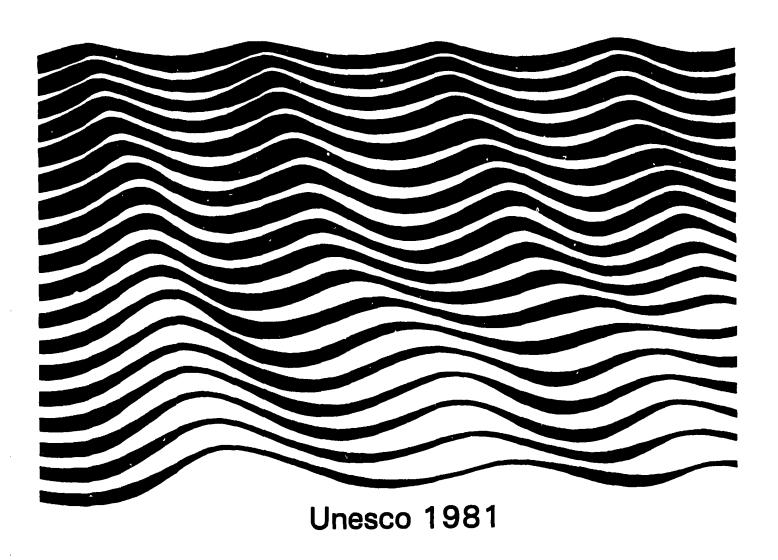
# Tenth report of the joint panel on oceanographic tables and standards

Sidney, B.C., Canada 1-5 September 1980 sponsored by Unesco, ICES, SCOR, IAPSO



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| graphy. Report of working group sponsored<br>by the Unesco Scientific Co-operation Bure<br>Europe and the Division of Marine Sciences   | i<br>au for    | •          | 33  | published in 1981  Coastal lagoon research, present and future.  Proceedings of a seminar, Duke University,   | 1981 | -          |
| An intercomparison of some current meter<br>Report on an experiment carried out from  |                |            |     | August 1978. (Unesco, IABO). To be published in English   | 1981 | -          |
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# I. TENTH REPORT OF THE

# JOINT PANEL CN OCEANOGRAPHIC TABLES AND STANDARDS

Sidney, B.C., Canada, 1 - 5 September 1980

# 1. Opening of the Meeting

The meeting was opened by the Chairman, J. M. Gieskes, after having been convened in the Institute of Ocean Sciences in Sidney, British Columbia. Dr. E. L. Lewis, largely responsible for the organization of the meeting, welcomed the membership and guests to the Institute of Ocean Sciences. Dr. Selim Morcos (Unesco) also welcomed the Panel and expressed his best wishes for a fruitful meeting.

The following members of the Panel attended the meeting:

| Dr. J. M. Gieskes<br>(Chairman) | Scripps Institution of Oceanography,<br>La Jolla, CA 92093,<br>U. S. A.   | SCOR   |
|---------------------------------|---|--------|
| Dr. F. Culkin                   | Institute of Oceanographic Sciences,<br>Wormley, Godalming,<br>Surrey GU8 5UB,<br>U. K.   | ICES   |
| Dr. N. P. Fofonoff              | Woods Hole Oceanographic Institution,<br>Woods Hole, MA 02543,<br>U. S. A.  | IAPSO  |
| Prof. W. Kroebel                | Institut für Angewandte Physik,<br>Olshausenstrasse 40-60,<br>D-2300 Kiel,<br>F. R. GERMANY.  | IAPSO  |
| Dr. E. L. Lewis                 | Frozen Sea Research Group,<br>Institute of Ocean Sciences,<br>P.O. Box 6000,<br>9860 W. Saanich Road,<br>Sidney, B.C. V8L 4B2,<br>CANADA. | SCOR   |
| Dr. O. I. Mamayev               | Department of Oceanology, Moscow State University, 117234 Moscow, U. S. S. R.   | UNESCO |
| Mr. M. Ménaché                  | 7, rue de Reims,<br>75013 Paris,<br>FRANCE.   | UNESCO |

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UNESCO

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Bedford Institute of Oceanography,

P. O. Box 1006,

Dartmouth, N. S. B2Y 4A2,

CANADA.

**ICES** 

In addition, the following invited experts participated in the meeting:

Mr. J. Crease, Institute of Oceanographic Sciences, Wormley, Godalming, Surrey GU8 5UB, U. K.

Dr. T. M. Dauphinee, National Research Council, Montreal Road, Ottawa 7, Ontario KlA OR6, CANADA.

Dr. F. Fisher, Scripps Institution of Oceanography, La Jolla, CA 92093, U. S. A.

Dr. Selim Morcos, Division of Marine Sciences, Unesco, 7 Place de Fontenoy, 75700 Paris, FRANCE.

