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Third report of the Joint Panel on Oceanographic Tables and Standards

Berne, 4-5 October 1967
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UNESCO TECHNICAL PAPERS IN MARINE SCIENCE, No.8

THIRD REPORT OF THE JOINT PANEL ON OCEANOGRAPHIC TABLES AND STANDARDS

Berne, 4-5 October 1967

jointly sponsored by the

United Nations Educational, Scientific and Cultural Organization

International Council for the Exploration of the Sea

Scientific Committee on Oceanic Research

International Association of Physical Oceanography

1968

The scientific views expressed here are those of experts participating in the work of the Panel and not necessarily those of Unesco or other sponsoring organizations.

The following members of the Panel attended the meeting in Berne, Switzerland, on 4 - 5 October 1967:-

Prof. Dr. G. Dietrich	-	Federal Republic of Germany
Dr. N.P. Fofonoff	-	U.S.A.
Mr. F. Hermann	-	Denmark
Dr. G.N. Ivanov-Frantzkevich	-	U.S.S.R.
Prof. Dr. W. Kroebel	-	Federal Republic of Germany
Dr. F.H. Fisher	-	U.S.A.
Dr. F. Culkin	-	United Kingdom

Professor O. Saelen (Norway) sent apologies for his unavoidable absence.

Other participants of the meeting included:-

Mr. J. Crease	-	United Kingdom
Prof. C. Eckart	-	U.S.A.
Mr. G. Girard	-	France
Dr. K. Grasshoff	-	Federal Republic of Germany
Mr. M. Menache´	-	France
Prof. Y. Miyake	-	Japan
Dr. J.S.M. Rusby	-	United Kingdom
Mr. M.J. Tucker	-	United Kingdom
Prof. W.S. Wooster	-	U.S.A.
Dr. K.N. Fedorov	-	UNESCO

In opening the meeting, Dr. Fedorov referred to the sad death of the Panel's Chairman, Dr. R.A. Cox, in March 1967, and the Panel observed one minute's silence in his memory. Mr. F. Hermann was then elected Chairman and Dr. F. Culkin was asked to act as Rapporteur.

Reports were given to the Panel on the progress of work in various laboratories. The following is a summary of these reports:-

Dr. G. Reusmann
Institut für Meereskunde
Niemannsweg 11
23 Kiel
Federal Republic of Germany

The following determinations have been carried out on more than 50 samples collected from different depths and different water masses in the Baltic:

Chlorinity
Specific gravity
Conductivity ratio
Salinity (gravimetric)
Major anions and cations

In this work it was considered necessary to equilibrate the samples with air before measuring conductivity because of the influence of the CO_2 system (as indicated by pH) on the conductivity. The most serious problem encountered has been that of temperature measurement. It has not been possible to have the Quartz Crystal Thermometer calibrated to better than 0.002°C because of instrumental instability. The results of the investigation suggest that some of the calcium in Baltic sea water is complexed by carbonate and sulphate and hence does not contribute as much to conductivity as was previously thought. It is intended to continue these investigations for several years in order to study the effect of stagnation periods. Then, from the final collection of data, a regional correction table with a simple chemical property as basis, will be prepared.

Dr. G.Y. Ryskin
Institute of Technical Physics
Academy of Sciences of the USSR
Leningrad
U.S.S.R.

Dr. Ivanov-Frantzkevich reported that determinations of density and thermal expansion of sea water were being carried out by Dr. Ryskin, using a float method which has an accuracy of $\pm 1 \times 10^{-6}$. (English translations of two articles by Dr. Ryskin are appended to this report as Annex I.) It is hoped to carry out measurements on a number of samples which were supplied by Dr. R.A. Cox.

Professor Dr. W. Kroebel
Institut für Angewandte Physik der Universität Kiel
Neue Universität, Haus 34
23 Kiel
Federal Republic of Germany

The following work is in progress:-

1) Measurement of conductivity as a function of pressure, temperature and salinity.

2) Measurement of ion mobility in sea water after the Hall effect.

3) Density as a function of sound velocity, temperature and conductivity with a view to arriving at explicit expressions.

4) The absolute determination of sound velocity as a function of pressure, temperature and salinity.

Dr. F.H. Fisher
Marine Physical Laboratory
Scripps Institution of Oceanography
San Diego, California 92152
U.S.A.

The following work on sea water is proposed:-

1) Density.

2) Sound velocity.

3) Electrical conductivity.

4) Dielectric constant.

5) Viscosity.

6) Transport numbers of individual ions.

7) Thermal expansion by the Rayleigh Benard method.

8) Specific heat at constant pressure.

9) Thermal conductivity

National Institute of Oceanography
Wormley, Godalming
Surrey
England

Absolute electrical conductivity of sea water
(Mr. M.J. Tucker and Mr. C. Clayson).

Mr. Tucker gave an account of some of the proposed modifications to the existing apparatus. These include a longer quartz cell and an interferometric method of

measuring the electrode displacement. The National Physical Laboratory have reported that the Quartz Crystal Thermometer can only be calibrated to 0.002°C because of instrumental instability but it is hoped to overcome this problem.

Specific gravity (Mr. M.J.M. McCartney).

Dr. Culkin reported that a series of measurements at 17.5°C, on sea waters covering the range 0 - 42‰, was almost complete. It is intended to carry out similar measurements at other temperatures, though some difficulties were expected at temperatures higher than 20°C. because of bubble formation on the float (Professor Kroebel suggested that this might be avoided by subjecting the sample to a short ultrasonic vibrational treatment before immersing the float.

Refractive index anomaly (Dr. J.S.M. Rusby).

The results of this investigation have recently been published (Deep-Sea Res. 1967, 14, 427-39) and will form the basis of an addition to the International Oceanographic Tables later this year (1967). Dr. Rusby discussed some of the problems involved in developing a routine method for obtaining salinity from refractive index anomaly at sea.

K. Schleicher and A. Bradshaw
Woods Hole Oceanographic Institution
Woods Hole, Massachusetts 02543
U.S.A.

Dr. N.P. Fofonoff reported that Schleicher and Bradshaw were making measurements of the thermal expansion of water under pressure. Measurements were also being made on sea water of salinity 35‰ over the temperature range -2°C. to 30°C. (2° intervals).

Mr. F. Hermann
Charlottenlund Slot
Charlottenlund
Denmark

Mr. Hermann presented his provisional report "The production and analysis of the chlorinity of a new primary standard sea water" and said that he hoped Professor D. Carritt would also determine the chlorinity of the new standard.

There was some discussion about the preparation of samples for specific gravity and electrical conductivity measurements. Mr. Menaché considered that the reference water for the specific gravity measurements should be free from dissolved gases, for the reasons outlined in the communication "Le problème du liquide de référence pour la détermination de la masse volumique de l'eau de mer", a copy of which is attached to this report as Annex II. Dr. Culkin and Dr. Grasshoff felt that, although such a reference liquid would have certain advantages they were outweighed by the difficulty of preparing and working with it. The Chairman pointed out that the difference in density between air saturated and air-free waters was only about 0.003 in 6_t.

Dr. Grasshoff stressed that it was essential in conductivity measurements that all samples should have the same pH. The simplest way of achieving this was to equilibrate the sample with air. The Chairman asked Dr. Grasshoff to prepare a report on the effect of change of pH on conductivity. This report will be published as a separate scientific paper.

Mr. Menaché recommended that several batches should be made of the specific gravity reference standard by the method of Cox and McCartney and that samples of each batch should be analysed for oxygen-18 and deuterium by several different laboratories. He also offered to make enquiries about having these analyses carried out.

The Chairman suggested that he, Mr. Menaché and Mr. Girard should assess the effect of natural variations in isotopic ratios on density.

Distribution of International Oceanographic Tables

Dr. Fedorov reported that UNESCO had distributed free copies of the new Tables to approximately 1000 laboratories. Copyright had been granted to the USSR authorities to reproduce and distribute further 2000 copies for internal use. The Bissett-Berman Co. were now including copies of the new Tables in the handbook of their inductive salinometer. Misprints had been noted in the Introduction to the International Oceanographic Tables and it is intended to correct these in new introductory pages which will be issued to all users of the Tables. Dr. Fedorov said that the refractive index tables were now being printed and should be ready by the end of 1967. Professor Wooster suggested that announcements of the issue of additional tables should be made in oceanographic journals and Dr. Fedorov said that this would be done. The Panel then discussed future additions to the Tables.

