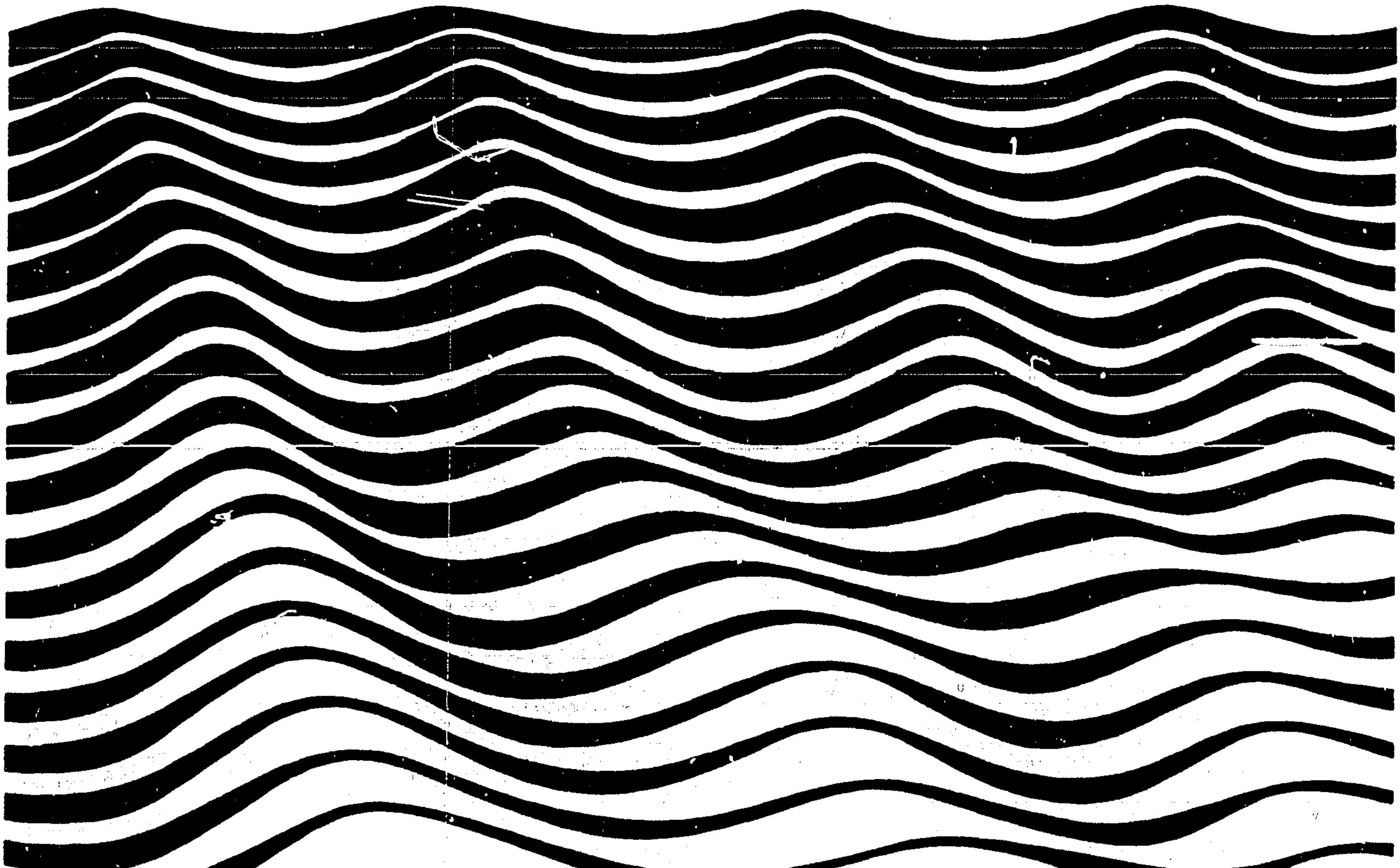
Unesco technical papers
in marine science 16

Sixth report of the Joint Panel on Oceanographic Tables and Standards

Kiel,
24-26 January 1973
sponsored by
Unesco, ICES, SCOR, IAPSO



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UNESCO TECHNICAL PAPERS IN MARINE SCIENCE

			SCOR
1.	First report of the joint panel on oceanographic tables and standards held at Copenhagen, 5-6 October 1964; sponsored by Unesco, ICES, SCOR, IAPO	1965	WG 10
2.	Report of the first meeting of the joint group of experts on photosynthetic radiant energy held at Moscow, 5-9 October 1964; sponsored by Unesco SCOR, IAPO	1965	WG 15
3.	Report on the intercalibration measurements in Copenhagen, 9-13 June 1965; organized by ICES		—
4.	Second report of the joint panel on oceanographic tables and standards held in Rome, 8-9 October 1965; sponsored by Unesco, ICES, SCOR, IAPO	1966	WG 10
5.	Report of the second meeting of the joint group of experts on photosynthetic radiant energy held at Karuizawa, 15-19 August 1966; sponsored by Unesco, SCOR, IAPO	1966	WG 10
6.	Report of a meeting of the joint group of experts on radiocarbon estimation of primary production held at Copenhagen, 24-26 October 1966; sponsored by Unesco, SCOR, ICES	1967	WG 20

(Note : Nos. 1 to 6 are out of stock)

7.	Report of the second meeting of the Committee for the Check-list of the Fishes of the North Eastern Atlantic and of the Mediterranean, London 20-22 April 1967 Procès-verbal de la 2è réunion du Comité pour le catalogue des poissons du Nord-Est atlantique et de la Méditerranée, Londres, 20-22 avril 1967	1968	—
8.	Third report of the joint panel on oceanographic tables and standards, Berne, 4-5 October 1967; sponsored by Unesco, ICES, SCOR, IAPO	1968	WG 10
9.	Report on intercalibration measurements, Leningrad, 24-28 May 1966 and Copenhagen, September 1966; organized by ICES	1969	—
10.	Guide to the Indian Ocean Biological Centre (IOBC), Cochin (India), by the Unesco Curator 1967-1969 (Dr. J. Tranter)	1969	
11.	An intercomparison of some current meters, report on an experiment at WHOI Mooring Site "D", 16-24 July 1967 by the working group on Continuous Current Velocity Measurements; sponsored by SCOR, IAPSO and Unesco	1969	WG 21
12.	Check-list of the fishes of the north-eastern Atlantic and of the Mediterranean (report of the third meeting of the Committee, Hamburg, 8-11 April 1969)	1969	—
13.	Technical report of sea trials conducted by the working group on photosynthetic radiant energy, Gulf of California, May 1968; sponsored by SCOR, IAPSO, Unesco	1969	WG 15
14.	Fifth report of the joint panel on oceanographic tables and standards, Kiel, 10-12 December 1969; sponsored by Unesco, ICES, SCOR, IAPSO	1970	WG 10

(Note : No. 14 is out of stock)

15.	Monitoring Life in the Ocean; sponsored by SCOR, ACMRR, UNESCO, IBM/PM	1973	WG 29
16	Sixth report of the joint panel on oceanographic tables and standards, Kiel, 24-26 January 1973; sponsored by Unesco, ICES, SCOR, IAPSO	1974	WG 10
17.	An intercomparison of some current meters, report on an experiment of Research Vessel Akademik Kurchatov, March-April 1970, by the working group on Current Velocity Measurements; sponsored by SCOR, IAPSO, Unesco	1974	WG 21

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Unesco 1974

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INTRODUCTION

The members of the Joint Panel of Experts on Oceanographic Tables and Standards were invited to attend a meeting in Kiel from 24 to 26 January 1973. The meeting was held at the new Institute for Marine Research at the University.

