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The Isotopic Composition of Sea Water

BY EDWARD SMITH GILFILLAN, JR.[1]

At the suggestion of Dr. W. D. Urry, the specific gravity of a sample of deep-sea water taken in Lat. 36°27″ N. Long. 68°38″ W. at a depth of 4500 meters by the Woods Hole Oceanographic Institution has been determined. On the basis of the Boltzmann distribution theorem it can be shown that *if* in the deeper parts of the ocean statistical equilibrium has been reached, pure water from a depth of 4500 meters should be heavier by a maximum of 7 parts per million than water from the surface, due to separation of the various isotopic species in the gravitational field. A difference of 2.3 parts per million between deep-sea water and the laboratory distilled water was found, but we were greatly astonished to discover that surface sea water shows the same difference. This indicates that the sea has not reached statistical equilibrium, and that the observed difference between sea and land water is perhaps due to distillation.

From the experiments of Washburn, Smith and Frandsen[2] the magnitude of the effect to be expected on distillation can be calculated. They found that water of specific gravity 1.001376 (supposedly due to heavy hydrogen) boiled 0.02° higher than ordinary water. Assuming Raoult's law and the known variation of the vapor pressure of water with temperature, one finds that water vapor contains 2.8% less H^1H^2O than the liquid water with which it is in equilibrium. Using the value for the ratio of the amounts of H^1 and H^2 found by Bleakney and Gould[3] (1 in 5000) one finds that the first liquid distilling from a large amount of water should be lighter by 0.3 part per million due to H^2 alone. If one now assumes that the effect of the substitution of O^{18} for O^{16} in the vapor pressure of water is the same as the substitution of H^2 for H^1 and uses the estimate of Mecke and Childs[4] (1 in 630) for the abundance of O^{18} one obtains an effect of 5.0 parts per million. This calculation indicates that the observed effect may be assumed due to O^{18}.

Dr. E. W. Washburn and his associates at the Bureau of Standards observed the effect for deep-sea water during a survey of the density of water from a variety of natural sources in the summer of 1933, but as it was of the same magnitude as their experimental error they did not consider it significant. Dr. Washburn now writes: "... we have rechecked our results and find a value which agrees with yours; that is, there is a real but very small difference between the density of sea water and laboratory distilled water."

Experimental Part

Precise specific gravity measurements by means of totally immersed floats have been made by Richards and Shipley[5] and by Lamb and Lee;[6] the former varied the temperature and the latter used a magnetic control. We have found it convenient and sufficiently accurate to hold the temperature constant at the ice-point and alter the buoyancy of the float by varying the hydrostatic pressure. The measurements were made in test-tubes connected to a pump and manometer system by means of ground joints. The tubes were kept immersed in an ice thermostat and the movement of the float was observed through a double-walled evacuated window by means of a telescope giving three-fold magnification.

The constants of the floats are given in Table I.

TABLE I

Float	Vol. in cc.	Constant[a]	Probable error of single detn., p. p. m.	Probable error of calibration, %
I	3	0.97	1.3	0.4
II	1.5	7.20	4.0	.5
III	0.1	1.75	3.5	1.0
IV	35	0.0293	0.3	3.0

[a] The constant gives the change in specific gravity in parts per million corresponding to a change of 1 mm. of mercury in the hydrostatic pressure. Floats I, II and III do not give a strictly linear relation between pressure and specific gravity and had to be calibrated over their entire ranges.

The floats are made of Pyrex glass and weighted with mercury. Float II was not used in this investigation. The value obtained with Float

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(1) National Research Fellow in Chemistry.

(2) E. W. Washburn, E. P. Smith and M. Frandsen, *Bur. Standards J. Res.*, **11**, 453 (1933).

(3) W. Bleakney and A. J. Gould, *Phys. Rev.*, **44**, 265 (1933).

(4) R. Mecke and W. H. J. Childs, *Z. Physik*, **68**, 362 (1931).