Additions to the International Oceanographic Tables

Dr. Grasshoff reviewed the literature on the solubility of oxygen in seawater and concluded that the recently published figures by E.J. Green and D.E. Carritt were the most reliable. The Sub-Committee on Chemical Analysis of Sea Water intends to recommend to the Hydrographic Committee of ICES that this data should be used as the basis of new tables of oxygen saturation of sea water. The Panel resolved that, if its recommendation were accepted, Dr. Green and Dr. Grasshoff should be asked to prepare the tables, which would then be distributed by UNESCO as a new instalment of the International Oceanographic Tables.

There was some discussion on the desirability of publishing chlorosity tables. Professor Wooster considered them unnecessary but other members of the Panel felt that they would be very useful to laboratories which had no computing facilities. It was decided that a Sub-Committee consisting of the Chairman, Mr. Menaché and Dr. Grasshoff should prepare the necessary tables.

The following is a list of proposed future additions to the International Oceanographic Tables:-

1) Refractive index anomaly/salinity (Dr. J.S.M. Rusby) - in print.

2) Oxygen saturation values for sea water (Dr. E.J. Green, Massachusetts Institute of Technology, and Dr. K. Grasshoff) - ready for printing in 1967 if ICES accept the recommendation that the data published by Green and Carritt should be used.

3) Chlorosity from chlorinity or salinity (Mr. F. Hermann, Mr. Menaché and Dr. K. Grasshoff) - ready early in 1968.

4) Specific gravity from salinity or conductivity. (Mr. M.J.M. McCartney and the late Dr. R.A. Cox, NIO) - probably late 1968.

5) Absolute electrical conductivity of sea water (Mr. M.J. Tucker, Mr. C. Clayson and the late Dr. R.A. Cox, NIO) - probably 1969.

In the concluding session Professor Wooster asked for a statement on present knowledge of the equation of state of sea water and the Panel was addressed by Professor Eckart and Dr. Fofonoff. It was suggested that a monograph should be written on the equation of state of sea water to clarify the situation and to show the oceanographer which measurements are still needed. Professor Eckart said he was working on such a monograph.

Dr. Fedorov said that it had been the intention of Dr. R.A. Cox to write a monograph on salinity of sea water and its determination, to be published by UNESCO. The Panel felt that the monograph should still be written, preferably by someone from NIO, and Mr. Crease and Dr. Culkin agreed to collaborate on this.

Changes in Membership

Professor G. Dietrich, a founder member and former Chairman of the Panel, expressed his wish to resign and proposed that he should be replaced as SCOR representative by Dr. K. Grasshoff.

Mr. F. Hermann proposed that ICES should be asked to nominate Dr. F. Culkin as their representative, to replace the late Dr. R.A. Cox.

Dr. Fedorov proposed that Mr. Menaché should be a UNESCO representative on the Panel. Mr. Menaché was also asked to represent the Panel on the IUGG Committee on Critical Data.

The revised list of the Panel's members is given as Annex III.

A draft resolution was then submitted by the Panel to IAPO requesting approval of the new definition of salinity in terms of electrical conductivity. It was understood that the definition may be subject to modification when the effect of pH on conductivity is known. The General Assembly of IAPO * approved the above draft. The approved Resolution is given in Annex IV.

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* Now IAPSO - International Association of Physical Sciences of the Ocean.

Translations into English

of papers by B. Konstantinov, G.Ia. Kyskin and others on methods of measurements of the coefficients of expansion and compressibility.

Zhurnal Tekhnicheskoi Fiziki, 28, No. 8, 1740-1747, 1958.
Translation from:- Soviet Physics - Technical Physics, 3, (8), 1604-1611, 1958.

ИЗМЕРЕНИЕ КОЭФФИЦИЕНТОВ РАСШИРЕНИЯ NaCl, LiF, KCl, KBr ФЛОТАЦИОННЫМ МЕТОДОМ

Б. П. Константинов, З. Н. Ефремова и Г. Я. Рыскин

MEASUREMENT OF THE COEFFICIENTS OF EXPANSION OF NaCl, LiF, KCl and KBr BY THE FLOTATION METHOD

B. P. Konstantinov, Z. N. Efremova and G. Ia. Ryskin

The technique of the measurement of coefficients of expansion by the flotation method is described and the results of measurements for NaCl, KCl, KBr and LiF are given. The values obtained are in close agreement with the corresponding data of x-ray and interferometer measurements. The error of the method does not exceed 0.5-1.0%.

The coefficients of thermal expansion of NaCl, KCl, KBr and LiF have been repeatedly measured by several methods. The results of the measurements are in agreement within the limits of error of the measurements, which are about 1% for interferometer and x-ray methods and 3-5% for dilatometer measurements. Evidently, the interferometer and the x-ray data are to be regarded as being the most reliable.

In a recently published communication [1], a new flotation method was proposed for measuring the coefficients of volumetric expansion, γ_c, of crystals. Estimation of the error of this method showed that the error of a single measurement ought not to exceed 1% of the measured magnitude. The paper did not, however, give data on the experimental confirmation of the method.

The present paper describes the technique of the measurement of γ_c by the flotation method and gives the results of measurements for NaCl, KCl, KBr and LiF.

The flotation method of measuring the coefficient of volumetric expansion γ_c is based on the accurate measurement of the difference in the densities of a float of known coefficient of expansion and of the investigated crystal. It is necessary to measure directly merely the flotation temperatures of the float and crystal in the two flotation liquids and the coefficients of expansion of these liquids.

The mean value of $\bar{\gamma}_c$ in the temperature range T_{1c}-T_{2c} is calculated from these data by means of formula (1)

$$\bar{\gamma}_c = \frac{\bar{\beta}_{2\,liq}(T_{2c}-T_{2f}) - \bar{\beta}_{1\,liq}(T_{1c}-T_{1f}) + \bar{\beta}_f(T_{2f}-T_{1f})}{\bar{\rho}_c(T_{2c}-T_{1c})} \qquad (1)$$

where T_{1f} and T_{1c} are the flotation temperatures of float and crystal in the first liquid and T_{2c} and T_{2f} are the corresponding values for the second liquid; $\bar{\beta}_f$, $\bar{\beta}_{2\,liq}$, $\bar{\beta}_{1liq}$ are the mean density variations for a temperature variation by 1°C: $\bar{\beta}_f$ – for the float in the range $T_{2f} - T_{1f}$; $\bar{\beta}_{1liq}$ for the first liquid in the range $T_{1c} - T_{1f}$; $\bar{\beta}_{2\,liq}$ for the second liquid in the range $T_{2c} - T_{2f}$; $\bar{\rho}_c$ is the mean value of the density of the crystal in the temperature range $T_{2c} - T_{1c}$.

Experimental Setup

The measurement of $\bar{\gamma}_c$ consists of the following operations: 1) growing the crystals of the investigated compound; 2) preparing the floats; 3) preparing the flotation mixtures; 4) measuring the flotation temperatures of crystals and float; 5) determining $\bar{\beta}_{liq}$ of the flotation mixtures.

The following is a description of the operations enumerated.

1. Production of crystals. For the measurement of the coefficient of expansion by the flotation method, any crystals are suitable, either natural or artificial, provided they have no inclusions of foreign matter and no cracks. In our measurements we used crystals grown from melts of the well purified compounds. The degree of purity was checked by spectrum analysis. The crystals were grown on the end of a platinum point and had the form of hemispheres 2-4 mm in diameter.

2. Preparation of the floats. The floats were made from fused quartz. For measuring γ_c of NaCl and KCl, the density of which is less than that of quartz, the floats used contained air bubbles, and for measuring the coefficients of expansion of KBr and LiF, floats with platinum fused internally in them were used.

The technique of preparing the floats differs little from the methods described in the literature for the preparation of floats used in the analysis of the isotopic constitution of water [2]. The accurate adjustment of the density of the floats was effected by etching them in a saturated aqueous solution of ammonium fluoride. By comparing from time to time the flotation temperature of the floats and corresponding crystals, it was possible to obtain floats, the density of which differed from the density of the given crystal by an amount which was as small as desired. It should be noted that when the floats are etched in a solution of NH_4F, their surface remains smooth and bright.

3. Preparation of the flotation mixtures. A liquid having at the given temperature a density equal to the density of the investigated crystal was prepared by mixing two components, one of which had a density greater than that of the crystal and the other a density less than that of the crystal. The density of such a flotation mixture must remain constant in the limits of accuracy of the flotation measurements (0.2-0.5γ), at least for a time sufficient to permit measurement of the flotation temperature. To satisfy this fundamental requirement, the following conditions must be satisfied: 1) the solubility of the crystal investigated must be negligibly low; 2) the components of the mixture must be chemically stable in the temperature range investigated; 3) evaporation of the liquid must be small and not accompanied by any change in density.