The members present were :

Dr. Frede Hermann	ICES
Prof. Dr. O. Saelen	
Dr. Fred Culkin	
Dr. N.P. Fofonoff	IAPSO
Prof. W. Kroebel	
Prof. Dr. K. Grasshoff, Chairman	SCOR
Dr. F. Fisher	
Prof. Dr. J. Gieskes	
Mr. M. Menaché	UNESCO

Dr. G.N. Ivanoff-Frantzkevich of the Institute of Oceanology, Academy of Sciences, USSR, was unable to attend the meeting.

The observers present were :

Dr. O.I. Mamayev	UNESCO

Dr. A. Poisson, Centre national de la recherche scientifique, Paris
Dr. K. Kremling, Institut für Meereskunde, Kiel

Prof. B. Kullenberg, Göteborg, who was invited as an expert, was unable to attend because of illness.

The Director of the Institut für Meereskunde welcomed the panel, noting that it was the first international working group to meet in the new building of the institute.

The revised agenda as proposed by the chairman was adopted as follows :

1) Additional tables to be included in the "International Oceanographic Tables" (oxygen, chlorosity, refractive index) published by Unesco and the National Institute of Oceanography, United Kingdom .
2) Report on the state of the art in measurements of the absolute conductivity of sea water.
3) Intercalibration of salinometers (international experiments to be carried out in 1973).
4) Absolute determination of the density of water.
5) Recent precision measurements of the specific gravity of sea water in the lower salinity range.

6) Progress report of the comparison measurements between real densities and calculated densities (the question of the significance of the third decimal in salinity). Experiments carried out by Dr. Kremling.

7) Problems related to in situ measurements of salinity $S = f(P,T,R_T)$.

8) The "Kullenberg" formula for the calculation of the density of sea water.

9) Sigma-t tables to be included in the "International Oceanographic Tables".

10) The entropy of sea water, state of the art and future work. Possible actions of the panel.

11) Recent precise measurements of the velocity of sound in sea water.

12) Election of a new chairman.

13) Other business.

14) Future meetings and membership of the panel.

REPORTS ON AGENDA ITEMS

1. Additional tables to be included in the "International Oceanographic Tables"

a) Oxygen saturation tables

At the fifth meeting of the Joint Panel of Experts on Oceanographic Tables and Standards (December 1969) it was decided to use the formula published by Weiss (Deep-Sea Research, 1970, 17, 721-736) for the compilation of oxygen solubility tables for inclusion in volume 2 of the International Oceanographic Tables . The panel recognized that both the original data and the treatment of the data for the solubility of oxigen in sea water might be improved in future but there was general agreement that publication of the tables should proceed on the basis of the most recent measurements. The tables will be used mainly for calculation of saturation data from routine field measurements which, even under the best conditions, will have a probable error of ± 0.02 to ± 0.04 ml/l (or cm3/dm3). The panel felt that any future improvement of solubility values will be within the limits of this error and therefore the tables will be applicable also in the future. Full reference to the source of the solubility data used is given in the introduction to the tables. Unfortunately there was some delay in the preparation of the tables but they should be delivered to Unesco for distribution by the end of April 1973.

The panel was of the opinion that all possible means should be used to make the oxygen solubility tables known to the oceanographic community. In particular, it was proposed that a statement, signed by the Presidents of SCOR and IAPSO and the chairman of the panel, recommending that these tables and the formulae contained therein be exclusively used for the calculation of oxygen saturation data, should be forwarded to the main oceanographic journals, the data centres and to Unesco for inclusion in their communication channels.

With the completion of these tables the commitment of the panel with respect to oxygen solubility tables has now been fulfilled.

b) Tables for conversion of relative conductivity to salinity

The panel was informed that a second edition of Volume 1 of the International Oceanographic Tables (conductivity ratio/salinity) was printed in 1972 and that Unesco and the National Institute of Oceanography now have stocks of these tables. The panel discussed the problem of some salinometer manufacturers supplying with their instruments conversion tables which differ from the official Unesco tables. The panel felt that this practice should be strongly discouraged and decided to ask its sponsors to again recommend that only the official "International Oceanographic Tables" should be used for the conversion of conductivity ratio to salinity. It was also recommended that the chairman of the panel should write to the manufacturers of salinometers urging them to supply only official tables with their instruments. Because of the low cost of these tables compared with the price of an instrument this would not increase total costs significantly. The panel felt very strongly that unofficial tables should be removed from circulation as soon as possible.

c) Tables for conversion of salinity to chlorosity

The panel was informed that these tables, which were compiled at Kiel, will be published as part of Volume 2 of the International Oceanographic Tables by the end of April 1973. The commitment of the panel is therefore fulfilled in this respect.

d) Tables of refractive index of sea water

These tables are a supplement to Volume 1 of the International Oceanographic Tables . At its last meeting the panel recommended that the measurements by J.S.M. Rusby should be repeated by at least one other laboratory to give an independent check. However, it was recognized that it will certainly not be an easy undertaking to repeat the measurements with the same degree of accuracy as has been obtained by the above author.

The panel was informed that Prof. Ivanoff from the Laboratoire d'océanographie physique de l'Université de Paris intends to repeat the refractive index measurements if the necessary funds can be obtained. This was welcomed by the panel.

The panel discussed the procedure for the compilation and preparation of future tables. It was suggested that, if possible, a member of the panel who is associated or familiar with the work leading up to the table should be responsible for the preparatory work on the table in question and that editing, supervision of the printing, etc.. should also in future be handled by the N.I.O. The panel received with gratitude a guideline paper from Unesco giving information on what is needed by Unesco to provide a closer collaboration between the panel and the Division of Oceanography of Unesco. The panel discussed the matters raised in the informative paper from Unesco but felt that it might be difficult, if not impossible, to meet the request to give an 8-year projection of the appearance of additional tables. The panel could certainly agree on the time of the next meeting, but could only have a rough idea about meetings to come later than the next meeting. This is due to the fact that the meetings of the panel are arranged according to the needs and to matters arising but are not scheduled on a regular basis. The panel agreed on the following procedure for additional tables to be published as parts of the "International Oceanographic Tables" :

1) At a particular meeting, the panel will decide that a certain table should be compiled and would also propose the format of this table, after having thoroughly studied and discussed the data and measurements as well as the mathematical treatment leading to the tables.
2) The panel recommends to Unesco that the table should be included in the series "International Oceanographic Tables".
3) Having received a positive answer, the panel nominates a member to be responsible for the preliminary compilation of the tables and for writing the introductory remarks. (To avoid delay in the work the responsible person may already be nominated at the meeting where the new table is recommended by the panel.)

4) After preliminary compilation of the new table it will be circulated in draft form to the members of the panel and, if desired, also to other interested experts.

5) After incorporation of the remarks the tables will be sent to the N.I.O. for a final revision and for editing and will then be handed over to the printer.

2. Measurements of the absolute conductivity of sea water

The panel received a report of progress at N.I.O. in the development of an instrument for measuring the absolute electrical conductivity of Standard Sea Water. The apparatus is at present being re-assembled after some modifications to the optical system which will be used to measure the movement of the electrode. The precision of the measurements will be limited by the accuracy of the temperature measurement and the temperature control but it is hoped it will be of the order of 2 in 10^5. Calibration of the Quartz Crystal Thermometer at the National Physical Laboratory, U.K. showed a drift of less than 3×10^{-3}°C in two years but more frequent calibration is planned in future. It is intended to carry out reproducibility tests very soon. If these prove satisfactory it will then be necessary to have the dimensions of the cell measured and the resistors and thermometer calibrated. Because of their high cost these measurements were left until the design had been finalized. It is therefore not yet possible to say when work on Standard Sea Water will start.

The panel unanimously agreed that measurement of the absolute conductivity of sea water is still of the utmost importance. The calibration of the Standard Sea Water in figures of absolute conductivity will provide for the conversion of relative conductivities of sea water sample measurements into absolute figures and for the long-term quality check of the standards.

The panel was informed that the work at the N.I.O. is at present financed only from national sources. The panel strongly recommended that the work in connexion with the absolute conductivity should be continued and that, if possible, an independent cross-check should be made by another institute, possibly also on the basis of KC1 as standard.

