in the physical condition of the particles which continue for a long time may be accompanied by the evolution of appreciable quantities of heat, thus explaining the low value obtained in measuring directly the heat of hydration.

Summary and Conclusions

1. The value 276.3 cal.$_{20°}$ per gram or 15.49 kg. cal.$_{20°}$ (64.76 kj.) per mole was obtained for the heat of hydration of CaO in saturated lime water at 20°.
2. This value is 2.6 cal. per gram lower than the value (278.9 cal.$_{20°}$ per gram, 15.64 kg. cal.$_{20°}$ per mole) obtained by calculation from the heats of solution of calcium oxide and calcium hydroxide in $HCl \cdot 200H_2O$.
3. Microscopic examination indicated that physical changes in the hydrated material continue for a long time after the temperature of the calorimeter comes to apparent constancy. It is suggested that changes in the energy of surface and of crystal lattice may be responsible for the discrepancy between the observed and calculated results for the heat of hydration of calcium oxide.

SASKATOON, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

IONIC RATIOS IN THE WATERS OF THE NORTH PACIFIC OCEAN[1]

BY THOMAS G. THOMPSON AND CALVERT C. WRIGHT

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During the past sixty years a number of papers[2] have appeared giving the analyses of sea water from various regions of the world. From some of these data the ratios of the various ions occurring in the waters of the several oceans may be calculated. Such ratios give valuable information as to the constancy of composition of sea water; and, once established and referred to the chlorinity[3] as unity, may be used to calculate the con-

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[1] Paper read before the Pacific Intersectional meeting of the American Chemical Society held at Berkeley, California, June 21, 1929.

[2] (a) Thorpe and Morton, *Ann.*, **158**, 122 (1871); (b) Dittmar, "Reports of H. M. S. "Challenger," *Phys. and Chem.*, **1884**, Vol. 1; (c) Schmidt, *Bull. Acad. St. Petersburg*, **24**, 231 (1878); (d) Schmelck, "Den Norske Nordhavs-Exped.," Part 9, **1882**, p. 1; (e) Forsberg, "Vega Exped. Rept.," **1883**, Vol. 2, p. 376; (f) Kolotoff, *J. Russ. Phys.-Chem. Soc.*, **24**, 82 (1893); (g) Makin, *Chem. News*, **77**, 155 (1898); (h) Natterer, *Monatsh.*, **13**, 873 (1892); **14**, 624 (1893); **15**, 530 (1894); **16**, 405 (1895); **20**, 1 (1899); **21**, 1037 (1900); (i) Schloesing, *Compt. rend.*, **142**, 320 (1906); (j) Coppock, *Chem. News*, **96**, 212 (1907); (k) Wheeler, THIS JOURNAL, **32**, 646 (1910); (l) Bertrand, *Compt. rend.*, **174**, 1251 (1922).

[3] The chlorinity of sea water is defined as the number of grams of chloride ions contained in a kilogram of water, assuming that the small amounts of bromide ions and traces of iodide ions have been converted to chlorides.

centrations of the several ions when only the chlorinity of the water is known. The constancy of the sulfate chlorinity ratio was recently demonstrated for the waters of the North and Northeast Pacific.[4]

In the present investigation special attention has been given to the calcium and magnesium ions in the waters of this same region. A critical examination was first made of the different methods used in the determination of calcium and magnesium ions in sea water and the most accurate methods accordingly adopted.

After a study of the literature, particularly the conclusions of Giral,[5] and considerable laboratory experience, the authors became convinced that many of the discrepancies in the calcium–magnesium ratios calculated from the data of other investigators were due to faulty methods of analysis, or to the tendency of investigators to report results to a degree of accuracy not warranted by evident experimental errors.

Methods of Analysis

To ascertain the most accurate method for the determination of calcium and magnesium in sea water, standard solutions of pure magnesium sulfate and calcium chloride were prepared. These solutions were used in the preparation of a synthetic sea water, in which only carefully purified and analyzed chemicals entered. This water had the following composition

Mg^{++}	$1.1506^0/_{00}$	Na^+	$13.0^0/_{00}$
Ca^{++}	$0.3750^0/_{00}$	Cl^-	$17.0^0/_{00}$
K^+	$0.37^0/_{00}$	$SO_4^=$	$4.6^0/_{00}$

Throughout all of the analytical work the following precautions were taken: (a) every reagent was tested for its purity; (b) ignitions were all made in platinum crucibles; (c) constant weight was considered to have been obtained only when three weighings checked to within 0.1 milligram; (d) all weighings were made at constant temperature.

Determination of Calcium.—In previous determinations of calcium in sea water, the oxalate method with ignition of the precipitate to the oxide has been exclusively used. The chief variation in the method has been the number of precipitations of the calcium oxalate. In a few instances only one precipitation was used but in the majority of cases three or the equivalent were considered necessary. Thus Dittmar used a single precipitation for individual samples, but combined the ignited calcium oxide precipitates, analyzed them by double precipitation and corrected the original results. Natterer used a double precipitation but boiled the second precipitate with dilute ammonium oxalate solution.

The data presented in Table I demonstrate that at least three precipitations of the calcium oxalate are necessary.

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[4] Thompson, Lang and Anderson, *Publ. Puget Sound Biol. Sta.*, **5**, 277–292 (1927).