The preparation of liquids satisfying the conditions enumerated usually does not give rise to any difficulties. We used mixtures of bromoform and ethylene bromide, bromoform and n-hexanol, and others. The bromoform, ethylene bromide, and other halogen derivatives were dehydrated by means of phosphorus pentoxide, and the alcohols by boiling with shavings of metallic calcium under a reflux condenser. After this treatment, the liquid was distilled in a vacuum (5-15 mm Hg). The distilled reagents and mixtures were kept in stoppered vessels in desiccators with fused KOH.

4. Measurement of the flotation temperature. The crystals and floats were lowered into a measuring test tube containing the flotation mixture in an amount of 1.5-2 mm^3. The test tube was closed with a ground-glass stopper and placed in the socket of a thermostat. The temperature in the thermostat was regulated with an accuracy of up to 0.002°C by means of a laboratory autotransformer by varying the current passing through the winding of an electrical heating element immersed in the thermostat.

The movements of floats and crystals were observed through a microscope (MIR) fixed to a stand, set up in front of the thermostat. Fixed to the same stand was a microscope for reading a Beckmann thermometer graduated in 0.01°C.

The actual measurement of the flotation temperature was carried out as follows. The temperature in the thermostat was raised and lowered continuously, so that the crystal (float) correspondingly sank and floated. The interval between the temperatures of floating and sinking was gradually narrowed until it was 0.002-0.004°C. The temperature corresponding to the mean of the last interval was equal to the flotation temperature of the crystal (float) with an error not exceeding half the interval.

5. Determination of $\bar{\beta}_{liq}$ of the flotation mixtures. The temperature coefficient of the density of the flotation mixtures was determined by the piknometer method. A quartz piknometer with a capacity of 24 cc and a capillary 0.1 mm in diameter was used for this purpose. The piknometer was filled and emptied by means of a fore-vacuum pump.

For measuring $\bar{\beta}_{liq}$ in the range $T_1 - T_2$ where $T_1 < T_2$, the piknometer was filled with the investigated liquid at a temperature below T_1 and then placed in a thermostat heated to T_1. The temperature in the thermostat was kept constant with an accuracy of ±0.002°C and was measured by means of a very accurate thermometer

(of the Beckmann type) graduated in 0.01°C.

The liquid escaping from the piknometer during the heating of the latter was removed from the end of the capillary by means of filter paper. Ten to fifteen minutes after the escape of liquid had stopped and its meniscus stood at the level of the capillary tip, the piknometer was removed from the thermostat, washed with distilled ethyl alcohol from a wash bottle, and weighed on an analytical balance. The accuracy of weighing was ± 0.2 mg.

In this way, the weight of piknometer with liquid was determined, corresponding to several temperatures within the range $T_1 - T_2$, separated from each other by about 1°C. At the same time, the range of measurement $T_1 - T_2$ was selected so as to comprise the points T_{2c} and T_{1f} of interest to us and so that all the temperature variations could be measured on one thermometer, i.e., within the limits of 5°C.

The piknometer measurements of $\bar{\beta}_{liq}$ were very long and tedious. In this connection, it should be noted that in a number of cases, the value of $\bar{\beta}_{liq}$ for the mixtures can be calculated from the values of β_1 and β_2 given in the tables for the pure components of which the mixture consists. Calculation is based on the assumption that $\bar{\beta}$ is additive and is carried out according to the formula

$$\bar{\beta}_{mix} = \beta_1 x + \beta_2 (1 - x), \tag{2}$$

where x is the proportion by volume of the first component of the mixture.

Experimental confirmation of formula (2) for mixtures of bromoform and ethyl bromide showed that within the limits of accuracy of the measurement of β (0.5%), the calculated values agreed with the experimental values.

Another method of determining β will be described below, the two-float method, giving a considerable reduction in the number of piknometer measurements.

II. Results of the Measurements

Sodium chloride. The crystals of NaCl were grown from a melt of the salt NaCl, mark "khch" (chemically pure). The coefficient of expansion of a natural crystal of NaCl (rock salt) was measured at the same time. The basic flotation liquid used was ethylene bromide, the density of which coincides with the density of NaCl at about 26.4°C. Bromoform was added to it for measurements at higher temperatures, and n-hexanol for measurements at lower temperatures.

The temperature coefficient of the density of pure ethylene bromide, measured by the piknometer method and in the temperature range 28-25°C, was found to be

$$\beta_{liq} = 2.091 \cdot 10^{-3} \text{g.cm}^{-3} \cdot \text{deg}^{-1}.$$

The measurement of β of other flotation liquids required for the flotation measurements of the coefficient of expansion of NaCl was carried out by the two-float method. The essence of this method consists in the following. The difference in the flotation temperatures of two quartz floats in the investigated liquid and in a liquid for which the value of β is known, for example ethylene bromide, is measured. Since the difference in density $\Delta\rho$ of the two floats is constant, it is evident that

$$\beta_x \Delta T_x = \beta \Delta T, \tag{3}$$

where ΔT_x and ΔT are the differences in the flotation temperatures of the two floats in the investigated liquid and in pure ethylene bromide. From this we find the temperature coefficient of the density of the investigated liquid

$$\beta_x = \frac{\Delta T}{\Delta T_x} \beta. \tag{4}$$

For ΔT equal to 3-4°C, the relative accuracy of the measurement of β_x by the two-float method is about 0.1%, if the true value of β is known. The results of the measurements of all the quantities (except β_f) required for the calculation of γ_c of the crystals according to formula (1) are given in Table 1. In the designation of the

TABLE 1

Results of Measurements of the Coefficient of Expansion of NaCl

Specimen	Composition of flotation mixture	T_c, °C	T_f, °C	$\beta_{liq} \cdot 10^3$, $cm^{-3} \times deg^{-1}$	ρ_{liq}, g/cm^{-3}	$\bar{\rho}_c$, g/cm^{-3}	$\bar{\gamma}_c$, deg^{-1}
Crystal No. 1 grown from the melt	$C_2H_4Br_2$ + n-$C_6H_{11}OH$	22.602	23.973	2.073	2.166	2.164	120.3
	$C_2H_4Br_2$ + $CHBr_3$	33.322	33.359	2.116	2.163		
	$C_2H_4Br_2$ + n-$C_6H_{11}OH$	22.599	23.973	2.073	2.166	2.164	120.3
	$C_2H_4Br_2$ + $CHBr_3$	33.427	33.464	2.116	2.163		
Crystal No. 2	$C_2H_4Br_2$ + n-$C_6H_{11}OH$	33.325	33.359	2.116	2.166	2.164	121.3
	$C_2H_4Br_2$ + $CHBr_3$	22.592	23.973	2.073	2.163		
	$C_2H_4Br_2$ + n-$C_6H_{11}OH$	22.594	23.973	2.116	2.166	2.164	120.5
	$C_2H_4Br_2$ + $CHBr_3$	33.421	33.464	2.073	2.163		
Rock salt	$C_2H_4Br_2$ + n-$C_6H_{11}OH$	33.304	33.359	2.116	2.166	2.164	120.6
	$C_2H_4Br_2$ + $CHBr_3$	22.582	23.973	2.073	2.163		
	$C_2H_4Br_2$ + n-$C_6H_{11}OH$	22.582	23.973	2.116	2.166	2.164	120.0
	$C_2H_4Br_2$ + $CHBr_3$	33.403	33.464	2.073	2.163		
Crystal No. 1	$C_2H_4Br_2$ + $CHBr_3$	33.322	33.359	2.116	2.163	2.161	121.1
		49.781	47.638	2.156	2.159		
		33.427	33.464	2.116	2.163	2.161	121.1
		49.772	47.830	2.156	2.159		
Crystal No. 2	$C_2H_4Br_2$ + $CHBr_3$	33.325	33.359	2.116	2.163	2.161	120.8
		49.776	47.838	2.156	2.159		
		33.421	33.464	2.116	2.163	2.161	121.3
		49.771	47.830	2.156	2.159		
Rock salt	$C_2H_4Br_2$ + $CHBr_3$	33.304	33.359	2.116	2.163	2.161	121.2
		49.751	47.638	2.156	2.159		
		33.403	33.464	2.116	2.163	2.161	121.6
		—	—	2.156	2.159		
Crystal No. 1	$C_2H_4Br_2$ + $CHBr_3$	33.322	33.359	2.116	2.163	2.159	121.5
		63.388	59.853	2.185	2.155		
Crystal No. 2	$C_2H_4Br_2$ + $CHBr_3$	33.325	33.359	2.116	2.163	2.159	121.4
		63.388	59.853	2.185	2.155		
Rock salt	$C_2H_4Br_2$ + $CHBr_3$	33.304	33.359	2.116	2.163	2.159	121.2
		63.357	59.853	2.185	2.155		

columns corresponding to these quantities, the indices "1" and "2" have been omitted. Of the two lines arranged in pairs, the values given in the first line correspond to the index "1" and those in the second line to the index "2".