The panel was informed that Dr. Poisson from the Centre national de la recherche scientifique is prepared to carry out cross-check measurements on the basis of KC1. This proposal was welcomed by the panel.

3. Intercalibration of salinometers

The number of manufacturers of salinometers has increased in recent years. Most salinometers are constructed on the basis of measuring the conductivity by means of inductive coupling of torroids through the sea water sample. It is frequently stated by the manufacturers that the accuracy of the measured conductivity relative to the standard used is greater than .003‰ over the entire range of salinities (2-42‰) but at present there is no means of confirming such statements. In fact, there has been strong evidence that the performance of salinometers is not as good as stated and that aging of the circuits or of the geometry may cause disturbance of the original calibrations. Furthermore it is not known how the manufacturers are setting up their calibrations. It has therefore been recommended by ICES in collaboration with IAPSO and SCOR that an international intercalibration exercise be carried out on the basis of sea water samples with exactly known salinities of 38.4‰ and 8‰. These samples will be prepared by the Standard Sea Water service and distributed to interested institutes at their own expense (at a somewhat lower price than that of the normal standards).

It is recommended that such institutes who wish to be informed about and to take part in the intercalibration test should indicate their interest to Mr. Hermann, Standard Sea Water Service, Copenhagen-Charlottenlund. It is desirable that as many institutes as possible take part in this exercise. Drs. Gieskes and Fofonoff will provide a list of institutes and people from the United States who may wish to take part in the intercalibration. A realistic estimate shows that about 1,000 ampoules of the higher and 500 ampoules of the lower salinities are needed. The test will be carried out under the guidance of Mr. F. Hermann and Prof. Dr. K. Grasshoff. It is intended to distribute the samples during 1973.

The panel discussed a number of details with respect to the performance and the "unknowns" in the test.

Technical details about the intercalibration and test of salinometers will be forwarded to the institutes together with the samples.

The panel discussed also the possible risk of degassing of the standard sea water when it is introduced into the measuring cells of salinometers if used at temperatures higher than 25°C. The panel was informed that this problem has been overcome by the Standard Sea Water Service and that the standards will now not degas if used below 26°C.

4. Absolute determination of the density of water

The panel recalled recommendation No.1 from its last meeting as endorsed by the sponsors. Mr. Menaché reported on the efforts of the "Bureau International des Poids et Mesures" (BIPM) to implement the recommendation and submitted a report from the bureau which reads in its main part as follows :

"After the meeting of the Joint Panel on Oceanographic Tables and Standards held in Kiel from 10-12 December 1969, the text of recommendation No.1 from the panel was submitted to the president of the Comité International des Poids et Mesures (CIPM) concerning the problem of the absolute density of water and that of its thermal expansion coefficient.

This recommendation was submitted to the XVth General Assembly of the International Association for the Physical Sciences of the Ocean, which was held in Tokyo in September 1970. The Assembly endorsed this recommendation and passed its resolution No.1, which is in agreement with the recommendation of the panel. In turn the International Union of Geodesy and Geophysics, whose XVth General Assembly took place in Moscow in August 1971, supported this recommendation and voted its Resolution No. 18. The secretary general of IUGG submitted the text of the resolution and expressed the hope that the large national metrological laboratories would agree to undertake the desired studies.

These questions moreover had already been the subject of preliminary discussions by the CIPM at its session in 1970. The members of the CIPM, who are for the most part directors of large national laboratories, are conscious of the importance of this problem and have promised to examine this question. The following replies have been received by the Bureau International des Poids et Mesures :

The National Research Council of Canada and the Physikalisch-Technische Bundesanstalt of F.R.G. cannot for the time being contemplate such studies. The National Bureau of Standards is concentrating for the moment on establishing a series of standards for absolute density constituted by solid samples. Only the National Standards Laboratory in Australia, in conjunction with the nuclear research and oceanographic laboratories, has a project for measuring the absolute density of water and its thermal expansion coefficient. The method consists of using a hollow sphere of a known mass, the volume of which would be determined by mechanical measurements of its diameters. This sphere, by hydrostatic weighings, would make it possible to determine the absolute density of water at several temperatures, 4°C and every 5 or 10°C up to 40°C. The measurement of the thermal expansion coefficient of water would be carried out also by hydrostatic weighings, taking bearings on the above absolute measurements with the help of a sphere constructed from some very slightly expansive material.

The Institut Océanographique in Paris has, on the other hand, in cooperation with the BIPM, written an article (see appendix No.1) setting forth these two problems and stressing the urgent need for new measures".

The Soviet Academy of Science has also expressed its interest in these problems and strongly endorsed the recommendation of the panel. The panel was of the opinion that the echo caused by the Recommendation No.1 was rather positive and was unanimously of the opinion that these determinations are still of the utmost importance.

5. Recent precision measurements of the specific gravity of sea water in the lower salinity range

Dr. Kremling reported to the panel about his work on the chlorinity-salinity-conductivity-specific gravity relationships at lower salinities. About 250 samples are being investigated and complete chemical analyses of the main constituents are being carried out on most of the samples. There is clear evidence that the conversion of chlorinity to salinity and vice versa by the factor 1.80655 should not be applied to salinities below 20‰ if accuracies better than 0.05‰ are desired. The conversion by means of equations of the type $S = A \cdot Cl + B$ with different A's and B's for the different regions and depths will give a more accurate conversion for Baltic waters. The "real" salinities may be better determined by conductivity measurements and will under most circumstances deviate from the chemically determined salinity $\Sigma(K^+ + A^-)$ by less than 0.02‰.

The specific gravities of most samples from this programme have also been determined.

The panel discussed the problem of whether the density measurements from the Baltic should be used to improve conductivity-density conversion formulae in the low salinity range. It is, however, quite possible that the composition of sea water at lower salinities deviates to such a degree that each region with brackish water needs another conversion factor. It is the intention of the Institut für Meereskunde to collect also samples from other regions e.g. Black Sea, Caspian Sea and compare the conductivity-density relations of these areas with those for the Baltic.

There are actually no precise and extended laboratory experiments on measuring the specific gravity of sea-water in the range of salinity 0 - 10‰. It was recommended that further measurements should be made of specific gravity of low salinity waters at low temperatures.

6. Comparison measurements between real densities and calculated densities

It was announced at the last meeting of the panel that the Institut für Meereskunde intended to collect sea water samples from several parts of the world oceans and compare the calculated specific gravities, as derived from conductivity-salinity measurements, with measured specific gravities. Most of the samples which have been collected, with the help of several other laboratories, from the Pacific, Atlantic and Mediterranean have now arrived in Kiel. Comparison measurements have been made at N.I.O. and I.f.M. The standard pure water used by these two laboratories was prepared by the same method of triple distillation of Mediterranean deep water and it has been shown that there is no significant difference in isotopic composition between the two standards. For technical reasons the instrument which is to be used at Kiel for measuring high precision specific gravities has been out of order for some time so it has not been possible, so far, to make any measurements. It is expected, however, that the measurements will be completed by the middle of 1973 and the results will be available by the end of 1973. With these measurements the question of whether the third decimal place in salinity has any significance, or in other words whether calculated and real densities do agree, will be answered.

Dr. Kremling reported on his experiments on cross-check of N.I.O. values of specific gravity (polynomial expression by Cox, McCartney and Culkin) with the aid of new precise density apparatus (cf. paper by Kremling in "Deep-Sea Research", 1972, vol. 19, pp. 377-383). For all temperatures and salinities the mean deviation was (Cox-Kremling) = - 0.004 (in sigma-T values). The experiments of Dr. Kremling will be finished this year and the results reported in "Deep-Sea Research".