Mr. R. Perkin, Institute of Ocean Sciences, P. O. Box 6000, 9860 W. Saanich Road, Sidney, B. C. V&L 4B2, CANADA.

Panel member Prof. K. Grasshoff was unable to attend.

# 2. Adoption of the Agenda

The following agenda was adopted:

- 1. Opening of the Meeting
- 2. Adoption of the Agenda
- Overview of Previous Work and Present Task of the JPOTS
- 4. Conductivity and Salinity Definition
  - 4.1 Definition of the Practical Salinity Scale, 1978
  - 4.2 Standard Seawater Service
- 5. International Equation of State of Seawater
  - 5.1 One Atmosphere Equation (Millero, Poisson)
  - 5.2 Combined Equation
- 6. Unesco Reports and Publications
- 7. Other Definitions/Equations
  - 7.1 Oxygen Solubility
  - 7.2 Freezing Point
  - 7.3 Entropy of Seawater
  - 7.4 Speed of Sound
- 8. Future Activities of the JPOTS
- 9. Membership of the Joint Panel

# 3. Overview of previous work and present task of the JPOTS

The chairman pointed out that the present meeting of the Panel was called in order to draft a document on the "Practical Salinity Scale and the International Equation of State of Seawater". This work did occupy the bulk of the time of the meeting. Whereas during the meeting of the Panel in Paris in 1978 (UNESCO, 1979) there were still apparent discrepances in the data for the one atmosphere equation of state, these differences have been resolved. Data reports on the background data for the definition of practical salinity as well as for the International Equation of State will shortly be available in the form of Unesco Technical Papers.

In addition to the drafting of the above mentioned document, the meeting was intended to briefly review the Panel's previous recommendations on various physical and chemical properties of seawater, as well as to outline further areas where attention should be focussed on more precise data or formulations of such properties.

# 4. Conductivity and Salinity Definition

# 4.1 Definition of the Practical Salinity Scale, 1978

The new practical salinity is based on two sets of measurements (a total of 152 data points) of conductivity ratio of standard seawater solutions obtained by weight dilutions with distilled water or by evaporation. A precisely specified solution of potassium chloride has been chosen as a reproducible electrical conductivity standard. All the considerations which led the JPOTS to adopt the new practical salinity are reported in detail in the Unesco Technical Papers in Marine Science (UNESCO 1981, a).

Though during the Meeting of the Panel in Paris, 1978 (UNESCO, 1979) the new definition of practical salinity was adopted, some additional discussions on this topic were held during this meeting in order to further refine the definition and the algorithm for the practical salinity, which are now presented in Annex 1 on "The Practical Salinity Scale, 1978 and the International Equation of State of Seawater, 1980".

In particular, the numerical values to be assigned to the practical salinity were considered. Though the Panel realizes that absolute salinity in terms of SI units should be reported, for instance, as 0.035 23 or 35.23 x 10<sup>-3</sup>, the practical salinity can be most conveniently expressed as 35.23 rather than 0.035 23, thus yielding values 1000 times larger than salinities based on previous scales (c.f. Annex 1). A major reason for this decision was that the numerical values of practical salinity would be similar to the numerical values of previous salinity data, when expressed in \(^{\textstyle 0}\)oo.

The Panel unanimously passed the following recommendation:

### Recommendation No. 1

For reasons of simplification, the Joint Panel on Oceanographic Tables and Standards, during its meeting held at the Institute of Ocean Sciences in Sidney, B. C., Canada, from September 1 to 5, 1980, considers it more advantageous that the values of practical salinity be expressed by numbers one thousand times larger than those used in previous definitions. Thus in the new scale, which has been defined, the value of a practical salinity will be written, for instance, as 34.527 in place of 34.527°/oo or 0.034 527 which would have been obtained under previous usage.

The Joint Panel on Oceanographic Tables and Standards submits this rule for adoption by its sponsor organizations and requests that these organizations recommend the strict use of this concept in the future.

After some further discussion, the definition as presented in Annex 1 was accepted.

# 4.2 Standard Seawater Service

Standard seawater ( $S=\underline{ca}$  35, P series) will be calibrated in  $K_{15}$  before the end of 1981. The value of  $K_{15}$  will be labelled on the ampoules. The chlorinity which will also be included on the label should be regarded as a separate independent variable for describing the properties of seawater. As salinometers are calibrated at a single point and often have linear offsets, a low salinity standard ( $S=\underline{ca}$  30, L series) will be made available by the Standard Seawater Service before the end of 1981. This standard will also be calibrated in  $K_{15}$  and chlorinity (c.f. Annex 1).

