzalez and Ward (1976) was adopted as part of the equation of state of seawater. Recent measurements of Poisson and Brunet (unpublished) on the density of seawater disagrees with this equation at high temperatures (See Table I).

We recommend that:

1. A working group of Millero and Poisson look into these differences. Measurements with the suspension balance in the two laboratories at 25, 30, 35 and 40°C on 35‰ Standard Seawater should clear up this discrepancy. (The differences between the two sets of data at a given temperature as a function of salinity (See Table II) appear to be in excellent agreement, with a maximum difference of $4 \times 10^{-6} \text{ g cm}^{-3}$ in density.)

Table I
Comparisons of the Measured Densities (g cm^{-3}) of seawater (d)
relative to pure water (d_0) of Poisson and Brunet at
 $s = 35\%$ and the 1976 Equation of Millero et al.

<u>Temp.</u> °C	<u>Measured</u> ($d-d_0$) 10^3	<u>Calculated</u> ($d-d_0$) 10^3	<u>10^6</u>
1.169°C	28.133	28.127	6
1.176	28.128	28.126	2
1.195	28.124	28.124	0
2.373	27.988	27.991	- 3
7.120	27.509	27.508	1
7.120	27.509	27.508	1
10.423	27.219	27.219	0
10.498	27.218	27.213	5
15.682	26.829	26.828	1
15.682	26.829	26.828	1
19.695	26.574	26.577	- 3
19.715	26.574	26.576	- 2
24.235	26.329	26.336	- 7
25.360	26.276	26.283	- 7
25.597	26.261	26.273	-12
30.000	26.075	26.083	- 8
30.000	26.075	26.083	- 8

Table II
Comparisons of the Density Differences of Poisson
and Millero et al. at various temperatures
after adjustment to zero at 35 ‰ salinity

$\times 10^{-6} \text{ gm/cm}^3$

Temp	5‰	10‰	15‰	20‰	25‰	30‰	35‰	40‰
0	1	0	-1	-1	-2	-1	0	2
5	4	4	3	3	2	1	0	-2
10	4	4	4	4	3	2	0	-1
15	1	1	0	0	0	0	0	1
20	0	0	-1	-2	-2	-2	0	3
25	-1	-1	-3	-4	-4	-3	0	4
30	-2	-1	-3	-3	-3	-2	0	4

overall average = $2.1 \times 10^{-6} \text{ gm/cm}^3$

2. Since the two data sets are internally consistent, both be used to derive a new 1 atm equation of state for seawater (after the discrepancies are cleared up).

3. This new 1 atm equation of state be combined with the high pressure equation of state for seawater and be adopted by the sponsoring organizations.

Recommendation 4/1978

Format for Numbers

We recommend that:

1. In accordance with standard usage suggested by the 9th Conférence Générale des Poids et Mesures (1948, Resolution 7), the International Organization for Standardization (International Standard ISO 31/0-1974 (E), p. 11) and by several International Scientific Unions (e.g. IUPAC, Royal Society), to facilitate the reading of numbers with many digits, these may be grouped in threes about the decimal sign, but no comma or point should be used except for the decimal sign.

2. The Division of Marine Sciences of Unesco apply the above rule to publication of future Oceanographic Tables.

Annex 2

Dr. T. M. Dauphinee, Dr. F. Culkin and Dr. A. Poisson

Preparation of Potassium Chloride (KCl) Standard

The solutions used in the determination of the KCl electrical conductivity equivalent of Standard Seawater were prepared by 3 laboratories using variations of the following procedures.

Making up a standard KCl solution of precisely known concentration involves three basic steps:

- a) preparation of dry, pure KCl in a form suitable for weighing;
- b) introduction of a precisely known amount of the dried KCl into a preweighed mixing flask; and
- c) introduction of an appropriate amount of distilled water into the flask, and determining the weight of the total amount of solution.

Suitable procedures for these steps follow:

a) Experiments have confirmed that "Suprapur" Merck KCl is sufficiently reproducible and can be dried completely by (1) air drying at a temperature of at least 250°C for at least 1 day, or (2) fusion and resolidification. Process (2) requires the least amount of time and is recommended. The fused KCl can be obtained in a form suitable for weighing by performing the fusion in a platinum crucible and pouring the melted KCl onto a cleaned and polished stainless steel plate 3-5 mm thick. The KCl will solidify, without sticking to the plate, into pieces which can be placed in the weighing boat with clean forceps (the film of condensed KCl powder on the plate should not be used).

b) The recommended method of weighing the KCl is to use a small boat with a pouring spout. The quantity of KCl poured into the mixing flask is determined by before-and-after weighing of the boat and therefore no error is incurred if some KCl sticks to it.

c) The amount of distilled water required to give the desired concentration is then added to the flask and stirred to dissolve the KCl and give a uniform solution. The total mass of solution is then determined from either (1) final flask and solution mass - empty flask mass, or (2) final flask and solution mass - (mass of flask + KCl) + (mass of KCl). The concentration is then calculated from the ratio of the mass of KCl alone to the mass of solution and will normally be expressed in parts per thousand .

(⁰/oo) i.e. $\frac{\text{mass KCl}}{\text{mass solution}} \times 1000$. It should be emphasized that all

weights must be corrected as appropriate for air buoyancy, taking account of temperature, relative humidity both inside and outside the flask, barometric pressure and density of containers, KCl and KCl solution (note — the average density of unmixed KCl and H₂O is not the same as the density of the resultant uniform solution). Before using the solution it is necessary to ensure that any condensation on flask surfaces is remixed with the solution. The flask should be kept sealed to prevent evaporation. However some evaporation, if it does occur, can be allowed for by reweighing to determine the new total solution mass and recalculation of the new concentration, since the mass of KCl will not have changed.