7. Problems related to in situ measurements of salinity $S = f(P,T,R_T)$

The panel discussed thoroughly the present situation in converting in situ conductivity measurements into salinity and density. It was recognized that there is at present no officially adopted conversion formula in spite of the fact that a great number of in situ STD recording instruments are on the market. The present situation is obviously such that the institutes and manufacturers are using individual conversion procedures. In some cases the conversion is made by means of a built-in analogue computer and in others the conversion is made either on line or later by a computer. The quantity of salinity data obtained by means of in situ instruments which is being received by the data centres is rapidly increasing and will eventually match that obtained by conductivity measurement or titration of discrete samples. It is essential, therefore, that the salinity data are comparable. The panel felt strongly that it will be an urgent task to improve the present rather unsafe situation and proposes that

a) means are undertaken to compile and critically investigate all types of conversion procedures which are at present applied for the conversion of in situ conductivity into salinity and density and,

b) a comparison and intercalibration of in situ salinometers (conductivity meters) should be organized including as many STD recording instruments as possible. Such an intercalibration should be organized by a joint special working group consisting of physical oceanographers, engineers, electronic engineers, mathematicians and statisticians. The test might be carried out with tank experiments and through field tests in areas with very small stratification of salinity but with great depths, e.g. Mediterranean or Red Sea. The funding of such an important intercalibration should ideally come from international sources;

c) special attention should be paid to the fact that there are gaps in our knowledge regarding precise measurements of conductivity ratios below 15°C and at elevated pressures;

d) the panel should investigate at its next meeting the possibilities of recommending a single conversion formula for in situ conductivities into salinity and density.

The considerations of the panel led it to adopt recommendation No.(1) 1973.

Recommendation 1/1973

Taking into account the rapidly increasing use of in situ measurements of conductivity for estimating salinity and considering that no internationally accepted conversion formulae have been recognized, the panel strongly recommends that IAPSO, IUGG, SCOR, ICES and Unesco take steps so that :

a) Precise measurements of conductivity ratios of sea water be carried out in the range -2 - 15°C to extend the range of present Unesco tables to lower temperatures;

b) precise measurements of conductivity ratio of sea water be carried out at elevated pressures to verify and extend the salinity range of the present Bradshaw and Schleicher formula;

c) after suitable evaluation, the panel propose a conversion procedure for estimating salinity from in situ measurements of conductivity, temperature and pressure for international use;

d) a working group be formed to initiate and carry out intercalibration procedures for in situ measurements of conductivity, temperature and pressure.

The panel notes with gratification Dr. Fisher's willingness to review existing literature related to the problem of converting conductivity measurements to salinity.

8. The "Kullenberg" formula for the calculation of the density of sea water

The panel was informed about the mathematical treatment of the calculation of σ_t from salinity and temperature as derived by Prof. B. Kullenberg, Göteborg, and presented at the Statutory Meeting of ICES, 1971. As quoted by the originator of the new formula, it should give an improved fit between the measured and computed σ_t values throughout the entire range of salinities as compared to the treatment of Cox, McCartney and Culkin. The latter author's formula leads to almost identical values in the higher ranges of salinities ($>9‰$) with comparable mean standard deviations (0.0113, Kullenberg; 0.113, Cox a.o.) but the deviations at lower salinities down to zero are expected to be considerably less with the Kullenberg treatment. The panel regrets that Prof. Kullenberg was unable to attend the meeting, because of illness, and the fact that his work has not yet been completed. The Kullenberg formula uses the temperature and salinity of the point of maximum density as parameters where

$$\sigma_m = 0.7737085\ S + 0.00059312\ S^2 + \frac{0.52553\ S}{S + 8.458}$$

$$\text{and } t_m = 3.9863 - \frac{0.22473\ S^2}{S + 0.941}$$

The formula for the calculation of σ_t is then :

$$\sigma_t = \sigma_m - a\,\frac{(t - t_m)^2}{t + b} + c(t - t_m)^2$$

where a, b, c are coefficients which have not yet been finally determined. At present Prof. Kullenberg is improving the coefficients on the basis of recent density measurements at low salinities.

The panel felt unable to give a full and competent judgement on the scientific value of the new formula until the work of Prof. Kullenberg is completed. There was a strong feeling that Prof. Kullenberg should be encouraged to finish his work. It was decided that the problem should be reconsidered at the next meeting of the panel. The panel was aware that the Cox-McCartney-Culkin formula does not represent an optimal fit between calculated and measured density data at low salinities. There is, however, the problem of to what extent differences in the chemical composition of brackish water may limit a single formula for uniform application in all enclosed seas with low salinities.

9. Sigma-t tables to be included in the "International Oceanographic Tables"

At its previous meeting the panel decided that Drs. Fisher, Fofonoff and Culkin should investigate by exchange of letters the format of future tables and/or nomographs of sigma-t to be included in the "International Oceanographic Tables". Dr. Fofonoff reported to the panel on the outcome of the discussions within the working party. The panel agreed with the opinion of the working party that at present no new sigma-t tables should be issued until the derivation of a suitable equation of state of sea water has been finished. There might be the risk that an edition of new sigma-t tables may be premature and that such tables or nomograms would have to be withdrawn because of a better mathematical treatment of the relationship between salinity, temperature, density and pressure through a uniform equation of state in the forseeable future.

It was the general opinion of the panel that, if possible, those tables which are included in the "International Oceanographic Tables" should represent a kind of finite treatment which should not be changed or improved at a later date other than through improving the accuracy by adding more significant decimals if needed.

It is, therefore, recommended that the old tables of Knudsen and nomographs derived from Knudsen's tables should be used until the equation of state is set up covering the whole range of temperatures and salinities. It was the opinion of the panel that such sigma-t tables, if issued now, will not improve significantly the old tables.

In addition most oceanographic data centres provide a service for the calculation of sigma-t from the basic data. Tables and nomographs are at present normally only used for a preliminary calculation of sigma-t. These practical reasons diminish the immediate need for new sigma-t tables.

The panel will reconsider the problem at its next meeting and find out whether the progress in the development of a suitable equation of state permits the compilation of new tables. In the meantime institutes should be encouraged to carry out precision measurements of densities at low temperatures, low salinities and at elevated pressure, which are lacking at present.

The panel considers that any sigma-t table and any form of the equation of state could give the density relative to the chosen standard pure water, on condition that the isotopic composition of this standard water is indicated. In this way, recalculation can be done when one or several absolute values of the density of pure water have been obtained with the required accuracy.

Sigma-t tables and equation of state could preferably give absolute density of sea water, taking :

$$\rho_{max}(\mathrm{SMOW})/(\mathrm{kg.m^{-3}}) = 999.975 + \varepsilon \text{ (see appendix 1),}$$

ρ_{max}(SMOW) being the maximal value of the absolute density of the SMOW free of dissolved gases and under one standard atmosphere.

The small systematic error, ε , thus made on all the density values will be eliminated later when we have the results of new absolute determinations at our disposal.

10. The entropy of sea water, state of the art and future work

On the basis of the presentation by Dr. O. Mamayev (see appendix 2 of this report) and on the deliberations by Drs Fisher and Gieskes the panel discussed the state of the art in the problems related to the entropy of sea water. The panel was of the opinion that a number of problems must be solved before the panel could consider presenting a comprehensive report on the entropy of sea water. The final discussion should therefore be postponed until

a) Dr. Fisher has completed his work on the equation of state;

b) Dr. Millero (Miami) has done more measurements and presented his own equations;

c) the density data by Drs Kremling, Millero and Culkin are complete.

The panel was informed that Drs Gieskes, Millero and Fisher would meet in the spring of 1973 to discuss the problems related to the entropy of sea water in greater detail. In general a workable equation of state might be developed by 1975 and the problem regarding the entropy of sea water can then be resolved, based on numerous new measurements. Unfortunately the situation is at present such that we have not yet found a dependable way of expressing the final equation of state nor are we yet able to calculate relative entropies. It is to be hoped that these objections may be overcome within the next two years. The panel is of the opinion that the state of the art is rapidly improving and strongly recommends that institutes involved in work related to the entropy of sea water should be encouraged to continue or even extend their activities. Such institutes are urged to communicate with Prof. Gieskes, member of the panel, about ongoing and planned work, in order to enable the panel to maintain a full record of the present situation.

