The Specific Gravity of Sea Water at Zero Degrees in Relation to the Chlorinity.

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1. Introduction.

The relationship between the chlorinity and specific gravity of sea water was first definitely established by Prof. KNUDSEN and co-workers (1) about 1900. The results of this work in the form of tables (2) are extensively used in hydrodynamical investigations of the oceans. These tables afford a rapid and accurate means of calculating the specific gravity of sea water directly from an easily-performed chemical determination. The direct estimation of specific gravity is very difficult, involving apparatus and precautions which can only be obtained and realized in a well-equipped land laboratory. Since 1900, however, no attempts have been made to recheck the values given in the tables. At the request of Prof. KNUDSEN the present investigation was undertaken on a series of samples obtained from various regions of the world, through the co-operation of the International Council for the Exploration of the Sea, the International Fisheries Commission, the Scripps Institution of Oceanography, and the Carnegie Institution.

2. Experimental Procedure.

A. The Determination of Specific Gravity. Two pycnometers of the type recommended by PARKER and PARKER (3) but made of fused silica were employed in the present investigation. These pycnometers contained about 150 cubic centimeters and 175 cubic centimeters respectively, and when filled, weighed approximately 250 and 275 grams. Silica was utilized in order to minimize the errors due to thermal expansion.

An ice bath of the type used by the Parkers was also employed.

A temperature of $0° \pm .002°$ C. was easily maintained, as was determined by the use of a Beckmann thermometer which had just been calibrated using pure water.

A balance with a capacity of one kilogram and a sensitivity of one-tenth of a milligram was used. The weights were of the ordinary brass type, calibrated by the modified method of T. W. RICHARDS (4). Tares of pyrex glass and of the approximate weight and volume of the full pycnometers were also used.

In order to determine the constants of each pycnometer, the capillary stem was first calibrated with mercury by accurately measuring the lengths of the mercury threads. These were subsequently weighed. The stem calibrations were carefully checked and a table made of the equivalents of the stem readings in centimeters. It was found that .01 centimeter on the capillaries of the two pycnometers were equivalent to 0.048 and 0.076 milligrams of water respectively. Since the height of the liquid in the capillary could be accurately determined to 0.02 centimeter, any experimental reading could be reduced to an arbitrary standard without introducing abnormal error.

The total volume of the pycnometer to the arbitrary stem reading was determined by weighing the instrument when filled with pure gas-free water. This water was prepared by passing carbon dioxide free air through a slightly acid (sulfuric acid) solution of ordinary distilled water for a few hours, then distilling directly into a pyrex bottle. The receiver, containing the hot distillate, was evacuated, and the dissolved air removed by boiling. The water was then siphoned directly into the pycnometer, which had been previously filled with hydrogen gas (hydrogen being about $1/_{60}$ as soluble by weight as air). Long glass tubes were fastened to the pycnometer stems and filled with the same water, so that during the process of bringing to constant temperature at $0°$ no dissolved air would diffuse into the pycnometer bulb. The instrument was then placed in the ice bath and allowed to come to equilibrium. It was found that no further cooling took place after three hours. The pycnometer was allowed to stand in the ice bath for six hours after which the protective tubes were removed, the overflow tube quickly dried and a reading taken on the calibrated stem. The pycnometer was of such construction that when the overflow tube was carefully dried out, the water came just to the top of the capillary below it, and also stood at a convenient height in the other calibrated capillary.

The pycnometer was then removed from the ice bath, rapidly brought to room temperature and weighed as soon as it had come to temperature equilibrium with the balance. Three weighings were made a half hour

apart, the temperature of the balance case and the atmospheric pressure being recorded each time. If the weight did not change by more than 0.2 milligram between the first and last weighing, the last weight was taken as the true weight of the pycnometer, after making the corrections necessary to reduce the weights to vacuum. The pycnometer was weighed against a tare which in turn was weighed against brass weights. The value of the specific gravity of pure gas-free water at $0°$ referred to water at $4°$ was taken as 0.9998681 (5). The density of air under the various conditions was taken from standard tables (6).

The empty pycnometer was weighed in exactly the same way except that only two weighings were made each time, as the empty instrument came to temperature equilibrium much more rapidly than when filled.

The actual volumes of the instruments and tares which were needed in order to calculate the vacuo corrections were determined by weighing in air and then in water.

The same procedure was followed for the determination on sea water except that no precautions were taken to protect the water from the air once it was in the pycnometer. The samples were never opened until just before making the determination, and were rapidly transferred into the pycnometer without coming into contact with the air.