(5) T. W. Richards and J. W. Shipley, THIS JOURNAL, **34**, 599 (1912).

(6) A. B. Lamb and R. E. Lee, *ibid.*, **35**, 1666 (1913).

III is given only for completeness; no weight is attached to it because of its large probable error. The first three floats are more compressible than water; Float IV is less compressible than water and rises with rising pressure. They were calibrated by floating them in potassium chloride solutions of known concentration. The following formula derived from the density data of Baxter and Wallace[7] and of Root[8] was used to compute the specific gravities

$$\delta = 0.7004\,\sigma - 0.244\,\sigma^{3/2} \qquad \delta = d^{0°}_{0°} - 1$$
$$\text{valid for } \sigma \text{ less than } 0.07$$

where δ is the excess of the specific gravity over unity and σ is the ratio wt. KCl in air/wt. water in air. The zero points (floating pressures in purified tap water) of the first three floats were found constant within the experimental error over a period of two months. The application of the method of least squares to the zero points of Float IV indicated that its volume becomes less at the rate of 0.075 p. p. m. per day. Account was taken of this in computing the results.

Water was purified by distillation first from alkaline permanganate and then from very dilute phosphoric acid directly into the tube in which it was measured. Small, equal head and tail fractions were rejected. The still was especially designed to trap spray. On one occasion a 2% solution of potassium chloride was distilled in it and the distillate was found not more than 1 p. p. m. heavier than the original water. To get rid of dissolved air the water was boiled, cooled in ice to about 50°, the float inserted, and the system at once pumped down to the vapor pressure of water. Air was readmitted only at the instant of making the pressure balance. It is thought that this procedure reduced the amount of dissolved air to less than one-tenth of the saturation amount. The difference in specific gravity of air-free and air-saturated water at 0° is 2.5 p. p. m.[9]

The results of the comparison of tap water and sea water are given in Table II. No determinations have been omitted. The specific gravity of the laboratory tap water has been arbitrarily taken as unity, and the fluctuations of individual determinations from this expressed in p. p. m.

TABLE II

Tap Water		Deep Sea Water	
Detn.	Result	Detn.	Result
	Float III		
1	−2.1	2	7.7
3	2.1		
	Float I		
1′[a]	0.8	2′	3.7
3′	− .8	5′	3.7
4′	7.1[b]	7′	1.5
6′	0.0	9′	2.4
8′	.7	Average	2.9
10′	− .8	Av. deviation	0.9
11′	.1		
Av. deviation	1.5		
	Float IV		
4	0.9[b]	5	1.6
6	.2	7	1.7
8	− .4	9	2.8
10	− .2	Average	2.1[c]
11	.2	Av. deviation	0.5
12	.2	Surface Sea Water	
15	− .1	13	1.7[d]
16	.7[e]	14	2.5
18	− .5	17	2.4[f]
21	.0[i]	19	2.1[g]
22	− .1[j]	20	2.9[h]
23	.0	Average	2.3
Av. deviation	.3	Av. deviation	0.3

[a] A prime indicates that the determination was made in the same water as the corresponding unprimed determination.

[b] Omitted in taking the average but included in the average deviation.

[c] Collected in Lat. 36°27″ N. Long. 68°38″ W. at a depth of 4500 meters. The final average for deep-sea water is 2.3, the results with float IV being given triple weight.

[d] The sample used in determinations 13 and 14 was taken in Lat. 38°47″ N. Long. 69°11″ W.

[e] This sample was distilled from the moist salt residue left after distilling the sample of sea water used in determination 17.

[f] This sample was collected in Lat. 39°25″ N. Long. 69°11″ W.

[g] Liquid residue from half-frozen surface sea water taken in Lat. 40°20″ N. Long. 70°20″ W.

[h] Melted ice from above experiment.

[i] Liquid residue from half frozen tap water.

[j] Melted ice from half frozen tap water.