11. Recent precise measurements of the velocity of sound in sea water

The members of the panel and the observers visited the Institute of Applied Physics, Kiel University, and were informed of the progress in the redetermination of sound velocity in pure water under atmospheric pressure in the institute of Prof. Kroebel.

12. Election of a new chairman

Prof. Grasshoff was reelected chairman of the panel for the coming period.

13. Other business

The panel informed Dr. Mamayev that no additional tables will be proposed for inclusion in the "International Oceanographic Tables" within the next two years. The panel felt unable to make a safe forecast but it might be expected that sigma-t tables and tables of the conductivity ratio at lower temperatures and at higher pressures may be compiled within the next four years. A table of the absolute conductivity of sea water at atmospheric pressure might also be generated within a four-to-eight-year period as well as tables of the viscosity of sea water at atmospheric pressure and of the thermal expansion.

14. Membership and future meetings of the panel

The panel was informed that Mr. Hermann and Prof. Saelen, both nominated by ICES, wished to resign as members. On behalf of the panel the chairman expressed thanks for their active collaboration in the work of the panel. There was a general feeling that the panel should always be a dynamic group, recruiting members according to its needs and the work. The chairman was asked to contact the Secretary General of ICES to bring up the question of future representation of ICES in the panel to the coming Statutory Meeting for discussion within the hydrographic committee and decision by the Executive Council of ICES. The panel felt strongly that Dr. Frank Millero, University of Miami, should be coopted as a member of the panel in order to enlarge the expertise in relation to the problems relating to the entropy of sea water.

The panel decided to hold its next meeting in connexion with the forthcoming General Assembly of IAPSO in Grenoble, France, in August 1975.

The chairman of the panel was asked by the Secretary of IAPSO to organize a part of the scheduled symposium with the topic "Thermodynamics of the Sea and the Equation of State". The panel welcomed the idea of the symposium which would bring together scientists involved in one of the main topics for the coming work of the panel.

The meeting was closed at 1 p.m., 26 January 1973.

K. Grasshoff

APPENDICES

1. SOME COMMENTS ON RECOMMENDATION 1969, No. 1

by

M. Menaché

The report of the Director of the Bureau International des Poids et Mesures (BIPM), addressed to the Chairman of the Joint Panel, Professor Grasshoff, proves the interest aroused by the Panel's Recommendation 1969, No. 1, and those which have followed and endorsed it (Resolutions No. 1, 1970 of the IAPSO and No. 18, 1971 of the IUGG.

In its Recommendation 1969, No. 1, the Panel expressed the desire to know, with an accuracy at least equal to 1×10^{-3} kg.m^{-3} :

1) one or several absolute values of the absolute density of water for a water having a definite isotopic composition;

2) its thermal expansion between 0 and 40°C.

These two problems have thus been brought to the attention of the important national metrological laboratories best qualified to undertake this study and achieve results, and there is no doubt now that, sooner or later, these two problems will be solved.

The first problem, that of finding out one or several absolute values of the absolute density of water, is extremely difficult to solve for it requires, first of all, the construction of a solid object of perfect geometrical form, and then the geometrical measurement of the dimensions of this object with a relative accuracy at least equal to $1/3 \times 10^{-6}$. If, for example, the absolute determination has to be made by hydrostatic weighings of a solid sphere, 10cm. in diameter, this diameter must be known at least to $\pm 0.03\,\mu$m.

Fortunately the solution to this problem does not seem to be the most urgent, especially for oceanographic needs. It is sufficient for the moment to choose a suitable numerical value to represent the absolute density of water, corresponding to definite values of its four parameters, and in particular of its isotopic composition, even if this numerical value is only known approximately.

With Mr. Girard of the BIPM, we have proposed to take as standard for the absolute density of water, the SMOW, itself the isotopic composition standard, and to attribute to it the following numerical value:

$$\rho_{\max}(\mathrm{SMOW})/(\mathrm{kg.m^{-}}) = 999.975 + \varepsilon$$

the uncertainty ε being very probably of the order of 1 to 3×10^{-3} kg.m^{-3}.

The adoption of this numerical value makes it possible to take into account the isotopic composition in calculating the absolute density of any sample of water. The results obtained for different samples of water with different compositions, would be obtained with the same error ε, and would thus become comparable. This error could be eliminated later when we have the results of new absolute determinations at our disposal. In any case, it is eliminated in calculations of differences in absolute density of water, which most interest oceanographers.

The problem of thermal expansion of water seems to require a more urgent solution.

As well as the study project of the NSL, information is to hand on some other projects which are still at the preliminary stage, in particular in German, Polish and Canadian laboratories.

It seems, however, preferable that a precise study of the influence of atmospheric gases dissolved in water should be undertaken before that of thermal expansion.

2. SOME THEORETICAL CONSIDERATIONS ON THE EQUATION OF STATE OF SEA WATER

by

O.I. MAMAYEV

> "There are occasions when mathematical beauty should take priority over (temporary) agreement with experiment".
>
> Paul Dirac

ABSTRACT

Considering that the density (specific gravity) of sea water, under constant pressure, according to Knudsen, follows, with a fairly good approximation, the Laplace equation with respect to T and S, the author proposes a numerical solution of the Laplace equation for the density of sea water. This solution can be based either on density values on a contour of the T - S diagram, including the ranges of T and S found in nature (Dirichlet's problem) or on the values of the derivatives of density with respect to T and S on the same contour (Neumann's problem). The comparison of the results of such calculations and of Knudsen's results might be helpful for the interpolation of new values of density based on accurate determinations of density or of its derivatives made only on the contour.

1. The present communication is devoted to an additional discussion of the hypothesis formulated by the author (Mamayev, 1970) that the density $\rho(S,T)$ (or the specific volume $\alpha(S,T)$) of sea water under constant pressure is a harmonic function of its salinity S and temperature T, in other words that it satisfies the Laplace equation for the variables S and T*

$$\nabla^2_{ST}\rho = 0 \qquad \left(\nabla^2_{ST} = \frac{\partial^2}{\partial S^2} + \frac{\partial^2}{\partial T^2}\right) \tag{1}$$

As this hypothesis, as we shall see later, is not proven, the present communication is of the nature of a discussion.

We shall first repeat briefly the considerations which lead to the statement of the validity of equation (1) (Mamayev, 1970).

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* We will consider the dimensionless S–T plane, on which $T = T'/T_o$, $S = S'/S_o$, where S' and T' are dimensional values of temperature and salinity, $T_o = 1^oC$'$S_o = 1^o/_{oo}$ constant values. This kind of setting retains numerical values of functions of the dimensional (ordinary) T–S diagram.

Let us consider two sets of orthogonal curves : of "isopycnal potential" ρ and of "density Flux" Ψ on the S-T diagram*. From the condition of orthogonality of these two sets of curves,

$$\frac{\partial\rho}{\partial T}\,\frac{\partial\Psi}{\partial T}+\frac{\partial\rho}{\partial S}\,\frac{\partial\Psi}{\partial S}=0, \qquad (2)$$

it follows that the Cauchy-Riemann equations for the S-T plane

$$\frac{\partial\rho}{\partial S}=\frac{\partial\Psi}{\partial T} \qquad \frac{\partial\rho}{\partial T}=-\frac{\partial\Psi}{\partial S} \qquad (3)$$

must be satisfied, as their substitution into (2) turns this condition into identity.

(Cf. Mamayev, 1970, p. 120 for the detailed discussion).

Differentiation of (3) leads to the equation (1) for ρ and an analogous equation for the function Ψ :

$$\nabla^2_{ST}\rho=0 \;; \qquad \nabla^2_{ST}\Psi=0 \qquad (4)$$

This is the result obtained by the author earlier (Mamayev, 1970) and to some extent discussed by him in the above work.

