Chemical Studies of the Western Pacific Ocean. III. Freezing Point, Osmotic Pressure, Boiling Point and Vapour Pressure of Sea Water.

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(Received January 9, 1939.)

Freezing Point. The freezing point of sea water was measured by Knudsen and Hansen(1) in 1903, and it is expressed by the following empirical formula:

$$\tau = -0.0086 - 0.064633\,\sigma_0 - 0.0001055\,\sigma_0^2$$

where τ is the freezing point, and $\sigma_0 = (S_0 - 1) \times 1000$, in which S_0 represents the specific gravity of sea water at 0°C. with reference to distilled water at 4°C. The relation between the freezing point and chlorinity,

$$\tau = -0.0966\,\mathrm{Cl} - 0.00000520\,\mathrm{Cl}^3$$

was derived by B. D. Thomas(2) from Knudsen-Hansen's formula. The present author has repeated the measurement of the freezing point of sea water and obtained a new empirical formula which seems to be more adequate than the former equations.

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(1) O. Krümmel, "Handbuch der Ozeanographie," Band 1, 240, Stuttgart (1907).
(2) *Bull. Nat. Research Council*, **85** (1932), 84.

Experimental. Sea water of known chlorinity was diluted with water into six samples. The chlorinity, the position, the depth and the date of collection of the original sea water are as follows: Cl, 18.54‰; N 39°46′, E 143°16′; 145 m.; March 17th, 1938. The measurements were made by the ordinary method. Into a beaker containing about 100 c.c. of sample water, a Beckmann's thermometer and a certified stem thermometer (−20° ∼ 50°C.) were inserted and the content was cooled indirectly with a cooling mixture under incessant stirring. The temperature of the water, taken at intervals of thirty seconds, was plotted giving the cooling curve. The freezing point was determined from the tangent of the curve after the state of supercooling was broken. At first, the freezing point of distilled water was carefully measured and the reading was used as a reference standard. The difference between the reading of a sample and that of the standard directly gives the depression ΔT of the freezing point of sea water.

Results of the Measurements. The results of the measurements are given in Table 1.

Table 1.

Cl (‰)	Salinity (‰)	Depression of the Freezing Point, ΔT
18.54	33.49	1.895
13.07	23.62	1.350
9.37	16.94	0.970
7.53	13.62	0.770
4.75	8.60	0.495
1.90	3.46	0.195

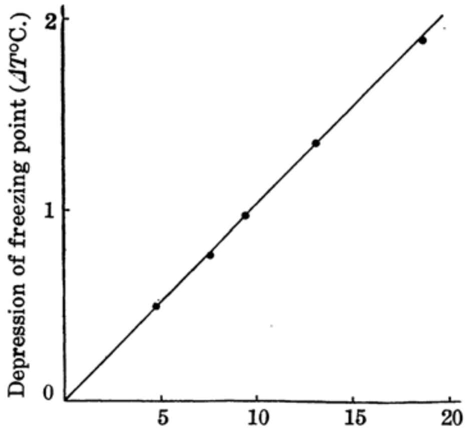

Fig. 1. The relation between freezing point depression and chlorinity.

As shown in Fig. 1, the relation between the chlorinity and the freezing point depression is almost linear and may be represented by the following simple formula:

$$\Delta T = 0.102710 \text{ Cl}.$$

A Comparison of Author's Formula with Knudsen-Hansen's Equation. The freezing point of sea water of various chlorinities was next measured. The results have been compared with the values calculated from the equation of Knudsen-Hansen and from the new formula. From the experimental results shown in Table 2, we can see that the values obtained by the present formula are in good agreement with the measurements, the average deviation between them being only $\pm 0.005_5$°C.; on the other hand, the values calculated from Knudsen-Hansen's formula constantly show a deviation of about 0.08°C, giving values that are too high. The comparison shows clearly that the new formula is superior to Knudsen-Hansen's formula.

Table 2.

Chlorinity	ΔT, observed	ΔT, calculated by the new formula	ΔT, calculated by Knudsen's formula
18.22	1.875	1.872	1.792
18.28	1.875	1.878	1.798
18.42	1.900	1.892	1.812
18.48	1.890	1.898	1.819
18.57	1.915	1.907	1.828
18.59	1.915	1.909	1.830
18.60	1.915	1.910	1.831
18.75	1.935	1.926	1.846
19.38*	1.985	1.991	1.911
19.39**	1.990	1.992	1.912

* The standard water supplied by the Imperial Fisheries Experimental Station, Japan.

** The standard water supplied by Prof. Knudsen.

The Calculation of the Osmotic Pressure of Sea Water: When the depression of the freezing point of a solution is known, its osmotic pressure can readily be estimated. The theoretical relation between osmotic pressure and freezing point depression is given by the next formula:

$$P_0 = \frac{41.35\ r\ \delta}{T_0} \Delta T(\text{atm.})$$

where P_0 is the osmotic pressure at 0°C.; r, the heat of fusion of water, 79.65 cal.; δ, the density of water at 0°C.; ΔT, the freezing point depression. Substituting numerical values in the formula, we obtain the simple equation:

$$P_0 = 12.06 \times \Delta T.$$

In Table 3, the osmotic pressure corresponding to various chlorinity values, calculated by the above formula with additional correction for the heat of solution, are given. The empirical relation between osmotic pressure, chlorinity and temperature is represented by the following equation:

$$P_t = 1.240\ \text{Cl} + 0.00454\ \text{Cl} \cdot t.$$

Table 3.

