Proposal for a IAPSO/SCOR Working Group on the
"Thermodynamics and Equation of State of Sea water"

Background

Defining the equation of state of seawater is fundamental to many activities concerned with observing the physical state of the oceans and representing ocean processes in numerical models. The work of the Joint (IOC/SCOR) Panel on Oceanographic Tables and Standards (JPOTS) during the 1970s and 80s provided the world with a much-needed way to determine the salinity and density of seawater much more accurately than had been previously possible. The equation of state needed to do this is presently defined in algorithms published by Fofonoff and Millard (1983).

Since the mid-1980s there has been little formal study of these issues and yet there have been advances that point to a need to revisit the work initiated by JPOTS.

Timeliness and relevance

The International Equation of State is written in terms of the 1968 temperature scale. Virtually all new high precision ocean measurements are now made in the 1990 temperature scale. A growing group of scientists are unaware of the 1990 change, and may therefore wrongly employ the equation of state without taking into account the temperature conversion. In addition the 1990/1968 conversion is done with an approximate linear formula, deemed to be "adequate" for oceanographic purposes, but is not rigorously precise.

Ocean modelling has made great advances driven by increased computing power, by improved physical understanding and by the need to better represent the oceans in climate models. Scientists who run global ocean models are keen to have an accurate equation of state and they need their equation of state to be expressed as a function of potential temperature rather than in terms of in situ temperature. Recent work by McDougall et al. (2003) and Jackett et al. (2005) has provided ocean modellers with such an algorithm based on Feistel and Hagen (1995) and Feistel (2003). In this way, the modern thermodynamic research of Feistel has made its way into ocean modelling, but this work has not yet been adopted by the observational oceanographic community.

The known thermodynamic quantities for which accurate measurements exist have now been incorporated into a Gibbs function for seawater (Feistel, 1993; Feistel and Hagen, 1995; and Feistel, 2003). The most recent study in this series, namely Feistel (2003), abbreviated below as F03, has carefully documented the known accuracy of each type of thermodynamic measurement. This work seems to represent the limit of accuracy that is available at this time to determine density and other properties of seawater. The relevance of this finding to the wider oceanographic community should be addressed.

While the bulk of research has applied to the range of temperature and salinities typical of the open ocean, its relevance to areas of extreme high and low temperature and salinity as well as of non-standard sea salt composition should be considered.

The case for SCOR sponsorship of the WG

SCOR has a long history of support of activities in this and related areas. Relevant past SCOR Working Groups that have studied related topics include:-

WG 4	Physical Properties of Sea Water
WG 6	Chemical Oceanography
WG 10	Oceanographic Tables and Standards (reconstituted as the Joint Panel on Oceanographic Tables and Standards (JPOTS)
WG 49	Mathematical Modelling of Oceanic Processes
WG 51	The acquisition, calibration, and analysis of CTD data
WG 77	Laboratory Tests Related to Basic Physical Measurements at Sea
WG 102	Comparative Salinity and Density of the Atlantic and Pacific Ocean Basins
WG 121	Ocean Mixing

This working group would continue that long association. Its co-sponsorship by IAPSO and the support for the working group expressed by IOC provides a link to the foundation laid by the JPOTS panel.

Its subject matter matches the physical emphasis expressed in call for new WG proposals.

While the topics to be addressed by this WG may appear esoteric, they have applications and relevance to a wide range of modelling, observational and practical issues. (e.g parameterisation of mixing in models, the calculation of density from temperature/salinity/pressure observations, the physics and chemistry of substances (such as liquefied CO_2) placed in the deep ocean).

In view of this wide relevance, the activities of the WG may be able to attract financial support other than that available from SCOR.

Terms of Reference

(1) To examine the results of recent research in ocean thermodynamics with a view to recommending a change to the internationally recommended algorithms for evaluating density and related quantities (including enthalpy, entropy and potential temperature). Such recommendations would take into account the reformulation of the International Temperature Scale (ITS-90). (This work is elaborated in the priority 1 issues listed below)

(2) To examine the most accurate recent knowledge of the freezing temperature of seawater, the calculation of dissolved oxygen, and the behaviour of seawater at high salinity.

(3) To examine the feasibility of using simple functions of three-dimensional space to take account of the spatially varying concentrations of alkalinity, total carbon dioxide, calcium and silica place on the determination of density in the ocean.

(4) To extend these concepts to a wider range of physical/chemical issues of relevance to the internal working of the ocean and of its interaction with the atmosphere and to present and potential future observational techniques.

(5) To write a set of related recommendations on the above topics in the form of a report to SCOR/IAPSO and a review or series of reviews to be published in the scientific literature.

Membership

Trevor McDougall (CSIRO, Hobart, Australia)
: Ocean physics/thermodynamics specialist (proposed chair of this WG)

Brian King (SOC, Southampton, UK)
: Observational physical oceanographer with interests in the precise measurement of temperature and salinity

Rainer Feistel (IOW, Warnemünde, Germany)
: Sea water thermodynamics specialist

Dan Wright (Bedford Institute of Oceanography, Dartmouth, Canada)
: Ocean modeller

Peter Brewer (MBARI, Monterey, USA)
: Ocean chemist/CO_2 specialist

Frank Millero (RSMAS, Miami, USA)
: Ocean composition and thermodynamics specialist (Past Chair SCOR WG 102)

Barak Herut (IOLR, Haifa, Israel)
: High-salinity seawater specialist

Giles Marion (DRI, Reno, USA)
: Ice and high-salinity chemistry specialist

Valentina Gramm-Osipova (Pacific Oceanological Institute , Vladivostok, Russia)
: Ocean chemistry specialist

Vladimir Tchijov (UNAM, Mexico City, Mexico)
: Specialist for ice physics.