2. Taking the equation of state of sea water at atmospheric pressure, $\rho=\rho(S,T)$, in Kundsen's form and forming the Laplacian $\nabla^2_{ST}\rho$, we obtain the following expression:

$$\frac{\partial^2\rho}{\partial S^2}+\frac{\partial^2\rho}{\partial T^2}=10^{-3}\left\{\frac{d^2\sigma_0}{dS^2}(1-A_T+2B_T\sigma_0)+2B_T\left(\frac{d\sigma_0}{dS}\right)^2+\frac{d^2\Sigma_T}{dT^2}\right.$$
$$\left.+(\sigma_0+0.1324)\left[-\frac{d^2A_T}{dT^2}+(\sigma_0-0.1324)\frac{d^2B_T}{dT^2}\right]\right\} \qquad (5)$$

Where Σ_T is 1000 times the excess over 1 of the density of pure water at T°C, A_T and B_T empirical functions of temperature, σ_0 is 1000 times the excess over 1 of the specific gravity of sea water at 0°C (function of salinity).

Therefore, formally speaking, Knudsen's equation satisfies not the Laplace equation (4), but the Poisson equation

$$\nabla^2_{ST}\rho=\delta(S,T) \qquad (6)$$

in which the character of the function $\delta(S,T)$ is unknown to us. The value of $\delta(S,T)$ in the oceanic range of S and T is extremely small:

$$\delta(ST)\approx 1.10^{-5}\div 2.10^{-5},$$

---

* Indication of the existence of the function Ψ conjugate to the density is contained in the works of Mamayev (1962) and Stommel (1962); development of theoretical questions concerning the function Ψ is contained in the above-mentioned work by Stommel (1962), the author's monograph (Mamayev, 1970) and the work of Veronis (1972). Stommel considers the linear approximation to the equation of state of sea water and denotes the function Ψ by q. Veronis denotes it by τ. See also the author's comments (Mamayev, 1973).

and is appreciably smaller than errors of determination of density by Knudsen et al.

The values of $\delta(S,T)$ are shown on the S-T diagram in Fig. 1; the graph is constructed using the values of the specific volume instead of density on the basis of precise tables of second derivatives of Fofonoff and Froese (1958).

The maximal values of δ lie in a domain of low temperature and low salinity. Do these values of $\delta(T,S)$ result from errors in the determination of density or from another source?

In putting this question it should be borne in mind that, as already stated (Mamayev, 1970), the experimental determination of the equation of state of any system on the basis of measurement of its parameters of state leads to various analytical expressions, the difference between which is revealed mainly in second derivatives.

Also, for the purpose of comparison, Fig. 2 shows on a T-S diagram the distribution of the differences between the densities (specific gravities) of sea water, calculated on the basis of results of recent determinations by Cox, McCartney and Culkin (1970) and the densities according to Knudsen. This graph demonstrates that the maximal discrepancies are also found in the region of low temperatures and salinities.

Many authors who have been investigating the equation of state recently confirm that their determinations revealed maximal errors in the range mentioned.

3. Let us now subject the considerations put forward in para. 1 above to an additional discussion.

From the condition of orthogonality (2) a more general case follows than stated above, i.e. that for the T-S plane the following equations are also satisfied :

$$\frac{\partial \varrho}{\partial S} = a(S,T)\frac{\partial \Upsilon}{\partial T} ; \qquad \frac{\partial \varrho}{\partial T} = - a(S,T)\frac{\partial \Upsilon}{\partial S} , \qquad (7)$$

where $a(S,T)$ is the function not yet determined. Substitution of these equations into the condition of orthogonality (2) also turns them into identity. Equations (7) as well as equations (3) also have an analogy in hydrodynamics: they correspond to the equations connecting velocity potential φ with the stream function ψ in the steady irrotational flow of a <u>compressible</u> fluid:

$$\frac{\partial \varphi}{\partial x} = \frac{1}{\varrho}\,\frac{\partial \psi}{\partial y} ; \qquad \frac{\partial \varphi}{\partial y} = - \frac{1}{\varrho}\,\frac{\partial \psi}{\partial x} , \qquad (8)$$

where $\varrho = \varrho(T,p)$ is density and p pressure (cf., e.g., Serrin, 1959, para. 43).

Equations (7) have been written by Veronis (1972) (his equation 6) but he does not mention the hydrodynamical analogy. Veronis names $a(S,T)$ an "arbitrary function of T and S"; we retain his letter denotation.

Here it is worth making the following important comment : while not determining in any way the function $a(S,T,)$, Veronis points out that, for the purpose of construction of the set of isolines of Υ, orthogonal to isopycnals, it suffices to take a = const. <u>In the present context this approximation is equivalent to the statement that Laplace equations (4) are satisfied for the S-T plane</u>: this follows from differentiation and addition of equations (7), taking a = const.

Nevertheless, let us proceed further, taking $a = a(S,T)$. Differentiating the first equation (7) with respect to salinity, and the second one to temperature, and adding them, we come to the following Poisson equation for density, after substitution of (7) :

$$\frac{\partial^2 \rho}{\partial S^2} + \frac{\partial^2 \rho}{\partial T^2} = \frac{1}{a}\left(\frac{\partial a}{\partial S}\frac{\partial \rho}{\partial S} + \frac{\partial a}{\partial T}\frac{\partial \rho}{\partial T}\right) \qquad (9)$$

and to the similar equation for γ

$$\frac{\partial^2 \gamma}{\partial S^2} + \frac{\partial^2 \gamma}{\partial T^2} = -\frac{1}{a}\left(\frac{\partial a}{\partial T}\frac{\partial \gamma}{\partial T} + \frac{\partial a}{\partial S}\frac{\partial \gamma}{\partial S}\right) \qquad (10)$$

If it is possible to prove that there exists such a form for the function $a(S,T)$, besides a = const. that simultaneously turns the right sides of the conjugated equations (9) and (10) into zero, then the problem put forward in this communication may be regarded as solved. We do not possess such a proof, and thus leave this question open.

4. For illustrative purposes Fig. 3 is introduced, showing the spatial representation of the equation of state of sea water (Weyl, 1970). The surface of densities may be regarded as a membrane, stretched on the figured boundary contour, shown by a heavy line. The function ρ has in the interior neither maximums nor minimums, but the condition of equality of any value of ρ and of the mean of its values for the four neighbouring points of the finite-difference grid is, strictly speaking, not fulfilled.

The author has prepared an algorythm for the solution of the Dirichlet problem for a quadrilateral domain (Fig. 1)

$$0 \leqslant S \leqslant 40\,‰ \; ; \quad -2 \leqslant T \leqslant 30\,^\circ\mathrm{C}$$

based, for test reasons, on Knudsen's values of density (specific volume) on its boundaries. The purpose of this calculation is to determine in which part of the T-S domain the maximal deviations will take place between the values of ρ obtained through the application of the Laplace equation and Knudsen's interior values.

5. For theoretical purposes, it might be considered that the density of sea water satisfies the Laplace equation (1), since the errors due to this approximation are extremely small ($\sim 1 \cdot 10^{-5} \div 2 \cdot 10^{-5}$); in other words, the equation of state might be approximated by assuming that it satisfies the Laplace equation.

However, as stated above, we do not possess a proof that the function ρ is harmonic in general (i.e. for constructing the true equation of state). Nevertheless, let us consider in a very general sense the problem of solving equation (1), bearing in mind how greatly we might thus reduce the volume of experiments for the determination of the equation of state.

The Dirichlet problem. The resolution of the Dirichlet problem under the boundary conditions formulated above is tricky, because two of the four boundaries of the oceanic range of sea water are arbitrary and the other two are the boundaries of phase transitions and processes of transformations within solutions.