# International Equation of State of Seawater, 1980

# 5.1 One Atmosphere Equation

At the Panel meeting held in Woods Hole in May 1977 (UNESCO, 1978), the one atmosphere equation of state of Millero, Gonzalez and Ward (1976) was suggested for use as the basis of a new equation of state in replacement of the earlier equation of Knudsen, Forch and Sörenson (1902). At the Paris meeting of the Panel in September 1978 (UNESCO, 1979), Poisson reported on a set of density measurements at one atmosphere which exhibited significant differences in the oceanic range of salinity and temperature from the set of data of Millero, Gonzalez and Ward (1976). A working group consisting of Millero and Poisson looked into these differences and prepared a comprehensive paper on the data treatment (Millero and Poisson, 1981, a). During the meeting, Dr. F. Millero presented his efforts, together with Dr. A. Poisson, to resolve these small differences which have now been overcome. The two sets of data (a total of 467 data points) were used to calculate the one atmosphere international equation of state recommended by the Panel (Annex 1). All the basic data and data treatment are reported in the Unesco Technical Papers in Marine Science, No. 38 (Millero and Poisson, 1981, b, in Unesco, 1981, b).

# 5.2 Combined Equation

At the Woods Hole meeting of the Panel in May 1977, five sets of data (a total of 2023 data points) were selected to construct the high pressure equation of state (UNESCO, 1978). A working group, consisting of Millero, Chen, Bradshaw and Schleicher, have prepared a comprehensive paper on the data treatment (Millero, Chen, Bradshaw and Schleicher, 1981) and the equation which they developed was recommended by the Panel in 1978 (UNESCO, 1979). This equation is presented in Annex 1. All the basic data and data treatment are reported in the Unesco Technical Papers in Marine Science, No. 38 (Millero, Chen, Bradshaw and Schleicher, 1981, in UNESCO, 1981, b).

# 6. Unesco Reports and Publications

The publication of the background data reports on which Annex 1 is based, as well as future tables, was discussed and the following recommendation was passed unanimously:

# Recommendation No. 2

The Joint Panel on Oceanographic Tables and Standards, meeting in Sidney, B. C., Canada, 1-5 September 1980,

Having adopted the new definition of the Practical Salinity Scale, 1978 and the International Equation of State of Seawater 1980, and recommended their use in future oceanographic work,

Being aware of the importance of communicating, as soon as possible, to the scientific community, the background and details of the research work involved, as well as the formulae, procedures and tables required for the application of the new definition of salinity and equation of state,

# Recommends to Unesco:

- (1) The publication of future volumes of the International Oceanographic Tables comprising the following:
  - a) Conductivity ratio conversion to Practical Salinity, 1978
  - b) Derived properties from International Equation of State of Seawater, 1980
- (2) The printing of the following published and unpublished papers on the Practical Salinity Scale, 1978, in the series Unesco Technical Papers in Marine Science:
  - Special Issue on the Practical Salinity Scale 1978, <u>IEEE Journal</u> of Oceanic Engineering, Vol. OE-5, No. 1, January 1980.
  - Poisson (1981), Conductivity Ratio Measurement of Diluted or Concentrated Standard Seawater and KCl Solution used to establish the new Practical Salinity Scale 1978 (unpublished report).

- Lewis and Perkin, (1981), the Practical Salinity Scale 1978: Conversion of Existing Data, Deep Sea Research, Vol. 28A, p. 307-328.
- (3) The printing of the following published papers and unpublished data reports on the equation of state of seawater in the series Unesco Technical Papers in Marine Science:
  - Millero and Poisson, 1981, International One Atmosphere Equation of State of Seawater, Deep Sea Research, Vol. 28A, p.625-629.
  - Summary of Data Treatment of One Atmosphere Equation of State, by Millero and Poisson (unpublished report).
  - Millero, Chen, Bradshaw and Schleicher, 1980, A New High Pressure Equation of State for Seawater, Deep Sea Research, Vol. 27Λ, p. 255-264.
  - Millero, Chen, Bradshaw and Schleicher, 1981, Summary of Data Treatment for the International High Pressure Equation of State (unpublished report).

The publishers of the above journals are requested to give their approval to the reproduction of these papers by Unesco.

# 7. Other Definitions/Equations

A discussion was held on issues covered in Agenda Item 7.

# 7.1 Oxygen Solubility

Though the International Oceanographic Tables, Vol. 2 (UNESCO, 1973) for the solubility of oxygen are essentially correct when the solubility is expressed in terms of  ${\rm cm}^3({\rm S},{\rm t},{\rm p})$  of real oxygen (per  ${\rm dm}^3$  or per kg of seawater), the tables in terms of molar concentrations (i.e.,  ${\rm \mu gat}~{\rm kg}^{-1}$  or  ${\rm \mu gat}~{\rm dm}^{-3}$ ) are not correct, because oxygen was considered as an ideal gas in the conversions in the UNESCO Tables. Hence, the real solubilities in terms of  ${\rm \mu gat}~{\rm kg}^{-1}$  are  ${\rm higher}$  by a factor of 1.000 98 or about 0.1%. This problem is discussed in Annex 2 of this report (R.F. Weiss, personal communication). In addition, it should be noted that preferably solubilities should be expressed in  ${\rm \mu mol}~{\rm kg}^{-1}$  of oxygen, rather than  ${\rm \mu gat}~{\rm kg}^{-1}$  of oxygen.