Corresponding members

David Jackett (CSIRO, Hobart, Australia)
: Mathematician and data specialist

Jim Swift (Scripps Institution of Oceanography, San Diego, USA)
: Observational physical oceanographer/Data specialist

Detailed explanation of the proposed remit for the Working Group

The WG will produce new "official" thermodynamic quantities of seawater (including the equation of state), taking into account recent developments in ocean thermodynamics and the reformulation of the International Temperature Scale (ITS-90).

The working group's main thrust would be to evaluate the recent Gibbs function that has been published by Feistel (2003), to decide on the limits of its accuracy, to weigh up its accuracy vis-a-vis the presently used international equation of state, with a view to recommending a change to the internationally recommended algorithms for evaluating density and related quantities (including enthalpy, entropy and potential temperature).

The following is a more detailed list of issues that would fall within the Terms of Reference of the proposed working group and that would be the focus of the WG. These have been separated into priority groups indicating the order in which they might be addressed.

Items in the first two priority categories should be achievable by the proposed Working Group within a time frame of two years.

Priority 1 issues:

1.1 Adopt the recent IAPWS*-95 international scientific pure water standard (Wagner and Pruß, (2002)) as the freshwater reference system for modern seawater thermodynamics.
1.2 Update all oceanic algorithms so that they are written in terms of the ITS-90 temperature scale and provide practical conversion algorithms between old and new parameters.
1.3 Examine F03's Gibbs function and the quantities that are derived from it and establish error estimates for the maximum errors that might arise from its oceanographic use.
1.4 Consider recommendations for chemical potential, specific entropy, enthalpy, internal energy or free enthalpy (Gibbs energy) of seawater, which were not part of the JPOTS standards, including the arbitrary reference state definitions.
1.5 Examine the accuracy of potential temperature that is determined by equating entropy based on F03's Gibbs function.
1.6 Examine the benefits of using potential enthalpy (or conservative temperature) as an oceanographic variable to represent "heat content" in oceanography, in particular, the potential enthalpy that is found from F03's Gibbs function.
1.7 Recommend the most accurate algorithms for the freezing temperature of seawater for pressures up to 3000db.

* IAPWS - International Association for the Properties of Water and Steam (http://www.iapws.org/)

Priority 2 issues:

2.1 Recommend the most accurate algorithms for saturated vapour pressure over seawater.
2.2 Examine whether modern data warrant a new algorithm for calculation of oxygen.
2.3 Examine the impact of air saturation on seawater properties.
2.4 Examine whether it might be possible to further increase the accuracy of the determination of density and other thermodynamic properties by a focused effort at collecting a limited number of extra data sets (e.g., data on the temperature of maximum density or on density below 0°C (Caldwell 1978))
2.5 Reconsider the practically widespread use of "dbar/db", "ml/l" or "psu" as units and recommend definitions and formula symbols for density anomaly, specific entropy, specific Gibbs energy, specific internal energy, sound speed, isothermal and adiabatic compressibility, or isothermal and adiabatic haline contraction coefficient.
2.6 Examine the possibility of optical determination of spatial and temporal distributions of density anomalies by using a refractive index sensor attached to standard CTD probes.
2.7 Write a set of related recommendations in the form of a review to be published in the scientific literature.

In addition to these tasks, there is a further set of issues (listed below) that should be addressed in order to progress this field even further. It is not clear at this time whether these issues are amenable to neat algorithmic solutions, and so it seems appropriate that the Working Group be asked to report back to SCOR after 12 months whether these issues seem amenable to further study by a Working Group or whether these issues, while being worthy research questions, are not close to yielding recommendations for changing the practice of oceanographers.

Priority 3 issues:

3.1 Examine the limits that the varying concentrations of alkalinity, total carbon dioxide and silica place on the determination of density in the ocean, and to examine whether a simple function of three-dimensional space might be used as a correction for some of this effect for the present ocean (Brewer and Bradshaw, 1975; Millero, 2000).

3.2 Examine the present knowledge of the ratio of absolute salinity to practical salinity and to determine whether it might be possible to construct a simple function of three-dimensional space to provide an estimate of this ratio for the present ocean.

3.3 Issue a recommendation on how standard formulas should be applied to waters with known density anomalies like the Baltic Sea.

3.4 Examine the possibility of a recommendation for artificial standard seawater chemical composition as reference for future models, theoretical work, or alternative measurement technologies, including recommended IUPAC* values for fundamental physical constants and atomic weights.

3.5 Examine the need for extending all the existing formulas to higher salinities/temperatures as already done up to salinities of 50 for conductivity and density.

3.6 Examine the possibility of a unified thermodynamic treatment of cold high-salinity seawater, ice, and sea ice (Herut et al., 1990; Feistel and Hagen, 1998; Marion et al., 1999; Feistel and Wagner, 2005)

3.7 Write a set of related recommendations in the form of a review to be published in the scientific literature.

* IUPAC- International Union of Pure and Applied Chemistry http://www.iupac.org/

Mode of Operation of the Working Group

As reported above, the priority 1 and 2 tasks should be able to be achieved by the Working Group over a two-year period, with two face-to-face meetings, one in the early months of the group's formation, in early 2006, and one after twelve or fifteen months of existence.

It is envisaged that at the first of these meetings the specific issues listed as priority 1 should be discussed and work be assigned to individual members (in collaboration with other members and non-members) to be performed out of session. This work would be reported and discussed at the second session. At the second meeting the Working Group would be in a better position to see if some or all of the priority 2 and 3 tasks could be fruitfully tackled by this or another Working Group, and if so, on what timescale.

In general, the work of this group would involve a small group of specialist participants, with inter-sessional targeted work having to be performed at their home institutions. Progress reports would be written and sent out to other experts for comment.

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