Two hours were allowed for the sample to come to equilibrium in the ice bath; the excess water in the pycnometer was then removed as before; and the reading taken. If there was no change in the height of the water in the calibrated capillary at the end of another hour, it was considered that all the water was at zero degrees.

The results were reported in terms of σ_0. If S is the specific gravity of sea water at $0°$ referred to distilled water at $4°$, then $\sigma_0 = (S-1)1000$.

B. The Chlorinity Determination. A modified Volhard method was used, in which approximately 25 grams of sea water were weighed to an accuracy of one milligram. A weighed excess of silver nitrate solution was added, the precipitated halides filtered off and the excess silver nitrate titrated with .05N ammonium thiocynate, using a micro buret. The silver nitrate was standardized against carefully purified sodium chloride and checked against the standard sea water of the Hydrographical Laboratories. Determinations by the Mohr method were made in order to check the values of THOMPSON (7) for changing chlorinity per liter to chlorinity per kilogram. Concordant results were obtained when based on the same standards used in deriving the Hydrographical Tables.

In order to compare the values of the present investigation with those of KNUDSEN, it was necessary to reduce the chlorinities to the basis of the 1900 atomic weights. It was found impossible to check the

standard sea water by using these 1900 atomic weights throughout in the calculations. On looking for an explanation of this, it was found that potassium chloride had been used by Prof. KNUDSEN as a standard, and that the atomic weights of potassium and sodium had not changed proportionately, as the following simple calculation shows:

	Gravimetric Factor for Cl in KCl	Gravimetric Factor for Cl in NaCl
1900 atomic weights	$\dfrac{35.453}{74.589} = 0.47531$	$\dfrac{35.453}{58.511} = 0.60592$
1930 atomic weights	$\dfrac{35.457}{74.553} = 0.47559$	$\dfrac{35.457}{58.454} = 0.60658$
Difference...	0.00028	0.00066

Taking this into account, the following results were obtained:

	Chlorinity 1930 atomic weights	Chlorinity 1900 atomic weights
Standard Sea Water .... (6—24—27)	19.378	19.367

The value reported by the Hydrographical Laboratories for this sample is 19.368.

All values of the chlorinity reported below (which is defined as the grams of chloride equivalent to the total halides in one kilogram of sea water) except those determined by the Mohr method were reduced to vacuum.

3. Discussion of Errors.

Since the errors in the specific gravity determination outweigh any that are made in the chlorinity determination, only the latter will be considered.

While each weighing is made to 0.1 milligrams, it is doubtful whether the value obtained can be considered more accurate than 0.3 milligram. Each value of the specific gravity depends moreover on two separate weights, the weight of the instrument filled with sea water and the weight of the empty instrument (not including an equal number of weighings made to determine the volume from the weight of distilled water). There is also the error made in reading the capillary stem, which, however, will not amount to more than 0.2 milligram.

Furthermore, the specific gravity of gas-free water is not known to

the accuracy indicated by its value as ordinarily given, since different authorities vary greatly among themselves. The value of the density of air as derived from the tables is also another limiting factor, especially as it is impossible to make adequate corrections for change in humidity.

4. Sources of Samples.

The samples of sea water used in this work were obtained from the following localities:

Mediterranean Sea. These samples were collected by the Snellius Expedition and by Professor J. GIRAL.

Baltic Sea. Samples collected by the Thalassological Institute of Helsingfors.

North Pacific. Samples collected by Mr. RICHARD VAN CLEVE of the International Fish Commission. These samples were all from one station in the middle of the Gulf of Alaska.

California Coast. Samples collected by Prof. E. G. MOBERG of the Scripps Institution of Oceanography. These samples were from one station twelve miles magnetic west of the institution pier at La Jolla.

Atlantic Ocean. Samples collected by the "Carnegie". These samples were contained in bottles not up to the specifications of the International Council for the Exploration of the Sea, and were run merely to show the large variations that occur when bottles of soft glass are used. Some of the glass goes into the solution.

5. Discussion of Data.

A summary of the data from this investigation is given in the following tables. The first column, under "Chlorinity", contains the results calculated on the basis of the 1930 atomic weights while those computed from the atomic weights of 1900 are given in the second column. The latter were used in the preparation of the Hydrographical Tables. Duplicate chlorinity determinations were made in all cases and the difference between duplicates is shown in the third column. The average variation between duplicates for the thirty-six samples studied was $0.001 \, ^o/_{oo}$ Cl. Such a variation would produce an error of 0.003 in the calculated specific gravity reported as σ_0 for samples having chlorinities of $18 \, ^o/_{oo}$, and 0.002 for Chlorinities of $21^o/_{oo}$.