Fig. 4 might explain this consideration. It should be noted here that at least the determination of the parameters of pure water in one series of experiments with sea water is absolutely necessary.

The Neumann problem for S–T plane is subject to the boundary condition

$$\oint \frac{\partial\rho}{\partial S}dS + \frac{\partial\rho}{\partial T}dT = 0 \qquad (11)$$

where $\oint$ denotes the line integral along a closed contour (circulation), with a given value of ρ at one point of the contour (say, at the point of maximal density of pure water on the T–axis). The concept of a line integral in the S–T plane was introduced by the writer (Mamayev, 1962); equation (11) follows from the work cited.

Empirical determination of thermal expansion $\frac{\partial\rho}{\partial T}$ and saline "contraction" $\frac{\partial\rho}{\partial S}$ has definite advantages in comparison with direct determination of the density ρ itself.

For other related problems, see Mamayev (1970).

Acknowledgement

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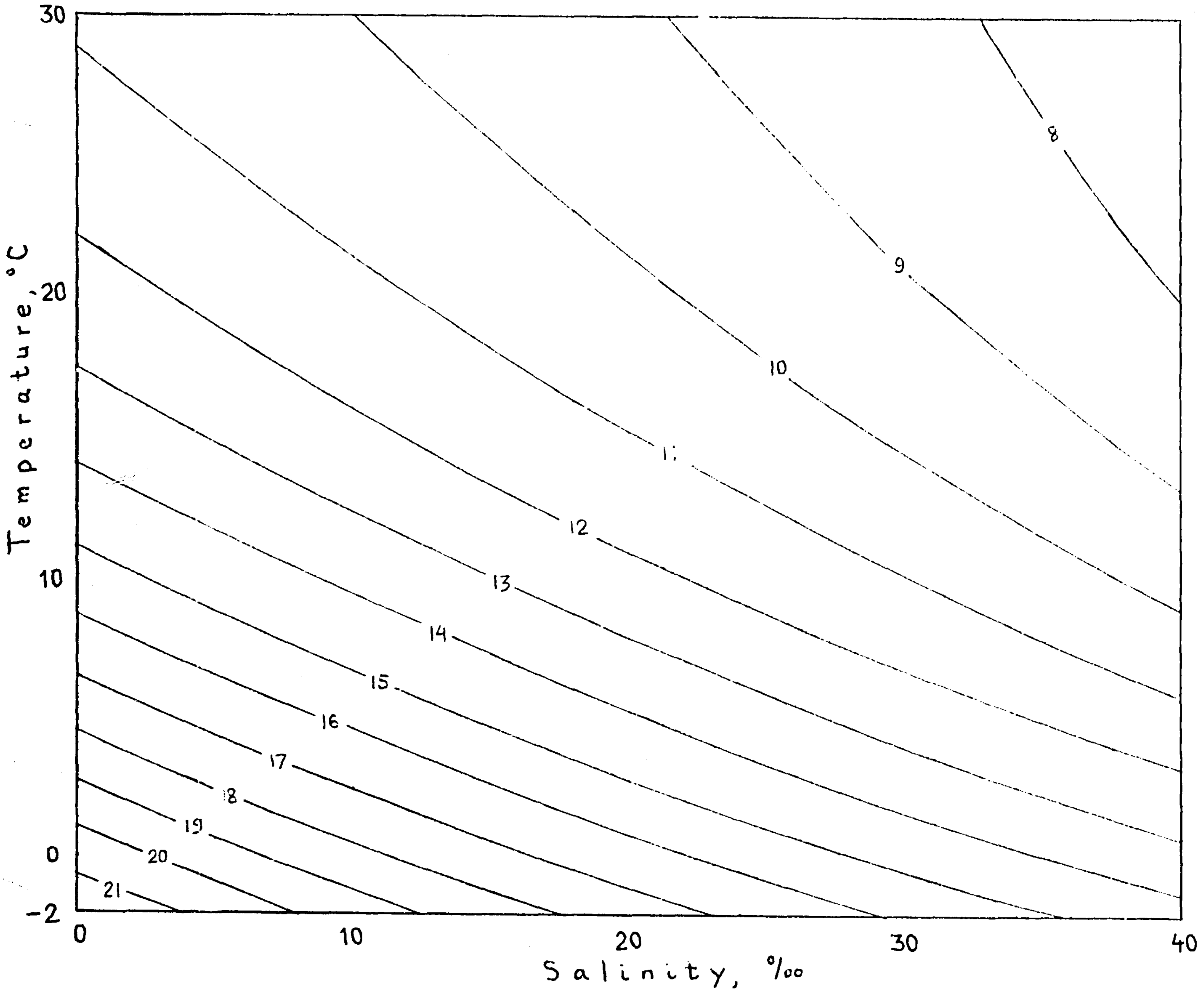

Fig 1 $10^6\left(\frac{\partial^2\alpha}{\partial S^2}+\frac{\partial^2\alpha}{\partial T^2}\right)=f(S,T,0)$