The Panel reconfirms its proposals on the following items :

# 7.2 Freezing Point

The Panel supports the equation developed by F. Millero as published in Unesco (1978).

# 7.3 Entropy of Seawater

The Panel noted the work of Millero and Leung (1976) on this matter. As little time was available and extensive data sets were lacking, the Panel could not discuss this matter in detail.

# 7.4 Speed of Sound

Prof. Kroebel presented briefly the state of his work on speed of sound in his laboratory. He confirmed that more precise data will be available in the near future (approx. 2 years).

# 8. Future Activities of the JPOTS

The following items were considered appropriate problems for consideration by the Panel in the future, i.e.:

- (1) Refractive index
- (2) Speed of sound
- (3) Heat capacity
- (4) Entropy
- (5) Adiabatic lapse rate

In addition to the above items, the Panel will consider the thermodynamic information necessary for calculations in the oceanic  $CO_2$  -  $CaCO_3$  system. A working party has already been constituted (Drs. Gieskes, Millero, Poisson, Pytkowicz, Skirrow, Dyrssen, Bates) for these purposes, and we propose a meeting on this subject by this group (plus, perhaps, a Japanese and Soviet representative) in September 1981.

# 9. Membership of the Joint Panel

The Panel proposed that the Panel Membership be reconstituted after the acceptance of its work on the definition of practical salinity and the International Equation of State of Seawater. The new membership should then represent the further interests and mandates of the Panel, i.e., items mentioned under item 8 of this report. This requires a membership not only including chemists, but also physicists/physical oceanographers. This matter will be discussed during the April 1981 SCOR meeting.

The Panel adjourned on September 4; a preliminary report was written on September 5 and subsequently checked by the membership.

### II. ANNEXES

### ANNEX 1

### The Practical Salinity Scale 1978

# and the International Equation of State of Seawater 1980

### Introduction

During the past 15 years, the UNESCO/ICES/SCOR/IAPSO Joint Panel on Oceanographic Tables and Standards has concerned itself with the precise definition of the equation of state of seawater as well as with the specification of salinity in relation to the electrical conductivity of seawater.

A new equation of state was considered desirable because recently acquired data indicated slight discrepancies with the Knudsen-Ekman's equation of state of seawater (Grasshoff, 1976). Whilst there is a systematic difference of order of 8.7 x  $10^{-6}$  cm<sup>3</sup> g<sup>-1</sup> in the Knudsen's equation for atmospheric pressure, this difference increases to 33 x  $10^{-6}$  cm<sup>3</sup> g<sup>-1</sup> at 500 bar and 89 x  $10^{-6}$  cm<sup>3</sup> g<sup>-1</sup> at 1000 bar pressure in Ekman's equation for elevated pressures (Grasshoff, 1976).

A new salinity scale was considered necessary in order that all oceanographers using conductivity temperature depth instruments be able to report their observations in a consistent manner. The existing International Tables (UNESCO, 1971), giving salinity as a function of conductivity ratio, do not go below 10°C which makes them unsuited for use in the majority of CTD applications. Salinity calculations have therefore been based on the data of Brown and Allentoft (1966) or a combination of these data with the International Tables. The two data sets are incompatible because they are:

- 1. derived from experiments on seawaters that did and did not vary in ionic composition as a function of salinity;
- 2. based on different "definitions" of salinity. In one case, a constant times chlorinity was used; in the other, the weight ratio obtained by diluting/evaporating a 35°/oo seawater with distilled water.

  35°/oo water from any ocean was defined in turn as having a conductivity ratio of unity with standard Copenhagen water.

In addition, errors in the data have been detected in the vicinity of  $0^{\circ}$ C. CTD data reduction equations produced in various attempts to resolve these conflicts yield salinities differing by up to  $0.005^{\circ}$ /oo for the same input in the oceanic range and up to  $0.02^{\circ}$ /oo in coastal waters. With in situ experimental resolutions of  $\pm 0.002^{\circ}$ /oo salinity available, it is essential that the existing algorithms be replaced by a single equation and that the chlorinity-salinity-conductivity ratio ambiguity which exists when ionic ratios change, be resolved (Lewis, 1980).