Cl (‰)	ΔT	P_0 (atm.)	Cl (‰)	ΔT	P_0 (atm.)
1	0.103	1.24	12	1.233	14.88
2	0.205	2.47	13	1.335	16.12
3	0.308	3.71	14	1.438	17.36
4	0.411	4.96	15	1.541	18.60
5	0.514	6.20	16	1.643	19.83
6	0.616	7.43	17	1.746	21.09
7	0.719	8.67	18	1.849	22.34
8	0.822	9.91	19	1.951	23.58
9	0.924	11.15	20	2.054	24.82
10	1.027	12.40	21	2.157	26.07
11	1.130	13.64	22	2.260	27.31

When the temperature is constant, the osmotic pressure increases by 1.24 atm. per unit increase in chlorinity. In Table 4 and Fig. 2, the osmotic pressures at 0°C. calculated by author's formula are compared with those by Krümmel and Stenius.⁽¹⁾ Here the concentration of sea salt is expressed in terms of salinity instead of chlorinity. As seen in this table and Fig. 2, author's values for the osmotic pressure are slightly larger than those of Krümmel and Stenius.

Table 4. Osmotic pressure of sea water at 0°C. (atm.)

Salinity (‰)	Krümmel-Stenius	Miyake
5	3.23	3.41
10	6.44	6.84
15	9.69	10.28
20	12.98	13.72
25	16.32	17.16
30	19.67	20.59
35	23.12	24.05
40	26.59	27.49

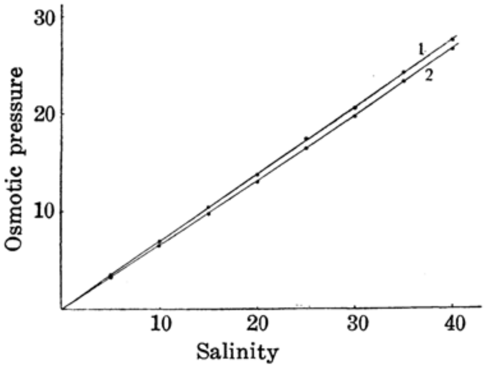

Fig. 2. The relation between osmotic pressure and salinity.
1: Miyake. 2: Krümmel-Stenius.

The Calculation of the Boiling Point Elevation. If we know the osmotic pressure of sea water, then we can estimate the boiling point elevation by the following equation:

$$P = \frac{41.35\ l\ \delta}{T} \Delta T,$$

where l is the heat of evaporation of water, i.e. 536.6 cal.

But, $$P = P_0\{1-0.00366(T-T_0)\}$$

Therefore, $$\Delta T = 0.02397\, P_0\,.$$

The numerical values calculated by this equation are shown in Table 5, where the results are compared with Krümmel's data.⁽¹⁾

Table 5. Boiling point elevation of sea water. ΔT°C.

Salinity (‰)	5	10	15	20	25	30	35	40
Miyake	0.08	0.16	0.25	0.33	0.41	0.49	0.58	0.66
Krümmel	0.08	0.16	0.23	0.31	0.39	0.47	0.56	0.64

The experimental formula between the salinity and the boiling point elevation may be expressed as follows:

$$\Delta T = 0.01645\,\mathrm{S}. \qquad \mathrm{S}:\ \text{the salinity.}$$

The Depression of the Vapour Pressure. We can easily calculate the vapour pressure depression for sea water at its boiling point when the boiling point elevation is known. There are two means of calculating the depression of the vapour pressure, i.e., one is from the pressure of saturated water vapour near 100°C. under the pressure of 760 mm. Hg (1); and the other is from the boiling point data of water at pressures slightly lower than 760 mm. Hg (2). These data have been quoted from Landolt-Börnstein's Tables, and the results of the calculation are as follows:

Table 6. The depression of the vapour pressure. (mm. Hg)

Salinity (‰)	5	10	15	20	25	30	35	40
From (1)	2.17	4.34	6.76	8.91	11.07	13.21	15.60	17.75
From (2)	2.17	4 33	6.77	8.93	11.07	13.20	15.62	17.75
Average	2.17	4.33_5	6.76_5	8.92	11.07	13.20_5	15.61	17.75
Krümmel	2.13	4.23	6.45	8.47	10.73	12.97	15.23	17.55

Summary.

(1) The freezing point of sea water from the Western Pacific Ocean has been measured and a new empirical formula for the relation between freezing point and chlorinity has been obtained, which seems to be more adequate than Knudsen-Hansen's equation.

(2) The osmotic pressure, the boiling point elevation and the depression of the vapour pressure of sea water have been calculated.

The author wishes to express his hearty thanks to Prof. T. Okada, Director of the Central Meteorological Observatory of Japan, for his kind guidance and the permission of publishing this report. He is also indebted to Mr. H. Matui for his earnest assistance throughout this work.

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Observatory of Japan.