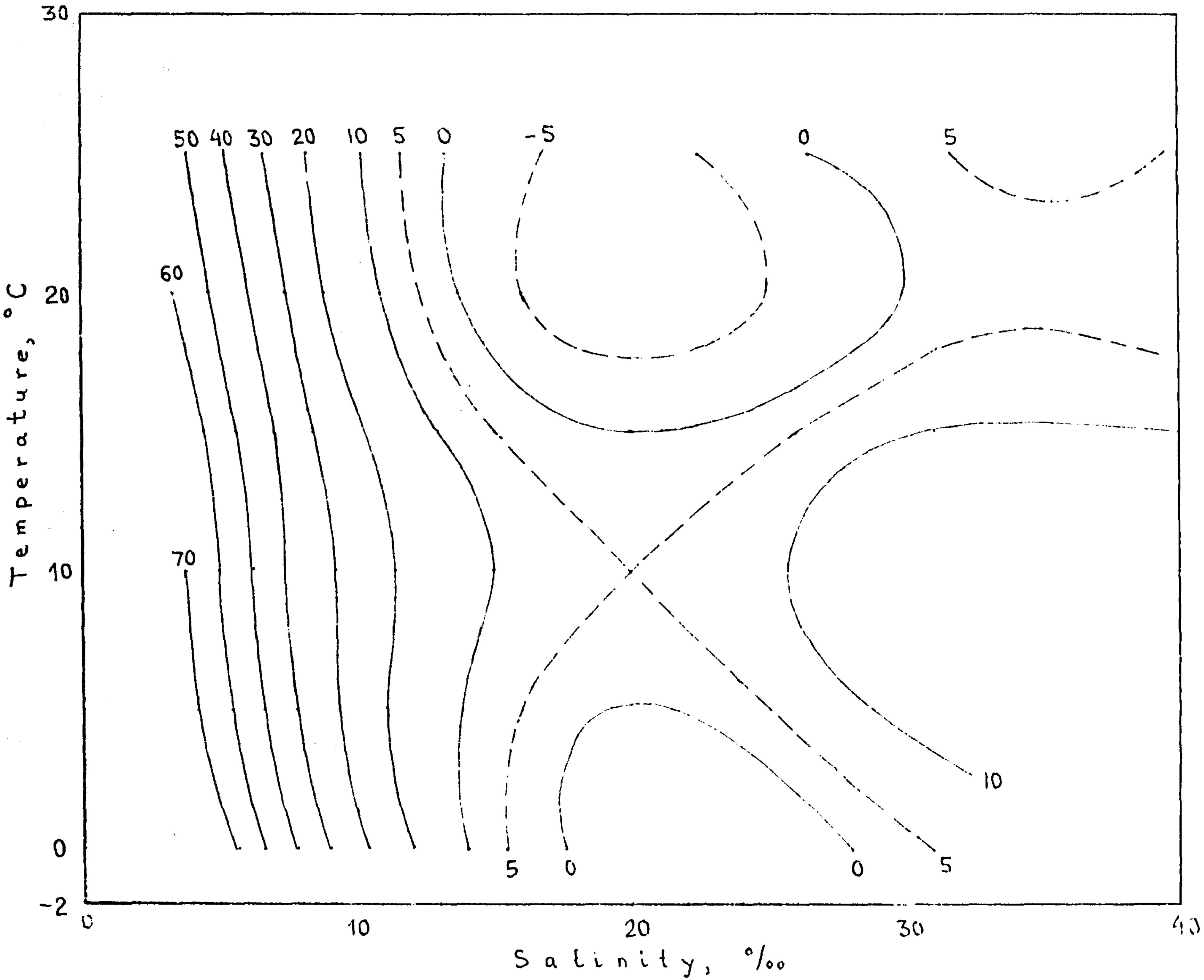

Fig. 2. $10^6[\rho_c - \rho_K] = f(S, T, 0)$

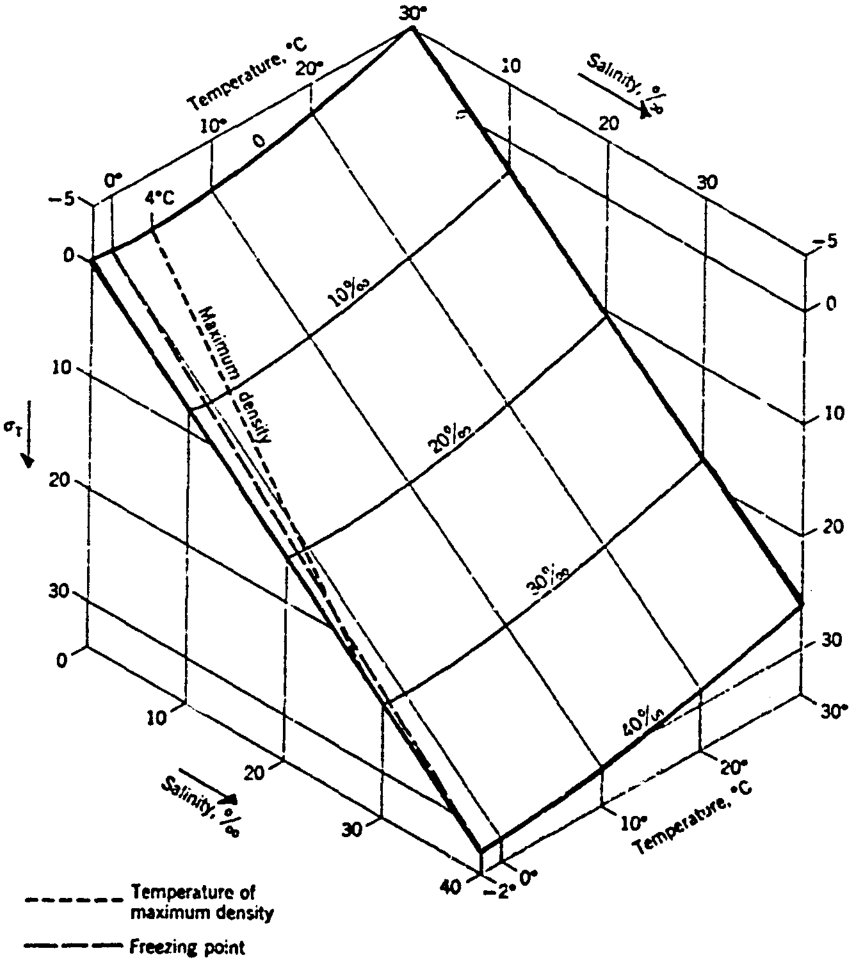

Figure 3 The density of sea water as a function of temperature and salinity at a pressure of one atmosphere: [σ_T = (density − 1) × 1000. e.g. $\sigma_T = 15$, density = 1.015 g cm^{-3}].

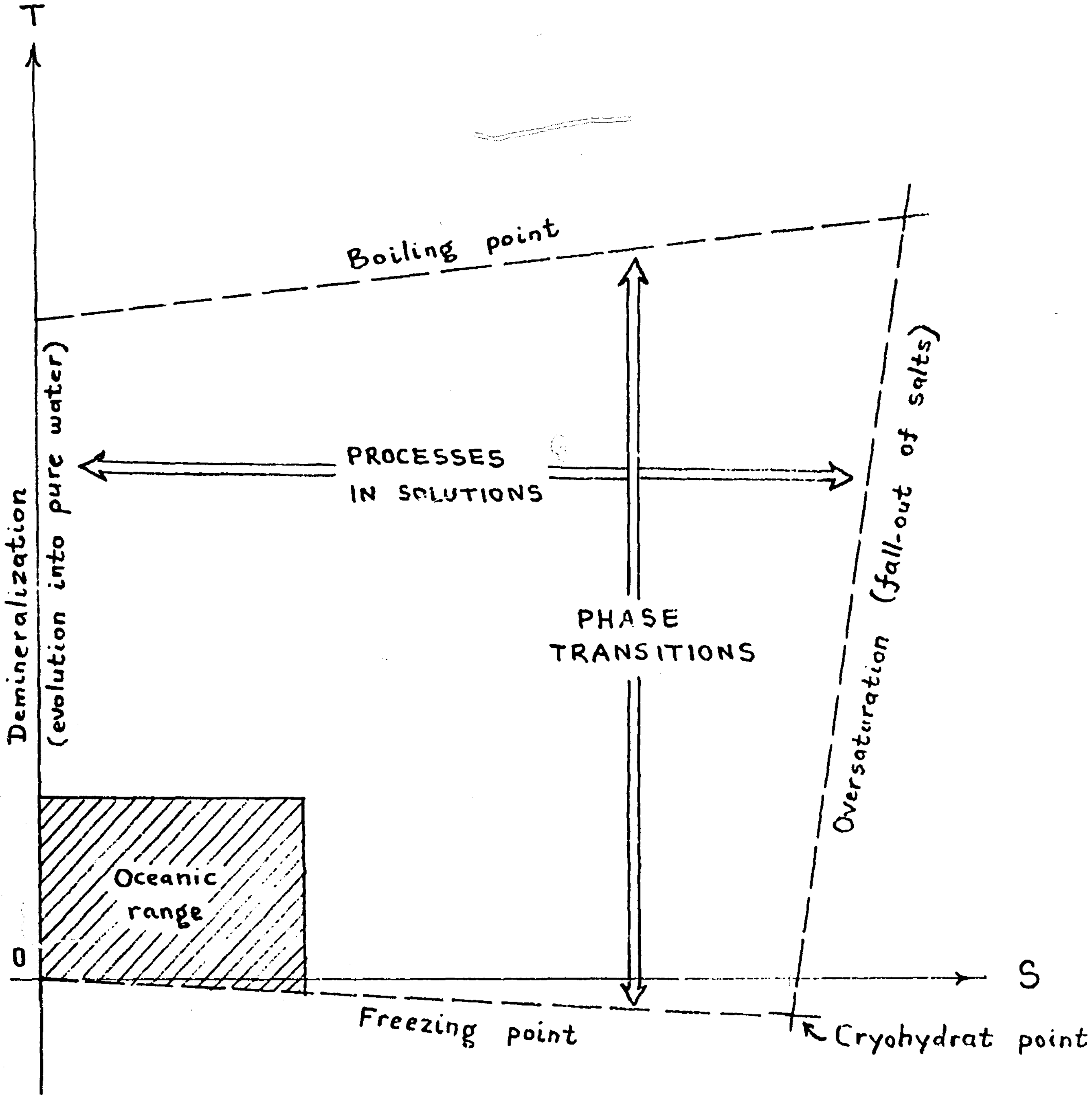
T
Boiling point
Demineralization (evolution into pure water)
PROCESSES IN SOLUTIONS
PHASE TRANSITIONS
Oversaturation (fall-out of salts)
Oceanic range
0
S
Freezing point
Cryohydrat point

Fig. 4 (cf. text)