During the course of the work of the Joint Panel (UNESCO, 1976, 1978), it became clear that there was a need for a reproducible electrical conductivity standard. A precisely specified solution of potassium chloride was chosen as this standard (Dauphinee, 1980). A concentration of potassium chloride was taken that would yield a conductivity ratio of unity at 15°C with respect to a North Atlantic seawater of a salinity of 35°/00 on the old salinity scale (equivalent to a chlorinity of 19.3740°/00) so as to ensure continuity at that salinity with the previous scale. Whereas the existing salinity scale was based on a conductivity-chlorinity relation using natural seawater, the new scale is different in that the standard seawater used was diluted by weight with distilled water or evaporated to obtain other salinity values. This procedure was followed to ensure the constancy of composition of this seawater over the salinity range of interest. The salinities obtained on this new scale will henceforth be referred to as practical salinities and will be reported as dimensionless quantities.

In the following we present:

- (a) The new definition of practical salinity;
- (b) The algorithms necessary for the calculation of practical salinity from the conductivity ratio at all temperatures and pressures over the range of oceanographic interest;
- (c) The International Equation of State of Seawater as a function of practical salinity, temperature and pressure.

### Definition of the Practical Salinity Scale, 1978

- 1. Absolute salinity, symbol  $S_A$  is defined as the ratio of mass of dissolved material in seawater to the mass of seawater. In practice, this quantity cannot be measured directly and a practical salinity is defined for reporting oceanographic observations.
- 2. The practical salinity, symbol S, of a sample of seawater, is defined in terms of the ratio  $K_{15}$  of the electrical conductivity of the seawater sample at the temperature of  $15^{\circ}\text{C}$  and the pressure of one standard atmosphere, to that of a potassium chloride (KCl) solution, in which the mass fraction of KCl is  $32.4356 \times 10^{-3}$ , at the same temperature and pressure. The  $K_{15}$  value exactly equal to 1 corresponds, by definition, to a practical salinity exactly equal to 35. The practical salinity is defined in terms of the ratio  $K_{15}$  by the following equation:

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

 $a_0 = 0.0080$   $a_1 = -0.1692$   $a_2 = 25.3851$   $a_3 = 14.0941$   $a_4 = -7.0261$   $a_5 = 2.7081$   $\Sigma a_1 = 35.0000$   $2 \le S \le 42$ 

### Supplementary Statement

As a consequence of this definition any oceanic water having a precisely known conductivity ratio of near unity at 15°C with the KCl solution is a secondary standard for routine calibration of oceanographic instruments. All seawaters having the same conductivity ratio have the same practical salinity. Chlorinity is to be regarded as a separate, independent variable in describing the properties of seawater.

It should be noted that the practical salinity values are 1000 times the values of the salinity of the same samples of seawater obtained on the previous scales. For instance, a sample of seawater having a salinity of  $0.035\ 12\ (i.e.,\ 35.12^{\circ}/oo)$  will have a practical salinity of 35.12.

# The Algorithm for Practical Salinity

If  $R_t$  is the ratio of the conductivity of seawater, at temperature t, to the conductivity of seawater of practical salinity 35 at the same temperature (both at a pressure of 1 standard atmosphere), then  $R_{15}$  will have the same value as  $K_{15}$  and may, therefore, be used to calculate practical salinity in equation 1. Since all practical salinity measurements are carried out in reference to the conductivity of standard seawater (corrected to S=35), it is the quantity  $R_t$  which will be available for salinity calculations.  $R_t$  is normally obtained directly by laboratory salinometers, but in situ measurements usually produce the quantity  $R_t$ , the ratio of the in situ conductivity to the standard conductivity at S=35,  $t=15^{\circ}C$ , p=0 (where  $P_t$  is the pressure above one standard atmosphere).  $P_t$  is factored into three parts, i.e.,

$$R = R_{p} r_{t} R_{t} \tag{2}$$

 $R_p$  is the ratio of the <u>in situ</u> conductivity to the conductivity of the same sample at the same temperature but at p=0;  $r_t$  is the ratio of the conductivity of reference seawater, having a practical salinity of 35, at temperature t, to its conductivity at  $t=15^{\circ}C$ . A knowledge of  $R_p$  and  $r_t$  allows the calculation of  $R_t$  from the <u>in situ</u> results, i.e.,

$$R_{t} = \frac{R}{R_{p}r_{t}}$$
 (3)