The values of $\bar{\rho}_c$ given in the penultimate column of Table 1 were assumed equal to

$$\bar{\rho}_c = \frac{\rho_{1c} + \rho_{2c}}{2} = \frac{\rho_{1liq} + \rho_{2liq}}{2}$$

To find the temperature coefficient of density of the float we made use of the values given in the "International Critical Tables" for the coefficient of expansion of fused quartz: $\gamma_f = 1.1 \cdot 10^{-6}$ deg^{-1} at 0°C and $1.5 \cdot 10^{-6}$ deg^{-1} at 50°C.

It is obvious that $\beta_f = \gamma_f \rho_f$, where ρ_f is the density of the float. The floats and flotation mixtures were selected so that in one liquid the difference $T_{1c} - T_{1f}$ was nearly zero.

If this condition is observed, there is no need to measure $\bar{\beta}_{1liq}$ and the error in the measurement of γ_c is reduced. If the difference $(T_{1c} - T_{1f})$ was not equal to zero but did not exceed 0.1°C, it was assumed in the calculation of γ_c that $\bar{\beta}_{1liq} = \bar{\beta}_{2liq}$.

The results obtained show that the divergence of the values of γ_c, calculated from different measurements

TABLE 2

Coefficient of expansion of KCl and KBr

Salt	Composition of flotation mixture	T_c, °C	T_f, °C	$\beta_{liq} \cdot 10^4$ / cm³ deg	ρ_{liq}, g/cm³	ρ_c, g/cm³	γ_c, deg⁻¹
KBr	$CHBr_3$ + $C_2H_4Br_2$	11.016	11.016	—	2.755	2.7515	117.0
	the same	29.685	27.354	2.546	2.748		
KBr	$CHBr_3$ + $C_2H_4Br_2$	11.016	11.016	—	2.755	2.7515	116.6
	$CHBr_3$ + n-$C_5H_{11}OH$	29.162	26.881	2.522	2.748		
KBr	$CHBr_3$ + $C_2H_4Br_2$	11.016	11.016	—	2.755	2.7485	117.6
	the same	49.664	44.872	2.581	2.742		
KBr	$CHBr_3$ + CH_4Br_2	11.016	11.016	—	2.755	2.7485	117.3
	$CHBr_3$ + n-$C_5H_{11}OH$	49.632	44.845	2.578	2.742		
KCl	C_2HBr_2 + $C_5H_{11}Br$	27.855	27.855	2.01	1.984	1.982	109.1
	the same	48.314	46.125		1.980		
KCl	Dibromopropane (1,3)	14.581	14.748	1.797	1.9894	1.9888	108.7
	the same + $CHBr_3$	19.836	19.377				

for the same crystal, do not exceed 0.7%, i.e., they confirm, in the case of NaCl, the estimation of the accuracy of the flotation method made in reference [1].

The results we have obtained do not confirm the difference observed by Srinivisan [3] between the coefficient of expansion of rock salt and crystals of NaCl grown from the melt. The temperature dependence of γ_c, according to our data, is less pronounced than would follow from Srinivisan's empirical formulas for synthetic crystals

$$\alpha = 39.2 \cdot 10^{-6} + 3.9 \cdot 10^{-8} t^\circ C \quad (5)$$

and for rock salt

$$\alpha = 40.7 \cdot 10^{-6} + 3.3 \cdot 10^{-8} t^\circ C, \quad (6)$$

where α is the coefficient of linear expansion.

Potassium chloride and potassium bromide. All the data required for calculating the coefficients of expansion of KCl and KBr and the results of the measurements are given in Table 2. As in the case of NaCl, the discrepancies between the repeated measurements do not exceed 0.5% and are in agreement with the estimation of the accuracy of the method given in [1]. In the measured temperature ranges, within the limits of accuracy of the flotation method, no temperature dependence of the coefficients of expansion was observed.

Lithium fluoride. The measurements were made on two crystals grown from melts. Mixtures of bromoform and ethylene bromide were used as flotation liquids.

The piknometer method was used for determining the density and temperature coefficient of the density for the mixture in which the flotation temperature of LiF crystals was equal to 29.19°C. In the temperature range 28-30°C, the value of $2.464 \cdot 10^{-3}$ g.cm^{-3} · deg^{-1} was obtained for β.

The measurement of β for the other flotation liquids was made by the two-float method. Unlike the measurements for NaCl, KCl and KBr, the flotation temperatures of LiF were measured in previously evacuated and sealed ampoules. This eliminated fluctuations in the flotation temperatures due to partial evaporation of the liquid, and improved the reproducibility of the results of the measurements. The ampoule containing the liquid, crystals and floats was cooled in liquid air, evacuated by means of a fore-vacuum pump, and then sealed.

The results of measurements of the coefficient of expansion of LiF at different temperatures are given in Table 3. In this series of measurements, special experiments were made to confirm the fundamental condition of

TABLE 3

Coefficient of expansion of LiF

Comp. of flotation mix.	Specimen	T_c, °C	T_f, °C	$\beta_{liq} \cdot 10^3$, g/cm³ · deg	ρ_{liq} g/cm³	ρ_c g/cm³	γ_c, deg^{-1}	γ, according to Sharma's formula
Bromoform and ethylene bromide	Crystal 1	18.00	17.23	2.413	2.639	2.6	96.7	102.8
		29.19	27.284	2.464	2.636			
		18.008	17.231	2.443	2.639	2.6375	96.7	
		29.19	27.284	2.464	2.636			
	Crystal 2	18.083	17.23	2.443	2.639	2.6375	96.04	102.8
		29.19	27.284	2.464	2.636			
		18.090	17.233	2.43	2.639	2.6375	96.05	
		29.19	27.284	2.464	2.636			
	Crystal 1	29.190	27.284	2.464	2.636	2.634	100.4	103.6
		44.525	41.037	2.496	2.632			
		29.193	27.284	2.464	2.636	2.634	100.4	
		44.525	41.037	2.496	2.632			
	Crystal 1	44.525	41.037	2.496	2.632	2.630	104.6	104.7
		55.264	50.674	2.520	2.6288			
		44.530	41.035	2.496	2.632	2.630	104.62	
		55.284	50.674	2.520	2.6288			
	Crystal 2	44.561	41.037	2.496	2.632	2.630	104.4	104.7
		55.284	50.674	2.520	2.6288			
		44.565	41.039	2.496	2.632	2.630	104.4	
		55.284	50.674	2.520	2.6288			
	Crystal 1	55.284	50.674	2.520	2.6288	2.627	108.3	105.8
		70.064	63.888	2.554	2.626			
		55.290	50.675	2.520	2.6288	2.627	108.26	
		70.064	63.888	2.554	2.626			

the applicability of the method: variations in flotation temperatures on transferring the crystals from one liquid to another are due solely to temperature expansion of liquid and crystal and not to other causes, which could produce a variation in density of the crystal (chemical reaction with the liquid, solution, cracks, etc.).

For this purpose, after each measurement in a given liquid, the crystals and floats were transferred to the same control liquid (T_c = 29.19°C).

Repeated measurements showed that in this control liquid, the different ($T_c - T_f$) for a given crystal and float was constant within the limits of accuracy of the flotation measurements, irrespective of whether the previous measurements had been made at high temperatures (up to 75°C) or low temperatures (10°C). The results given in Table 3 confirm the existence of an appreciable temperature dependence of the coefficient of expansion of lithium fluoride, as was obtained by Adenstedt [4] and Sharma [5]. According to our data, however, this dependence is more pronounced than follows from Sharma's empirical formula

$$\alpha = 0.043376 + 0.072054t + 0.0104885t^2 \qquad (7)$$

where α is the coefficient of linear expansion of LiF.

For comparison, the values of γ_c, calculated according to Sharma's formula, are given in the last column of Table 3.

The causes of the discrepancies between the corresponding values of γ_c, obtained by our flotation method and Sharma's interferometer method, have not yet been explained.

Comparison with Data in the Literature

Table 4 gives the results of flotation measurements of the coefficients of expansion of NaCl, KCl, KBr and LiF compared with the data of other authors. The discrepancies with recent x-ray and interferometer measurements do not, as a rule, exceed 2-3%.