Discussion of Results

Table II shows that, when purified as described above, different samples of sea water give the same specific gravity, while tap water so purified gives a definitely different value. The difference must be due either to a difference in isotopic composition or to an impurity present in one kind of water and not in the other. Experiments 16, 19, 20, 21 and 22 throw light on this

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(7) G. P. Baxter and C. C. Wallace, THIS JOURNAL, **38**, 72 (1916).

(8) W. C. Root, Thesis, Harvard University, 1932.

(9) Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5 Auflage, p. 73.

point. Determination 16 shows that tap water distilled from a residue from distilling sea water is only slightly heavier than ordinary tap water. Experiments 21 and 22 indicate that if tap water as purified contains an impurity it distributes itself equally between the phases when the water is frozen, which seems very unlikely. Experiments 19 and 20 indicate that if sea water as purified contains an impurity which increases its density it tends to stay with the ice rather than the liquid. I consider that these experiments prove that the difference in specific gravity is due to a difference in isotopic composition.

Summary

Pure water obtained from sea water has been found to have a specific gravity of 1.0000023 at 0 ± 0.0000002° compared with pure water obtained from Cambridge tap water at 0°.

A convenient method of measuring small differences of specific gravity has been described.

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NOTE

The Magneto-Optic Nicol Rotation Method for the Quantitative Analysis of Copper

BY EDNA R. BISHOP, IRENE G. OTTO AND LOUIS BAISDEN

An investigation has now been made of the use of the magneto-optic nicol rotation method[1] for the determination of copper.

Regular curves in which the angle of rotation of the analyzing nicol varied with the concentration of copper chloride and with the observer were obtained. These curves could not be superimposed on the previously reported curves for calcium[1] with the concentration expressed in grams of cation, grams of compound or molecules of compound per cc., although they were nearest together when the concentration was expressed in grams of cation per cc.

In the presence of excess NH_4OH, minima appropriate to $Cu(NH_3)_4Cl_2$ were found at scale readings of 30.20(2), 30.30(1) and 30.42(3). These scale readings represent the three isotopes of copper and their order of abundance, as shown by the magnitude of the angle at which minima could be read, is indicated by the numbers in parentheses and is the same as those of simple copper compounds.[2] The $Cu(NH_3)_4Cl_2$ solutions that were employed had a concentration of 1.457×10^{-5}, 1.457×10^{-8}, and 1.457×10^{-11} g. of Cu/cc. The angle of rotation for $CuCl^2$ and $Cu(NH_3)_4Cl_2$ was determined for each of these solutions. In every case the $CuCl_2$ minima became visible at the same nicol setting in the presence as in the absence of NH_4OH. The minima of $Cu(NH_3)_4Cl_2$, however, were seen at a larger angle than those of $CuCl_2$ when both were present in the same solution. When expressed in grams of cation, $Cu(NH_3)_4^{++}$, the points fit on the $CuCl_2$ curve.

Na^+, K^+, NH_4^+, H^+, Fe^{+++}, Ca^{++}, $SO_4^=$, $PO_4^{\equiv}$ and NO_3^- were added to a $CuCl_2$ solution but did not affect the angle at which the $CuCl_2$ minima could be seen. In the presence of excess of these four anions, the $CuCl_2$, $CuSO_4$, $Cu_3(PO_4)_2$ and $Cu(NO_3)_2$ minima all became visible at the same nicol setting.

The magneto-optic nicol rotation method should, therefore, be useful for the quantitative analysis of copper, especially at low concentrations or in complex mixtures since no preliminary separations are necessary. The range of concentrations at which this method can be employed is approximately 5×10^{-12} to 1×10^{-4} g. of Cu/cc. A calibration curve of nicol rotation *vs.* concentration must be made by the observer who is to make the analyses.

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(1) Bishop, Dollins and Otto, THIS JOURNAL, **55**, 4365 (1933).

(2) Bishop, *Phys. Rev.*, **40**, 16 (1932).