It has been found that  $R_p,\ r_t$  and  $R_t$  can be expressed as functions of the numerical values of the in situ parameters, R, t and p, when t is expressed in  $^{\circ}C$  and p in bars (105Pa), as follows

$$R_{p} = 1 + \frac{p(e_{1} + e_{2}p + e_{3}p^{2})}{1 + d_{1}t + d_{2}t^{2} + (d_{3} + d_{4}t)R}$$
(4)

where

$$e_1 = 2.070 \times 10^{-4}$$
 $d_1 = 3.426 \times 10^{-2}$ 
 $e_2 = -6.370 \times 10^{-8}$ 
 $d_2 = 4.464 \times 10^{-4}$ 
 $d_3 = 4.215 \times 10^{-1}$ 
 $d_4 = -3.107 \times 0^{-3}$ 

and

$$r_t = c_0 + c_1 t + c_2 t^2 + c_3 t^3 + c_4 t^4$$
 (5)

where

$$c_0 = 0.676 609 7$$
 $c_1 = 2.005 64 \times 10^{-2}$ 
 $c_2 = 1.104 259 \times 10^{-4}$ 
 $c_3 = -6.9698 \times 10^{-7}$ 
 $c_4 = 1.0031 \times 10^{-9}$ 

The effect of the relatively small differences between  $R_{\text{t}}$  and  $R_{15}$  at a given salinity can be accounted for by adding a correction,  $\Delta S_{\text{t}}$  to the practical salinity calculated by substitution of  $R_{\text{t}}$  for  $K_{15}$  in equation 1. The practical salinity, therefore, may be computed with the equation

$$S = a_0 + a_1 R_t^{1/2} + a_2 R_t + a_3 R_t^{3/2} + a_4 R_t^2 + a_5 R_t^{5/2} + \Delta S$$
 (6)

where

$$\Delta s = \frac{(t-15)}{1+k(t-15)} (b_0 + b_1 R_t^{1/2} + b_2 R_t + b_3 R_t^{3/2} + b_4 R_t^2 + b_5 R_t^{5/2})$$

with the constants  $\mathbf{a}_{\mathbf{t}}$  defined in equation 1 and

$$b_0 = 0.0005$$

$$b_1 = -0.0056$$

$$b_2 = -0.0066$$

$$b_3 = -0.0375$$

$$b_4 = 0.0636$$

$$b_5 = -0.0144$$

$$\Sigma b_1 = 0.0000$$

The equations 4, 5 and 6 are valid over the ranges of temperature  $(-2 \text{ to } 35^{\circ}\text{C})$ , pressure (0 to 1000 bars), and practical salinity (2-42) in the world ocean (Perkin and Lewis, 1980).

For laboratory salinometers the calculation of practical salinity requires only equation 6. For calculations based on  $\underline{in}$   $\underline{situ}$  measurements, one must compute  $R_p$  and  $r_t$  from equations 4 and 5 respectively, and then compute  $R_t$  from equation 3. Practical salinity can then be computed from equation 6.

The following values are provided for checking the correct use of the above equations.

| R    | t(°C) | p(bars) | Rp          | r <sub>t</sub> | R <sub>t</sub> | S          |
|------|-------|---------|-------------|----------------|----------------|------------|
| 1    | 15    | 0       | 1.000 000 0 | 1.000 000 0    | 1.000 000 0    | 35.000 000 |
| 1.2  | 20    | 200     | 1.016 942 9 | 1.116 492 7    | 1.056 887 5    | 37.245 628 |
| 0.65 | 5     | 150     | 1.020 486 4 | 0.779 565 85   | 0.817 058 85   | 27.995 347 |

# The International Equation of State of Seawater, 1980

A new equation of state of seawater diluted with pure water or concentrated by evaporation has been determined to be used with the practical salinity scale (Millero, Chen, Bradshaw and Schleicher, 1980; Millero and Poisson, 1981,a). This equation is more precise than the currently used equations (Knudsen, Forch and Sörensen, 1902; Ekman, 1908; Cox, McCartney and Culkin, 1970) and covers a wider range of temperature and pressure. Data reports describing the details of the fitting procedure are available (Millero, Chen, Bradshaw and Schleicher, 1981; Millero and Poisson, 1981,b in Unesco, 1981,b).

The density  $(\rho, kg m^{-3})$  of seawater as a function of practical salinity (S), temperature (t, C) and applied or gauge pressure  $(\rho, C)$  is given by :

$$\rho(S,t,p) = \rho(S,t,0)/\{1-p/K(S,t,p)\}$$
 (7)

where K(S,t,p) is the secant bulk modulus. The specific volume ( $v=1/\rho$ ,  $m^3kg^{-1}$ ) of seawater can be obtained from

$$v(S,t,p) = v(S,t,0)\{1-p/K(S,t,p)\}$$
 (8)

The density of seawater at one standard atmosphere (p = 0) can be determined from

$$\rho(S,t,0) = \rho_w + (b_o + b_1 t + b_2 t^2 + b_3 t^3 + b_4 t^4) S + (c_o + c_1 t + c_2 t^2) S^{3/2} + d_o S^2$$
(9)

$$b_0 = 8.244 \ 93 \ x \ 10^{-1}$$
 $c_0 = -5.724 \ 66 \ x \ 10^{-3}$ 
 $b_1 = -4.0899 \ x \ 10^{-3}$ 
 $c_1 = 1.0227 \ x \ 10^{-4}$ 
 $c_2 = -1.6546 \ x \ 10^{-6}$ 
 $c_3 = -8.2467 \ x \ 10^{-7}$ 
 $c_4 = 5.3875 \ x \ 10^{-9}$ 
 $c_6 = 4.8314 \ x \ 10^{-4}$ 