TABLE 4

Results of Measurements of $\bar{\gamma}$ for Some Halides

	Method	Temperature range	$\bar{T}$, °C	γ_c, deg^{-1}
		NaCl		
Our data, 1957	Flotation	22.6 - 33.3	27.9	120.3
Fiseau [6], 1867	Flotation	33.3 - 49.8	41.6	121.2
Henglein [7], 1925	Interferometer	15 - 65	40	120
Straumanis, Levins [8], 1938	Dilatometer	0 - 50	25	115
Srinivisan [3], 1955	x-Ray	18 - 67	43	121.5
	Interferometer		20	120
		KCl		
Our data	Flotation	27.9 - 48.3	32.1	109.1
Fiseau [6], 1867	Interferometer	15 - 65	40	114
Henglein [7], 1925	Dilatometer	0 - 50	25	110
Glover [9], 1954	x-Ray		40	108
Srinivisan [3], 1955	Interferometer		40	112.7
		KBr		
Our data, 1957	Flotation	11 - 29	15	116.8
Fiseau [6], 1867	Flotation	11 - 49.6	30.3	117.5
	Interferometer	15 - 65	40	126
Henglein [7], 1925	Dilatometer	0 - 50	25	118
Gott [10], 1942	x-Ray	18 - 100	59	116.4
Connell, H. Martin [11], 1951	x-Ray	18 - 100	59	116.4
		LiF		
Our data	Flotation	17.2 - 27.3	22.3	96.4
Straumanis, Levins, Karlsons [8], 1938	Flotation	27.3 - 41.0	34.2	100.5
	Flotation	44.5 - 55.3	49.9	104.5
	Flotation	55.3 - 70.1	62.7	108.3
Sharma [5], 1950	x-Ray	14.6 - 59.4	37	102.15
	Interferometer		30	103.26

SUMMARY

A detailed description is given of the technique of measuring the coefficients of expansion of crystals of salts by the flotation method.

A float method is proposed for measuring the temperature coefficient β of the density of a liquid, based on the measurement of the difference in flotation temperatures of two floats in the investigated liquid and in a control liquid, for which the true value of β is known.

The coefficients of expansion γ_c for NaCl, KCl, KBr and LiF have been measured close to room temperature. It is shown that the reproducibility of the measured values of γ_c is 0.5-1%. This is in agreement with the estimation of the accuracy of the method made by Konstantinov and Ryskin [1].

The measured values of γ_c are in satisfactory agreement with the results of recent interferometer and x-ray measurements of the coefficients of expansion of the corresponding salts.

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FLOTATION METHOD FOR MEASURING THE COMPRESSIBILITY COEFFICIENTS OF SOLIDS AND LIQUIDS

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Compressibility coefficients are usually measured by piezometric [1] or acoustic [2] methods.

The possibility of using a flotation method for density measurements or for compressibility investigations of solids and liquids was indicated in a previous publication [3].

The present paper derives the basic formulae and describes the measurement system and characteristics of a new flotation method for measuring compressibility coefficients.

Derivation of the Formulae for the Compressibility Coefficients of a Liquid

Let the flotation pressures of two floats at the same temperature in the liquid investigated be represented by p_1 and p_2.

It is clear that:

$$\left.\begin{aligned} \rho_1(p_1) &= \rho_1(p_1) \\ \rho_2(p_2) &= \rho_1(p_2) \\ \rho_2(p_2) &= \rho_2(p_1)[1 + \beta_f(p_2 - p_1)] \end{aligned}\right\}, \tag{1}$$

where $\rho_1(p_1)$, $\rho_2(p_1)$ and $\rho_1(p_1)$ are the densities of the first and second floats and of the liquid at a pressure p_1; and $\rho_2(p_2)$ and $\rho_1(p_2)$ are the densities of the second float and the same liquid at a pressure of p_2; $\bar{\beta}_f$ is the compressibility coefficient of the float.

From (1), the variation in the liquid density with variation in pressure from p_1 to p_2 is equal to:

$$\rho_1(p_2) - \rho_1(p_1) = \rho_2(p_1) - \rho_1(p_1) + \rho_2(p_1)\beta_f(p_2 - p_1). \tag{2}$$

The mean compressibility coefficient of the liquid over the range from p_1 to p_2 is:

$$\bar{\beta}_1 = \frac{1}{\rho_1(p_1)} \frac{\rho_1(p_2) - \rho_1(p_1)}{p_2 - p_1}, \tag{3}$$

and from (2) and (3) taking into account (1) we get:

$$\beta_1 = \frac{\Delta\rho_f}{\rho_1(p_1)} \frac{1}{p_2 - p_1} + \beta_f \frac{\rho_2(p_1)}{\rho_1(p_1)} \tag{4}$$

where $\Delta\rho_f = \rho_2(p_1) - \rho_1(p_1)$.

Since under experimental conditions $\rho_2(p_1)/\rho_1(p_1)$ is very close to unity, it is possible to use the simpler formula:

$$\beta_1 = \frac{\Delta\rho_f}{\rho_1(p_1)} \frac{1}{p_2 - p_1} + \beta_f . \tag{5}$$

The value of $\Delta\rho_f/\rho_1(p_1)$ can be determined by a flotation method. For this purpose it is sufficient to measure the flotation temperature of both floats T_1 and T_2 in a liquid with a known coefficient of thermal expansion $\bar{\gamma}_l$ at constant pressure and to know the coefficient of expansion of the float $\bar{\gamma}_f$

$$\frac{\Delta\rho_f}{\rho_1(p_1)} = (\bar{\gamma}_1 - \bar{\gamma}_f)(T_1 - T_2). \tag{6}$$

From (5) and (6) we get:

$$\beta_1 = (\bar{\gamma}_1 - \bar{\gamma}_f)\frac{T_1 - T_2}{p_2 - p_1} + \beta_f . \tag{7}$$

Thus, in order to measure the compressibility coefficient of the liquid it is sufficient to measure the flotation temperature of the two floats at constant pressure and the flotation pressure of the same floats at constant temperature.

Let us examine the accuracy of this method. The relative error $\delta(\bar{\beta}_l - \bar{\beta}_f)$ in measuring $(\bar{\beta}_l - \bar{\beta}_f)$ is $\delta(\bar{\beta}_1 - \bar{\beta}_f) = \delta(\bar{\gamma}_1 - \bar{\gamma}_f) + \delta(T_1 - T_2) + \delta(p_2 - p_1)$.

Normally $\bar{\gamma}_f \ll \bar{\gamma}_l$. Consequently $\delta(\bar{\gamma}_l - \bar{\gamma}_f) \approx \delta\bar{\gamma}_l$. With average pycnometer measurement accuracy it is possible to estimate the value of $\delta\bar{\gamma}_l$ as 0.1%. Assuming, on the basis of our experimental data and data contained in the literature, that the errors in determining the flotation temperature and pressure amount to ±0.002°C [4] and ±0.01 atm. respectively, we obtain a maximum measurement error of approximately 2% if $p_2 - p_1 = 5$ atm. ($\bar{\beta}_l = 50 \times 10^{-6}$ atm^{-1}, $\bar{\gamma}_l = 10^{-3}$ degree^{-1}). The error decreases as the pressure interval increases.

The compressibility of the liquid can be determined with a single float. If at pressures p_1 and p_2 the flotation temperatures are T_1 and T_2, respectively, we get:

$$\rho(p_1, T_1) = \rho_1(p_1, T_1), \tag{8}$$
$$\rho(p_2, T_2) = \rho_1(p_2, T_2). \tag{9}$$

From (8) and (9):

$$\rho_1(p_2, T_2) - \rho_1(p_1, T_1) = \rho(p_2, T_2) - \rho(p_1, T_1). \tag{10}$$

Expressing the density variations of the liquid and the float by corresponding compressibility and thermal expansion coefficients, we obtain from (10):

$$\rho_1(p_1, T_1)[\bar{\beta}_1(p_2 - p_1) - \bar{\gamma}_1(T_2 - T_1)] = \rho(p_1, T_1)[\bar{\beta}_f(p_2 - p_1) - \bar{\gamma}_f(T_2 - T_1)]. \tag{11}$$

From (8) and (11) we get:

$$\bar{\beta}_1 = (\bar{\gamma}_1 - \bar{\gamma}_f)\frac{T_2 - T_1}{p_2 - p_1} + \beta_f \tag{12}$$

Consequently, when using a single float, it is sufficient to measure the flotation pressure of the float p_2 and p_1 at two temperatures T_2 and T_1. The accuracy of this method determined in the same way as that of the two-float method described earlier, indicates a maximum relative error for an individual measurement of $(\bar{\beta}_l - \bar{\beta}_f)$ of 2% if the pressure difference amounts to 5 atm.