An operational procedure has been to make up a primary solution as above of about 100-200 ‰ KCl. This solution is then used as a stock solution to make several solutions bracketing the desired value by dilution with distilled water. The appropriate amount of distilled water is driven by air pressure into a small-mouth, weighed measurement flask and weighed. Stock solution is then added in the same manner, mixed and weighed, and the new concentration calculated from the dilution ratio and the original concentration. (Note, the distilled water should be added first to saturate the air otherwise the stock solution will change concentration by evaporation before mixing takes place.)

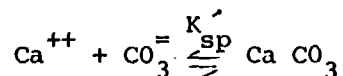
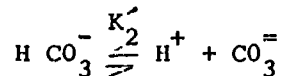
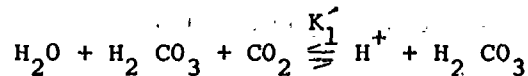
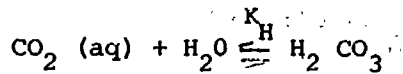
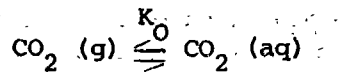
by Dr. J. Gieskes

Thermodynamics of the carbon dioxide system in seawater

During recent years the carbon dioxide system in seawater has received renewed attention, especially in view of the increasing concern regarding the fate of fossil fuel produced carbon dioxide in the ocean.

In order to study the distribution of carbon dioxide and its various dissolved species in the ocean, and in particular in order to monitor possible changes in concentration as a result of fossil fuel CO₂ input, special attention must be given to appropriate standardization of analytical methods. In addition, a detailed knowledge of the thermodynamics of carbon dioxide in seawater is required.

In principle the speciation and distribution of carbon dioxide in seawater is governed by the following equilibria:



The equilibrium constants for the above equations are functions of salinity, temperature and pressure, with the exception of K_H which is set equal to unity by the so called hydrate convention.

Prior to 1970, thermodynamic data on the above equilibrium constants were mainly based on information obtained by Buch and coworkers in Europe (Buch *et al.*, 1932) and Moberg and coworkers in the United States (Lyman, 1957). Additional work on pressure dependences was carried out by Pytkowicz and coworkers (Culberson and Pytkowicz, 1968). Much of this work was summarized by Edmond and Gieskes (1970) and by Gieskes (1974), who included new information on the solubility of carbon dioxide (K_O) of Murray and Riley (1971). Subsequent to this new sets of data on the thermodynamics of the carbon dioxide system have been obtained: dissociation constants of carbonic acid by Mehrbach *et al.*, (1973), dissociation constants of carbonic acid by Hansson (1973), and solubilities of calcite by Ingle (1975). Preliminary comparisons of these new data compared to those by previous workers have established small but significant discrepancies. This necessitates a revaluation of the thermodynamic information in order to obtain a more uniform set of equilibrium constants so that work by various workers will become comparable.

We propose the formation of a working party consisting of six persons with expertise in various areas of the carbon dioxide system. This group will be constituted to evaluate present knowledge of the carbon dioxide system and to propose:

- (i) appropriate analytical standards, and
- (ii) a "best" set of equilibrium constants recommended for use by workers in the CO_2 system.

Work should be concluded in a period of 12-18 months from date.

Annex 4

by Prof. W. Kroebel

Sound speed in seawater and its dependence on pressure is a basic parameter in oceanography. The best known tables have been given by Wilson (1960) and later by Del Grosso and others (1972). These authors used measuring equipment with small separations between the transducer and the receiver. This causes difficulties in the measurements because the phase planes do not have constant distances from one another so that the measured values must be corrected using a theoretical model of the acoustic field for the geometry of the transducer and the receiver. This correction was not applied by Wilson which resulted in deviations from true values of about 50 to 60 cm/sec at one atmosphere.

Deviations presumably also occur at higher pressures but are not accurately known. Del Grosso developed a sophisticated theory for the correction that has assumptions that are reasonable at atmospheric pressure but not at high pressures. For this reason, Kroebel and Mahrt (1975) investigated the sound speed using a method developed by Kroebel with large distances between transducer and receiver. At present, only measurements at one atmosphere have been made and agreement with Del Grosso and the best values of other authors is very good. The values given by Kroebel and Mahrt are probably the most precise available today.

It is now necessary to transfer the technique developed by Kroebel to high-pressure measurements. Our laboratory investigations are limited by the autoclave available. We have designed two different apparatuses, but these are not yet operational and we expect the first results in a few months. In addition, we have prepared an apparatus which has already been used for in situ measurements at depth where temperature and salinity are nearly homogeneous. The data from the first ocean test was disappointing and we have since improved our equipment to use on the next cruise. We hope to obtain precise results on sound speed at high pressures.

The effort described above to obtain standard values for sound speed in seawater refer to "pure" seawater. Our experience indicates that sound speed in real seawater depends not only on pressure, temperature and salinity but also on suspended particles. For this reason, we have always calculated the difference Δv between measured sound speed, v_{means} and calculated sound speed, v_{calc} , i.e. $\Delta v = v_{\text{means}} - v_{\text{calc}}$ using formulae of Wilson and Del Grosso. We have obtained many measurements that indicate that Δv can, in special cases, be a new parameter of importance. The results are now being collected and interpreted for publication.

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