The density of the reference pure water (SMOW) is given by (IUPAC, 1976)

$$\rho_{w} = a_{0} + a_{1}t + a_{2}t^{2} + a_{3}t^{3} + a_{4}t^{4} + a_{5}t^{5}$$
 (10)

where

$$a_0 = 999.842 594$$
 $a_1 = 6.793 952 \times 10^{-2}$ 
 $a_2 = -9.095 290 \times 10^{-3}$ 
 $a_3 = 1.001 685 \times 10^{-4}$ 
 $a_4 = -1.120 083 \times 10^{-6}$ 
 $a_5 = 6.536 332 \times 10^{-9}$ 

Should more reliable data for pure water become available in the future, equation 9 can be easily modified.

The secant bulk modulus (K) of seawater is given by

$$K(S,t,p) = K(S,t,0) + Ap + Bp^{2}$$
 (11)

where

$$K(S,t,0) = K_w + (f_0 + f_1t + f_2t^2 + f_3t^3)S + (g_0 + g_1t + g_2t^2)S^{3/2}$$
 (12)

$$f_0 = 54.6746$$
  $g_0 = 7.944 \times 10^{-2}$   
 $f_1 = -0.603 459$   $g_1 = 1.6483 \times 10^{-2}$   
 $f_2 = 1.099 87 \times 10^{-2}$   $g_2 = -5.3009 \times 10^{-4}$   
 $f_3 = -6.1670 \times 10^{-5}$ 

$$A = A_w + (i_o + i_1 t + i_2 t^2) S + j_o S^{3/2}$$
(13)

$$i_0 = 2.2838 \times 10^{-3}$$
  $j_0 = 1.910 \ 75 \times 10^{-4}$   
 $i_1 = -1.0981 \times 10^{-5}$   
 $i_2 = -1.6078 \times 10^{-6}$ 

$$B = B_{w} + (m_{o} + m_{1}t + m_{2}t^{2})S$$

$$m_{o} = -9.9348 \times 10^{-7}$$

$$m_{1} = 2.0816 \times 10^{-8}$$

$$m_{2} = 9.1697 \times 10^{-10}$$
(14)

The pure water terms of the secant bulk modulus are given by

$$K_{W} = e_{0} + e_{1}t + e_{2}t^{2} + e_{3}t^{3} + e_{4}t^{4}$$

$$e_{0} = 19 652.21$$

$$e_{1} = 148.4206$$

$$e_{2} = -2.327 105$$

$$e_{3} = 1.360 477 \times 10^{-2}$$

$$e_{4} = -5.155 288 \times 10^{-5}$$

$$A_{W} = h_{0} + h_{1}t + h_{2}t^{2} + h_{3}t^{3}$$

$$h_{0} = 3.239 908$$

$$h_{1} = 1.437 13 \times 10^{-3}$$

$$h_{2} = 1.160 92 \times 10^{-4}$$

$$h_{3} = -5.779 05 \times 10^{-7}$$

$$B_{W} = k_{0} + k_{1}t + k_{2}t^{2}$$

$$k_{0} = 8.509 35 \times 10^{-5}$$

$$k_{1} = -6.122 93 \times 10^{-6}$$

$$k_{2} = 5.2787 \times 10^{-8}$$
(15)

The International equation of state is valid for S=0 to 42; t=-2 to  $40^{\circ}C$ ; p=0 to 1000 bars.

The following values are provided for checking the correct use of the above equation. (Units :  $\rho$  in kg  $\text{m}^{-3}$  and K in bars)

| s  | t(°C) | p(bars) | ρ(S,t,p)    | K(S,t,p)      |  |  |
|----|-------|---------|-------------|---------------|--|--|
| 0  | 5     | 0       | 999.966 75  | 20 337.803 75 |  |  |
|    |       | 1000    | 1044.128 02 | 23 643.525 99 |  |  |
|    | 25    | 0       | 997.047 96  | 22 100.721 06 |  |  |
|    |       | 1000    | 1037.902 04 | 25 405.097 17 |  |  |
| 35 | 5     | 0       | 1027.675 47 | 22 185.933 58 |  |  |
|    |       | 1000    | 1069.489 14 | 25 577.498 19 |  |  |
|    | 25    | 0       | 1023.343 06 | 23 726.349 49 |  |  |
|    |       | 1000    | 1062,538 17 | 27 108.945 04 |  |  |