If, in the stead of the two-float method, the single-float method is used to determine compressibility coefficient: for the case of large pressure intervals, it becomes necessary to know the pressure dependence of $\bar{\gamma}_l$.

Derivation of the Formulae for the Compressibility Coefficients of Solids

The single-float method described above can be used to investigate the compressibility of solids. If the compressibility coefficient of the liquid $\bar{\beta}_l$ is known, then the compressibility of the float material can be determined from (12). The error involved is high, amounting to 40-50% if $\bar{\beta}_f < 5 \times 10^{-6}$ atm^{-1}.

A more accurate flotation determination of the compressibility of solids can be obtained by measuring the difference in the density of the crystal and float of known compressibility coefficient in two flotation liquids.

Indicating the flotation pressures of the float and crystal in the first liquid by p_{1f} and p_{1c}, the densities at these pressures by ρ_f (p_{1f}) and $\rho_c(p_{1c})$, and the corresponding values in the second liquid by p_{2f}, p_{2c} and $\rho_f(p_{2f})$, $\rho_c(p_{2c})$ respectively, we obtain:

$$\left.\begin{aligned} \rho_c(p_{1c}) &= \rho_{1l}(p_{1c}), \\ \rho_f(p_{1f}) &= \rho_{1l}(p_{1f}), \end{aligned}\right\} \tag{13}$$

$$\left.\begin{aligned} \rho_c(p_{2c}) &= \rho_{2l}(p_{2c}), \\ \rho_f(p_{2l}) &= \rho_{2l}(p_{2f}). \end{aligned}\right\} \tag{14}$$

From (13) and (14) we get:

$$\begin{aligned} &[\rho_c(p_{2c}) - \rho_c(p_{1c})] - [\rho_f(p_{2f}) - \rho_f(p_{1f})] = \\ &= [\rho_{2l}(p_{2c}) - \rho_{2l}(p_{2f})] - [\rho_{1l}(p_{1c}) - \rho_{1l}(p_{1f})]. \end{aligned} \tag{15}$$

From (3) and (15) we get:

$$\bar{\beta}_c = \frac{\bar{\beta}_{2l}(p_{2c} - p_{2f}) - \bar{\beta}_{1l}(p_{1c} - p_{1f}) + \bar{\beta}_f(p_{2f} - p_{1f})}{p_{2c} - p_{1c}}, \tag{16}$$

where $\bar{\beta}_c$ is the mean compressibility coefficient of the crystal over the range p_{1c} to p_{2c}; $\bar{\beta}_f$ is the mean compressibility coefficient of the float over the range p_{1f} to p_{2f}; $\bar{\beta}_{1l}$ and $\bar{\beta}_{2l}$ are the mean compressibility coefficients of the flotation liquids over the intervals p_{1c} to p_{1f} and p_{2c} to p_{2f}, respectively.

If the first liquid or the float is selected in such a way that $p_{1c} = p_{1f}$, the second term in the numerator on the right-hand side of (16) becomes zero and it is no longer necessary to determine $\bar{\beta}_{1l}$. In this case $\bar{\beta}_c$ is given by the simpler expression:

$$\bar{\beta}_c = (\bar{\beta}_{2l} - \bar{\beta}_f)\frac{p_{2c} - p_{2f}}{p_{2c} - p_{1c}} + \bar{\beta}_f. \tag{17}$$

Thus, in order to determine the compressibility coefficient of the crystal, it is necessary to select a pressure $p_{1c} = p_{1f}$ and a temperature value at which the densities of the float crystal are equal, and then measure the flotation pressures of the float and crystal at the same temperature in another liquid.

The maximum relative error for an individual measurement of $(\bar{\beta}_c - \bar{\beta}_f)$ is:

$$\delta(\bar{\beta}_c - \bar{\beta}_f) = \delta(\bar{\beta}_{sl} - \bar{\beta}_f) + \delta(p_{sc} - p_{lc}) + \delta(p_{sc} - p_{sf}) \quad (18)$$

The relative error in determining $(\bar{\beta}_{sl} - \bar{\beta}_f)$ does not exceed 2%. The accuracy in measuring the flotation pressues is ±0.01 atm; consequently $\delta(p_{sc} - p_{lc}) = 0.5\%$ if $p_{sc} - p_{lc} = 5$ atm. However, the error $\delta(p_{sc} - p_{sf})$ may be considerably larger. Thus, in the case of flotation of a NaCl crystal ($\bar{\beta}_c = 4.2 \times 10^{-6}$ atm^{-1}) and a quartz float ($\bar{\beta}_f = 2.6 \times 10^{-6}$ atm^{-1}) in ethylene bromide ($\bar{\beta}_{sl} = 62.7 \times 10^{-6}$ atom^{-1}) we get from (17):

$$p_{sc} - p_{sf} = \frac{\bar{\beta}_c - \bar{\beta}_f}{\bar{\beta}_{sl} - \bar{\beta}_f}(p_{sc} - p_{lc}) = 0.13 \text{ atmos.}$$

For the given flotation measurement accuracy $\delta(p_{sc} - p_{sf}) = 15\%$ and consequently $\delta(\bar{\beta}_c - \bar{\beta}_f) = 18\%$.

This does not take into account errors in the determination of the pressure and temperature at which the float and crystal densities are equal. In this case, the error $\delta(\bar{\beta}_c - \bar{\beta}_f)$ for NaCl would increase to 25%.

Increase in the difference $p_{sc} - p_{lc}$ to 20-30 atm would apparently decrease the error by 3 to 4 times.

Measurement Technique

The preparation of the flotation liquids and floats and the growth of the crystals were carried out as described in [4].

The experimental measurement system is shown in Fig. 1.

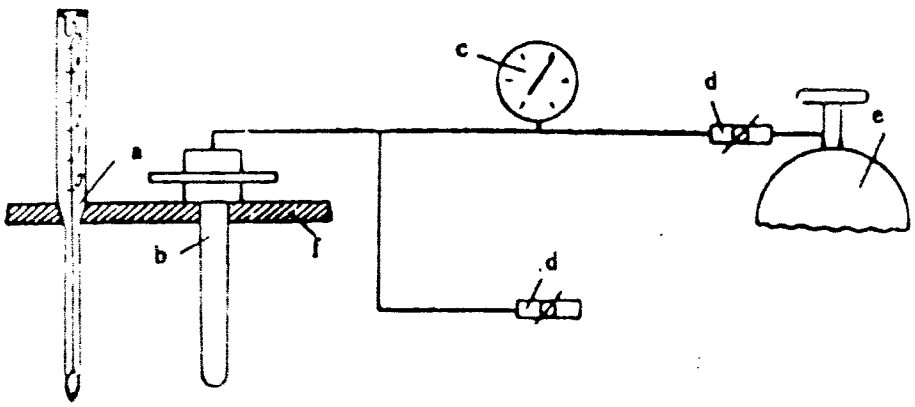

Fig. 1. Experimental arrangement. a) Beckmann thermometer; b) flotation test tube; c) manometer; d) reducer; e) compressed gas cylinder; f) thermostat cover.

The thermostat temperature could be measured with an accuracy of 0.001°C by means of the Beckmann thermometer a graduated in 0.01°C, using a MIR microscope giving sevenfold magnification. The pressure in the flotation tube was produced by means of compressed nitrogen fed from the gas cylinder f, via the reducer d, and was measured by a standard spring operated manometer c, grade 0.2 with an upper limit of 6 kg/cm^2. The reducer g served to relieve the pressure in the system.

Figure 2 shows the test tube and brass cap used for measuring the flotation pressure.* The test tube contains a small glass rod, the lower end of which is located 3 cm above the bottom of the tube but considerably below the level of the liquid in the tube. As a result any density variations arising in the surface layer of the liquid (e.g., due to the solubility of the gas) do not reach the lower level at which the float and crystal are located. This fact was established by special tests which showed that under constant pressure the flotation temperature remained unaltered for a considerable period of time (exceeding 8 hours).

*This construction of a test tube and brass cap was previously used by B. P. Konstantinov and Yu. B. Kesel'man for a similar purpose.

The flotation pressure p_{fl} was determined by finding the minimum pressure interval within the limits of which the float (crystal) changes its direction of motion. The midpoint of this interval was taken as the flotation pressure. It is clear that the error in determining p_{fl} does not amount to more than half of this interval. In our experiments the error amounted to ±0.02 atm. In order to increase the accuracy in determining the flotation pressure we measured the rate of movement of the float for a number of pressure values p close to p_f. These experiments showed that between the limits $p-p_{fl}$ = ±0.5 atm., the rate of movement was dependent on p. Using this relationship it was possible to determine the flotation pressure with an error of less than 0.01 atm.