There is a very marked relationship between specific gravity and chlorinity as shown by the empirical formula of KNUDSEN, where σ_0 is the specific gravity expressed as $(S—1)1000$ at $0°$ referred to distilled water at $4°$ and Cl. is the chlorinity per kilogram of sea water.

$$\sigma_0 = -0.069 + 1.4708\ Cl - 0.001570\ Cl^2 + 0.0000398\ Cl^3$$

The observed specific gravities of the various waters at $0°$ referred to distilled water at $4°$ are shown in the first column under "Specific Gravity" in the tables. These data are all averages of duplicate samples. The variation between duplicates is shown in the second column and avarages $0.004\ \sigma_0$. The third column gives the calculated densities from the Hydrographical Tables based on the 1900 atomic weights and Knudsen's formula. The differences between the observed and calculated are shown in the fourth column. The average variation for thirty samples was $+0.019\ \sigma_0$. In all cases the observed values were greater than the calculated. It is believed that the measurements of specific gravity reported herein are more accurate than those of 1900 because advantage has been taken of the improvements in apparatus and larger samples of water were used.

The fifth column gives the specific gravities calculated from chlorinities based on atomic weights of 1930. In the sixth column are given the differences between these calculated values and those actually observed. For all the samples examined the average difference is $\pm 0.006\ \sigma_0$. Two interesting facts are thus presented. First, assuming the specific gravities of the present authors are more accurate than those of KNUDSEN'S, the slight errors of experimentation in the data from which the Hydrographical Tables were computated, are very largely compensated for by the changes in atomic weights. In other words, the tables are more accurate using the atomic weights of 1930 than those of 1900. Second, the data tend to demonstrate a very slight difference in the waters of the several oceans, assuming a minimum experimental error. The waters from the Gulf of Alaska all gave a calculated value less than the experimental. The same statement applies to the Indian Ocean. The samples from the Mediterranean Sea showed conditions that were just the reverse. Rather abnormal conditions were obtained on the waters from the Pacific off the southern California coast.

These slight differences, which are either all plus or minus for all the waters examined from a given ocean, tend to indicate a very minute difference in the possible composition of sea waters. However, it may be possible that this slight variation may be due to differences in the concentration of certain dissolved gases.

6. Conclusions.

1) Accurate specific gravity determinations have been made on waters from the several oceans. The relationship between chlorinity and

Table I. Mediterranean Sea
Samples collected by the Snellius Expedition and Prof. J. Giral.
March and April, 1929.

Position	Depth Meters	Chlorinity			Specific Gravity					
		Based on Atomic Weights 1930 ‰	Based on Atomic Weights 1900 ‰	Difference between Duplicates ‰	Observed σ_0	Difference between Duplicates σ_0	Calculated from Hydrographical Tables σ_0	Difference σ_0	Calculated Atomic Weights 1930	Difference σ_0
36°42′ N 1°47′ E	0	20.171	20.159	0.003	29.281	0.004	29.269	+0.012	29.289	−0.008
37°13′ N 6°55′ E	900	21.278	20.267	.000	30.899	.001	30.883	+ .016	30.899	.000
35°06′ N 17°24′ E	900	21.436	21.424	.001	31.132	.000	31.111	+ .021	31.130	+ .002
33°59′ N 21°15′ E	0	21.215	21.203	.000	30.801	.004	30.789	+ .012	30.807	− .006
33°59′ N 21°15′ E	900	21.433	21.420	.001	31.114	.002	31.108	+ .006	31.125	− .011
33°06′ N 24°28′ E	0	21.412	21.401	.001	31.094	.014	31.078	+ .016	31.095	− .001
31°36′ N 30°12′ E	0	21.398	21.386	.001	31.072	.006	31.056	+ .016	31.074	− .002
Average...	..	..	..	.001	..	.004	..	+ .014	..	−.0037

Table II. Baltic Sea.
Samples collected by the Thalassological Institute of Helsingfors. July 1929.

Position	Depth Meters	Chlorinity			Specific Gravity					
61°58′ N 20°04′ E	0	3.031	3.030	0.002	4.402	0.003	4.374	+0.028	4.386	+0.016
60°20′ N 26°58′ E	0	2.116	2.114	.001	3.061	.007	3.033	+ .028	3.040	+ .021
Average...	..	..	..	.002	..	.005	..	+ .028	..	..

Table III. Indian Ocean.
Samples collected by the Snellius Expedition, April and May, 1929.