# Additional Remarks

## Limitation of the equations

The Practical Salinity Scale and the International Equation of State are meant for use in all oceanic waters. However, these equations should be used with caution in waters that have a chemical composition different from standard seawater. Salinities determined by laboratory salinometers operated at widely different temperatures may differ measurably due to possible changes in the temperature dependence of conductivity ratio with changing chemical composition. In such waters, densities derived with the methods described in this communication, i.e., based on practical salinity measurements and the International Equation of State, may deviate measurably from the true densities (Millero, Gonzales and Ward, 1976; Millero and Kremling, 1976; Millero, Gonzales, Brewer and Bradshaw, 1976; Millero, Forsht, Means, Gieskes and Kenyon, 1978; Poisson, Lebel and Brunet, 1980; Poisson, Lebel and Brunet, 1981). However, it is important to note that in water masses different in composition from standard seawater, the differences in densities derived by the new equations involve only very small errors (Lewis and Perkin, 1978). Corrections to the calculated densities can be made from direct density measurements or from calculations involving the use of partial molal volume data and conductivity data if the chemical composition is known (Brewer and Bradshaw, 1975; Poisson and Chanu, 1976 and 1980; Poisson, 1978; Millero, Forsht, Means, Gieskes and Kenyon, 1978; Poisson, Périé, Périé and Chemla, 1979).

# Conversion of existing data based on previous salinity scales

It should be emphasized that the use of the International Equation of State requires the use of the Practical Salinity Scale. Therefore, salinity based on previous scales must be converted to this new scale before it can be used in conjunction with this equation of state. Similarly, for comparison with new data, salinities based on previous scales must be converted to the Practical Salinity Scale. The conversion procedures are dealt with by Lewis and Perkin (1981).

# Practical Salinity Standards

Standard Seawater (S = ca 35, P series)

Following the adoption of the Practical Salinity Scale, 1978 and the associated equations, standard seawater (S =  $\underline{ca}$  35) will be calibrated in  $K_{15}$  starting 1 January 1982.

where

 $K_{15} = {conductivity \ of \ Standard \ Seawater \ at \ 15^{\circ}C \ and \ 1 \ standard \ atmosphere} \over {conductivity \ of \ KCl \ solution \ (32.4356 \ g \ KCl/kg)} \ at \ 15^{\circ}C \ and \ 1 \ standard \ atmosphere$ 

This value of  $K_{15}$  should be used for calibrating bench salinometers. Chlorinity, which will also be included on the label, should henceforth be regarded as a separate independent variable for describing the properties of seawater.

# Low Salinity Standard (S = ca 30, L series)

Salinometers are calibrated at a single point and often have linear offsets at other salinities. For work of the highest precision, it is necessary to determine the offset. For this purpose, the Standard Seawater Service will make available a second standard of salinity  $\underline{ca}$  30. This standard will also be calibrated in  $K_{15}$ , as defined above, and in chlorinity.

The (S =  $\underline{ca}$  35) standard seawater should be regarded as the main one for single point calibration, as in the past, with the (S =  $\underline{ca}$  30) standard seawater to be used only for checking salinometer offsets. The Standard Seawater Service will produce the (S =  $\underline{ca}$  30) standard as L series, to distinguish it from the P series for the (S =  $\underline{ca}$  35) standard.

# Future Unesco Tables

Tables for conversion of conductivity to practical salinity as well as of seawater properties derived from the International Equation of State are presently being prepared. Unesco is requested to publish these tables in future volumes of the International Oceanographic Tables, and to distribute them to the oceanographic community as soon as possible.

# ANNEX 2

# On the International Oceanographic Tables,

Volume 2, Unesco 1973

Oxygen Solubility in Seawater

by Ray WEISS (1)

I wish to draw to the attention of the Joint Panel on Oceanographic Tables and Standards a fundamental but relatively small and uniform error in the International Oceanographic Tables, Volume 2 (Oxygen Solubility Tables). This point came to my attention only recently when Dr. B. Benson (Department of Physics, Amherst College, Amherst, Mass. USA) claimed that my oxygen solubility functions did not fit the data on which they are based. Benson was using the International Oceanographic Tables as a representation of my data, and it soon became apparent that there is an error in the calculation due to the assumption that a mole of oxygen had the same volume as a mole of ideal gas. Thus, the factor of 89.23 used to convert  ${\rm cm}^3$  of oxygen at S,t,p to  ${\rm \mu g}$  atoms is incorrect. The correct factor, based on a molar volume of  $0_2$  at S,t,p of 22 391.6 cm<sup>3</sup> (Sengers et al., 1971), is 89.319. Thus all the values in the International Oceanographic Tables are low by 0.10%. Similarly, with a molecular weight of 31.9988 g, the conversion to mg from  $cm^3$  (S,t,p) should be 1.4291, not 1.428 as given in the International Oceanographic Tables.

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