Measurement Results

The flotation method was used to measure the compressibility coefficients of ethylene bromide, bromoform and NaCl crystals over the pressure range from 1 to 6 kg/cm² at temperatures of 26.4 and 61.6°C for the first, 25.9 and 69.2°C for the second and 26.4°C for the NaCl.

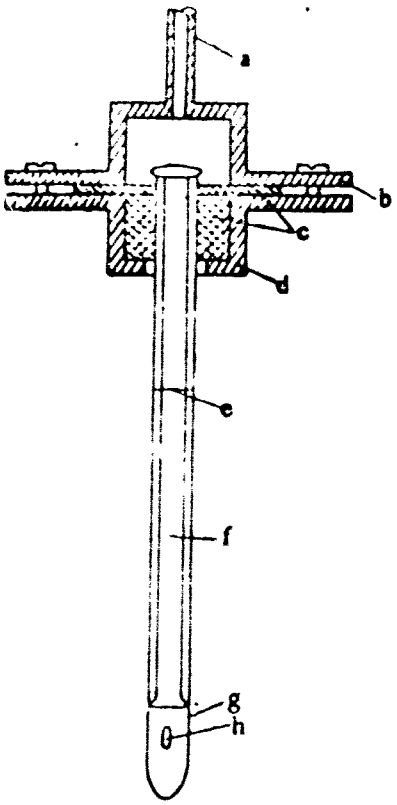

Fig. 2. Flotation test tube a) connecting tube; b) upper brass attachment; c) rubber gasket; d) lower brass attachment; e) liquid level; f) glass rod; g) test tube of length 27 cm, diameter 1 cm; h) float (crystal).

TABLE 1

Results of Compressibility Measurements for Ethylene Bromide at 26.4°C*

Expt. No.	$T_0 - T_1$, °C	$p_0 - p_1$, kg/cm²	$\beta_l \cdot 10^6$, cm²/kg
1	0.257	4.18	61.9
2	0.259	4.18	62.3
3	0.254	4.14	61.7
4	0.258	4.16	62.4
5	0.263	4.24	62.4
6	0.265	4.24	62.8
7	0.270	4.34	62.6
8	0.268	4.34	62.1
9	0.267	4.24	63.3
10	0.279	4.44	63.2
11	0.349	5.60	62.7
12	0.279	4.01	62.9
13	0.349	5.00	63.1
14	0.302	4.75	63.9
15	0.327	5.21	63.1
		Mean	62.7

* In experiments Nos. 1-11, 14 and 15 $\bar{\gamma}_l = 965 \times 10^{-6}$ degree^{-1}, $\bar{\gamma}_f = 1.3 \times 10^{-6}$ degree^{-1}; in experiments Nos. 12 and 13 $\bar{\gamma}_l = 965 \times 10^{-6}$ degree^{-1}, $\bar{\gamma}_f = 121 \times \times 10^{-6}$ degree^{-1}, $\bar{\beta}_f = 4.2 \times 10^{-6}$ cm²/kg (float – natural crystal).

The compressibility of the liquids was measured by means of a single-float method. In calculating $\bar{\beta}_l$ from (12) we used the values of $\bar{\gamma}_l$ given in [4] and tabulated values of $\bar{\beta}_f$ and $\bar{\gamma}_f$ for fused quartz: $\bar{\beta}_f = 2.6 \times \times 10^{-6}$ atm^{-1} [5] and $\bar{\gamma}_f = 1.3 \times 10^{-6}$ degree^{-1} [6].

Air films or bubbles attached to the floats had no significant effect on the values of $\bar{\beta}_f$ and $\bar{\gamma}_f$ obtained for the floats, since their relative volume was small (less than 3%).

The accuracy and reproducibility of the method are indicated by the measurement data given in Table 1 for ethylene bromide at 26.4°C and in Table 2 for sodium chloride at 26.4°C. The data show that the maximum

TABLE 2

Results of Compressibility Measurements for NaCl Crystals at 26.4°C*

Expt. No.	$p_c - p_{1c}$, kg/cm²	$p_{2c} - p_f$, kg/cm²	$(\beta_c - \beta_f) \cdot 10^4$, cm²/kg	$\beta_c \cdot 10^4$, cm²/kg
1	4.93	0.13	1.6	4.2
2	4.39	0.10	1.4	4.0
3	3.97	0.12	1.8	4.4
4	4.24	0.09	1.3	3.9
5	4.29	0.10	1.4	4.0
6	5.18	0.14	1.6	4.2
7	5.41	0.20	2.2	4.8
8	5.44	0.17	1.9	4.5
9	4.53	0.08	1.1	3.7
10	4.67	0.08	1.0	3.6
11	4.96	0.12	1.5	4.1
12	5.21	0.11	1.3	3.9
13	5.20	0.17	2.0	4.6
14	4.77	0.13	1.6	4.2
15	4.71	0.16	2.1	4.7
16	4.95	0.12	1.5	4.1
17	5.00	0.15	1.8	4.4
18	4.90	0.12	1.5	4.1
19	4.89	0.10	1.2	3.8
20	4.88	0.11	1.3	3.9
21	4.94	0.13	1.6	4.2
		Mean	1.6	4.2

*$\bar{\beta}_{2l} = 62.7 \times 10^{-6}$ cm²/kg, $\bar{\beta}_f = 2.6 \times 10^{-6}$ cm²/kg. Experiments 1 to 5 and 6 to 12 were carried out with crystals pulled from the melt; experiments Nos. 13 to 21 with a rock salt crystal.

TABLE 3

Compressibility Coefficients for Ethylene Bromide, Bromoform and Sodium Chloride

Material	Measurement method and literature reference	$\beta \cdot 10^6$ cm³/kg	T°C
Ethylene bromide	Piezometric method* [7]	61	26.4
	Contact piezometer** [8]	61.6	26.4
	Acoustic method [9]	53.1	26.4
	Flotation method	62.7 ±0.1	26.4
	Piezometric method* [7]	76	61.6
	Acoustic method [9]	77.7	61.6
	Flotation	78.0 ±0.2	61.6
Bromoform	Contact piezometer** [8]	57.6	25.9
	Acoustic method [9]	56.6	25.9
	Flotation method	56.0 ±0.2	25.9
	Flotation method	72.2 ±0.2	69.2
NaCl crystals	Two-dimensional compression** [11]	4.26	30
	Acoustic method** [12]	4.31	25
		4.2	25
	Contact piezometer** [10]	4.20 ±0.04	26.4
	Flotation method		

*Measurements within the limits 1-5.25 atm.

**Extrapolated to the pressure value p = 0.

deviation from the arithmetic mean of the complete series of measurements is approximately 2% for ethylene bromide, which is in agreement with the previous estimate of the error in determining liquid compressibility. In the case of NaCl, assuming the true value of $\bar{\beta}_f$ to be known, the maximum deviation from the mean value of $\bar{\beta}_c$ is approximately 15%. Examination of the data obtained indicates that the probable measurement error for liquids is 0.2% and for NaCl crystals 1%.

The results of all the measurements are summarized in Table 3, which for the purpose of comparison gives the isothermal compressibility coefficients of the same compounds measured by other methods. The latter are reduced to the same temperatures at which comparison was made with respect to the temperature dependence obtained in references [7, 9].

The data given in Tables 1 to 3 show that the flotation method is particularly suitable for investigating the compressibility of liquids. The accuracy achieved with this method is comparable with that of the acoustic method, which is generally estimated as 0.25-0.5%. The simplicity of the apparatus and of the experimental arrangement may be mentioned as advantages of the flotation method.

In conclusion it may be said that the flotation method appears very suitable for investigating the compressibility of polymers for which, as a rule, β is somewhat in excess of 10^{-5} atm^{-1}. In this respect it is interesting to note that the density and thermal expansion coefficient of the polymers can be measured simultaneously with the compressibility.

RESULTS

1. A new flotation method for measuring the compressibility coefficients of solids and liquids has been developed.

2. Measurements were made of the compressibility coefficients of ethylene bromide, bromoform and crystalline NaCl.

3. It is shown that the results obtained agree within 1-2% with the results obtained with the same compounds by other methods of measurement.

4. The suitability of the flotation method for investigating the compressibility of liquids and polymers has been demonstrated.