Position	Depth Meters	Chlorinity			Specific Gravity					
7°38′ N 55°43′ E	0	19.376	19.365	0.001	28.130	0.003	28.112	+0.018	28.129	+0.001
3°48′ N 63°48′ E	0	19.208	19.197	.001	27.889	.004	27.869	+ .020	27.885	+ .004
3°48′ N 63°48′ E	500	19.443	19.432	.001	28.228	.003	28.211	+ .017	28.227	+ .001
0°04′ S 79°43′ E	500	19.394	19.383	.000	28.163	.004	28.139	+ .024	28.156	+ .007
1°06′ S 94°56′ E	0	19.278	19.267	.000	27.992	.003	27.971	+ .021	27.987	+ .005
Average...	..	..	..	.001	..	.004	..	+ .020	..	+.0036

Table IV. Atlantic Ocean.
Samples collected by the „Carnegie", August, 1928. Samples stored in soft glass bottles.

Position	Depth Meters	Chlorinity			Specific Gravity					
42°10′ N 47°19′ W	82	19.689	19.678	0.001	28.639	..	28.566	+0.073	28.585	+0.054
	522	19.414	19.403	.000	28.269	..	28.169	+ .100	28.185	+ .084
	2074	19.325	19.314	.001	28.094	..	28.039	+ .055	28.055	+ .039
	4140	19.321	19.310	.002	28.099	..	28.034	+ .065	28.049	+ .050
Average...	..	..	..	.001	..	..	..	+ .074	..	+ .057

Table V. Gulf of Alaska.

Samples collected by the International Fisheries Commission, June, 1930.

Position	Depth Meters	Chlorinity			Specific Gravity					
		Based on Atomic Weights 1930 °/oo	Based on Atomic Weights 1900 °/oo	Difference between Duplicates °/oo	Observed σ_0	Difference between Duplicates σ_0	Calculated from Hydrographical Tables σ_0	Difference σ_0	Calculated Atomic Weights 1930	Difference σ_0
56°24′ N 144°4′ W	10	18.154	18.143	0.002	26.353	0.006	26.337	+0.016	26.352	+0.001
	25	18.159	18.149	.002	26.365	.004	26.346	+ .019	26.360	+ .005
	50	18.156	18.146	.002	26.366	.000	26.342	+ .024	26.356	+ .010
	100	18.176	18.166	.002	26.394	.007	26.370	+ .024	26.385	+ .009
	200	18.323	18.312	.001	26.620	.001	26.583	+ .037	26.598	+ .022
	300	18.354	18.344	.001	26.655	.010	26.629	+ .026	26.643	+ .012
	500	18.496	18.486	.002	26.860	.007	26.836	+ .024	26.850	+ .010
	1000	18.589	18.579	.002	26.992	.011	26.970	+ .022	26.985	+ .007
Average...	..	..	..	.002	..	.006	..	+ .024	..	+ .009

Table VI. Pacific Ocean.

Samples collected twelve miles off the coast of Southern California by the Scripps Institution of Oceanography. June, 1930.

Position	Depth Meters	Chlorinity			Specific Gravity					
32°52′ N 117°21′ W	0	18.609	18.599	0.002	27.010	0.004	26.998	+0.012	27.013	−0.003
	20	18.594	18.584	.002	26.988	.002	26.977	+ .011	26.992	− .004
	30	18.573	18.563	.001	26.954	.013	26.947	+ .007	26.961	− .007
	50	18.572	18.563	.001	26.967	.006	26.947	+ .020	26.960	+ .007
	75	18.753	18.742	.000	27.239	.010	27.208	+ .031	27.223	+ .016
	150	18.915	18.904	.001	27.461	.003	27.443	+ .018	27.460	+ .001
	200	18.945	18.934	.001	27.512	.003	27.481	+ .031	27.502	+ .010
	300	18.978	18.968	.000	27.566	.001	27.536	+ .030	27.550	+ .016
	400	19.005	18.994	.001	27.592	.005	27.574	+ .018	27.590	+ .002
	600	18.555	18.544	.001	26.934	.000	26.918	+ .016	26.936	− .002
Average....	..	..	..	.001	..	.005	..	+ .019	..	− .004 / + .008

specific gravity as established by Knudsen's formula, is again demonstrated.

2) There are slight differences between the values obtained and those calculated from the Hydrographical Tables. This small error is compensated by the use of the atomic weights for 1930.

3) There is a marked constancy in the relationship of chlorinity and specific gravity in the waters of the several oceans. The observed values and calculated values of the waters do not vary by more than $\pm\, 0.000006$ or $\pm .006\ \sigma_0$.

4) Very minute differences appear to exist between the waters of the several oceans.

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