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"Le probleme du liquide de référence pour la détermination de la masse volumique de l'eau de mer"

par

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1. PREAMBULE - Pour l'établissement d'une équation d'état de l'eau de mer, la masse volumique de l'eau de mer devrait être connue, en fonction des paramètres dont elle dépend, à la précision de 1.10^{-3} kg/m^3.

Des déterminations absolues de la masse volumique de l'eau de mer à la précision considérée ne semblent pas aujourd'hui à notre portée. Nous aurions en effet, pour ce faire, le choix entre deux méthodes de mesures:

1. la mesure géométrique directe d'un volume: celui du pycnomètre qui contiendrait l'eau de mer, ou du flotteur qui y serait immergé. Une telle mesure, parfaitement possible aujourd'hui, serait extrêmement coûteuse;

2. le recours à un liquide de référence dont la masse volumique soit connue à une précision d'au moins 1.10^{-3} kg/m^3, pour toutes les valeurs des paramètres dont elle est fonction.

Un tel liquide n'existe malheureusement pas encore. L'eau pure, qui a été utilisée jusqu'ici à cette fin, se révèle être un corps hétérogène, dont la masse volumique est connue avec une précision insuffisante. En effet:

1) La valeur de référence 999,972 kg/m^3 qui a représenté jusqu'ici la masse volumique de l'eau privée d'air à 4°C et sous une atmosphère normale, ne se rapporte pas à une composition isotopique bien définie et, de ce fait, se trouve entachée d'une incertitude de plusieurs unités de la 3ème décimale.

2) Les lois de variation de la masse volumique de l'eau en fonction de la température et de la concentration en gaz atmosphériques dissous sont insuffisamment connues. En particulier, la loi de variation avec la température est connue avec une incertitude qui devient sensible aux températures supérieures à 15°C, et qui croit avec la température.

L'"eau pure" ne convient donc pas comme liquide de référence, à la précision qui nous intéresse.

Il faut espérer qu'un jour proche, une nouvelle étude systématique de la masse volumique de l'eau serait entreprise; ou qu'il serait possible de construire un pycnomètre ou un flotteur dont le volume, dans des conditions physiques bien précisées, serait mesuré par voie géométrique avec une précision suffisante.

En attendant, la difficulté pourrait être tournée si nous pouvions disposer pour faire fonction de liquide de référence, d'un liquide pouvant être obtenu et conservé à l'état de parfaite homogénéité et de grande pureté, et dont la composition isotopique reste invariable. Ce liquide serait utilisé, pour les déterminations de masse volumique, dans des conditions physiques toujours les mêmes. Nous prendrions par exemple une eau pure,

de composition isotopique parfaitement définie et stable, exempte de gaz dissous, à 4°C et sous une atmosphère normale. La masse volumique d'un tel liquide serait une constante qu'on pourrait espérer déterminer plus tard, mais qui, en attendant, permettrait d'obtenir pour l'eau de mer les valeurs de la masse volumique à un facteur constant près, très voisin de 1.

2. CHOIX DU LIQUIDE DE REFERENCE - L'eau obtenue par la méthode de COX et McCARTNEY (1965) à partir de l'eau de mer semble répondre parfaitement aux conditions requises d'un "liquide de référence". Sa composition isotopique serait pratiquement identique à celle de l'eau de mer, laquelle est remarquablement constante. Si l'identité de la composition isotopique des deux liquides est bien établie, l'eau de COX et McCARTNEY aurait, dans des conditions physiques données, une masse volumique stable à $\pm 2.10^{-4} kg/m^3$ près.

Il faudrait, toutefois, bien s'assurer de l'identité de la composition isotopique de cette eau et de l'eau de mer. Cette identité a été vérifiée, à notre connaissance, par une seule série de déterminations, ce qui nous parait insuffisant.

Nous pensons nécessaire:

1) que plusieurs lots d'eau pure soient préparés à des dates différentes par la méthode de COX et McCARTNEY;

2) que des échantillons de chaque lot soient soumis dans plusieurs laboratoires différents, à des analyses isotopiques portant sur l'oxygène-18 et le deuterium. Des déterminations analogues devraient être faites par les mêmes laboratoires sur l'eau de mer à partir de laquelle a été préparé chaque lot d'eau pure.

Il serait en outre avantageux, par une modification appropriée de la méthode de COX et McCARTNEY, d'obtenir et d'enfermer dans les ampoules scellées, de l'eau privée de gaz atmosphériques dissous. Le liquide de référence devrait en effet, à notre avis, être défini comme exempt de gaz dissous pour les deux raisons suivantes:

1) les déterminations de masse volumique sur des liquides contenant une quantité appréciable de gaz dissous sont malaisées et incertaines, à cause de la formation sur les parois du pycnomètre ou sur le flotteur, de bulles de gaz qui faussent les résultats et qu'il est difficile de bien éliminer;

2) la loi de variation de la masse volumique en fonction de sa concentration en gaz dissous est peu précise, et pourrait, dans certaines circonstances, donner lieu à une erreur de l'ordre de $\pm 1.10^{-3}$ kg/m^3.

La proposition des auteurs, de procéder en cas de nécessité à une nouvelle distillation sous vide pour obtenir de l'eau exempte de gaz dissous, ne saurait être retenue, une pareille distillation entrainant inévitablement une modification de la composition isotopique du liquide.

Le choix de l'eau de COX et McCARTNEY aurait, en outre, l'avantage de permettre la préparation du liquide de référence quelques jours seulement avant son utilisation pour des déterminations de masse volumique. On éviterait ainsi les longues conservations en ampoules scellées susceptibles, à la longue, d'altérer la pureté du liquide.

Le moment venu, lorsqu'il sera possible de procéder à la détermination absolue de la masse volumique du liquide de référence, ce liquide pourrait être fraichement préparé en vue de cette détermination fondamentale.

Le liquide de référence pourrait donc être défini comme étant l'eau de COX et McCARTNEY (composition isotopique analogue à celle du S.M.O.W.), exempte de gaz atmosphériques dissous, à la pression d'une atmosphère normale et à une température t°C à choisir. Toutes les déterminations qui seraient faites sur ce liquide de référence devraient l'être dans des conditions aussi voisines que possible de celles figurant dans la définition.

Quelle valeur choisir pour la température t ?

La température du minimum de dilatation thermique de l'eau, 4°C, parait la plus avantageuse à deux points de vue:

1) elle permettrait de se montrer moins exigeant sur la constance et l'homogénéité de la température de l'eau au moment des déterminations. Des variations de quelques dixièmes de deg C au sein du liquide seraient sans conséquence sur la précision des résultats;

2) la loi de variation de la masse volumique en fonction de la concentration en gaz atmosphériques dissous est mieux connue au voisinage de cette température, ayant fait l'objet d'une étude particulière de CHAPPUIS (1910), étude qui a porté sur l'intervalle de température de 5 à 8°C. En cas de nécessité, les corrections correspondantes pourraient être faites avec un risque d'erreur plus faible.

La température 0°C ou celle du point triple de l'eau (+0,01°C) seraient également avantageuses à cause de leur facilité de production et de maintien durant de longues périodes de temps.

Il est toutefois difficile d'opérer à des températures très inférieures à l'ambiante, et de nombreux laboratoires préfèrent travailler à des températures voisines de 20°C. Le choix pour l'eau de référence d'une temperature égale ou supérieure à 20°C, s'il facilite ainsi le travail pratique, présente à la fois un avantage et un inconvénient.

L'avantage est qu'à ces températures, l'influence des gaz dissous devient, d'après MAREK (1891), négligeable.

L'inconvénient, et il est très sérieux, est qu'à ces températures, une variation de 1°C de la température de l'eau entraine pour cette eau

une modification de la masse volumique de l'ordre de $2.10^{-1} kg/m^3$. La constance et l'homogénéité de la température du liquide devraient, dans ces conditions, être assurées, durant les mesures, à quelques millièmes de degré Celsius près.

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Resolution No. 11

The International Association of Physical Oceanography,

Considering that the techniques for precise estimation of dissolved salts in sea water have been significantly improved during recent years, particularly by the introduction of conductivity methods;

Noting the careful experimental work establishing the relationship between conductivity ratio, chlorinity and temperature carried out under the leadership of the late Dr. R.A. Cox;

Further noting the review and endorsement of this work by the Joint ICES/IAPO/SCOR/UNESCO Panel of Experts on Oceanographic Tables and Standards, and the publication by UNESCO of the International Oceanographic Tables, based on this work;

Resolves to endorse the International Oceanographic Tables, and the definition of salinity and the relation between salinity and chlorinity contained in the introduction to Table 1a therein, and to recommend their use by oceanographers.