[5] Giral, *Mem. Inst. Español de Ocean*, **2**, 199 (1924).

TABLE I

DATA ON THE PRECIPITATION OF CALCIUM OXALATE

		Grams of Ca per kilo of synthetic sea water a	b	c	Mean	Variation
Calcium present		0.3750	0.3750	0.3750	0.3750	
Calcium found	Two pptns.	.3809	.3800	.3817	.3809	+0.0059
	Three pptns.	.3752	.3760	.3749	.3755	+ .0005

Titration of the calcium oxalate with potassium permanganate yielded varying results as shown by Hahn and Weiler[6] and accordingly was not considered. The determinations of calcium in samples of filtered sea water were carried out in much the same manner as that described by Fales.[7] Two hundred and fifty grams of the sea water was used, three precipitations of the calcium oxalate were made and the latter was finally ignited at a high temperature in an electric muffle to constant weight.

Determination of Magnesium.—The hydroxyquinoline method of Berg[8] and its modification for sea water by Matthews and Ellis[9] were studied. It was found that this procedure was far less accurate than Epperson's[10] modification of the magnesium ammonium phosphate method.

Previous workers in determining magnesium in sea water by the phosphate method considered two and in some cases one precipitation sufficient. The data of Epperson and the results reported in Table II show the fallacy of this assumption. Due to the peculiar composition of sea water, three precipitations of the magnesium ammonium phosphate are essential.

TABLE II

COMPARISON OF DIFFERENT METHODS AND MODIFICATIONS FOR THE DETERMINATION OF MAGNESIUM

	Grams of Mg per kilo of synthetic sea water a	b	c	Mean	Variation
Magnesium present	1.1506	1.1506	1.1506	1.1506	
Determined by Epperson's Method					
Two precipitations	1.162	1.149	1.157	1.156	+0.005
Three precipitations	1.149	1.152	1.152	1.151	.000
Determined by Berg's Method					
Two precipitations and drying 4 hrs. at 100°	1.206	1.250	1.176	1.211	+ .060
Matthews and Ellis' Modification					
Drying 2 hrs. at 100°	1.191	1.174	1.198	1.188	+ .037
Drying 6 days at 100°	1.169	1.155	1.181	1.168	+ .017

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[6] Hahn and Weiler, *J. prakt. Chem.*, **70**, 1 (1927).

[7] Fales, "Inorganic Quantitative Analysis," The Century Co., New York, **1925**, p. 198.

[8] Berg, *Z. anal. Chem.*, **71**, 23 (1927).

[9] Matthews and Ellis, *J. du Conseil*, **3**, 191 (1928).

[10] Epperson, THIS JOURNAL, **50**, 321 (1928).

This conclusion is partially corroborated by Bertrand,[11] who obtained high results on a synthetic sea water using only two precipitations.

The assertion made by several investigators[9,12] that a large error due to the solubility of the magnesium ammonium phosphate may enter into the determination seems to be unfounded, especially for Epperson's modification. The data given below were obtained from nine analyses of a solution of pure magnesium chloride containing 0.0919 grams of magnesium per kilo.

	a	b	c
1 Precipitation	0.0919	0.0919	0.0918
2 Precipitations	.0918	.0918	.0921
3 Precipitations	.0920	.0920	.0918

These data show that no error of solubility is introduced.

In determining the magnesium in sea water aliquot parts by weight of the filtrate from the calcium determination were taken and Epperson's procedure was followed, using three precipitations.

Source of Samples of Waters Studied

Puget Sound Biological Station, Friday Harbor, Washington.—The Puget Sound Biological station is situated in the San Juan Archipelago about 80 miles north of Seattle. From September, 1926, to September, 1928, samples of water were collected weekly at the surface and at a depth of 12.5 meters. Composite samples of about 2.5 liters, for each month, were made from the weekly samples, and used in the present investigation.

East Sound, San Juan Archipelago, Washington.—East Sound is an estuary about 10 miles in length, and its waters are characterized by an exceedingly rich diatom growth. Gran and Thompson[13] found as many as 1400 cells per milliliter of water. During the period of rich growth, 25 samples were collected from various parts of the sound and from these a composite sample was prepared.

Nanaimo Bay, British Columbia.—A 4-liter sample was collected through the courtesy of Professor Hutchinson of the University of British Columbia. The waters of the bay had a chlorinity much less than those of any region studied, resulting from the dilution of the waters of the Gulf of Georgia by the Fraser River.

Gulf of Alaska.—In 1928 a composite sample was made from 120 samples collected by the International Fisheries Commission at ten-mile intervals out from Ocean Cape, Cape Cleare and Cape Chiniak, Alaska, at depths varying between the surface and 1000 meters.

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[11] Bertrand, *Compt. rend.*, **174**, 1251 (1922).

[12] Schmelck, "Den Norske Nordhavs-Exped.," Part 9, **1882**, p. 1; Seidell, "Solubility of Inorganic Substances," 2d ed., D. Van Nostrand Company, New York., **1919**.

[13] Gran and Thompson, "Publ. Puget Sound Biol. Sta.," in press.

In 1929 three samples were collected for the authors in the Gulf of Alaska. No. 16 was taken at the surface, 14 miles from the coast, No. 370 was obtained at a depth of 1200 meters about 250 miles from shore, while No. 406 was taken at a depth of 375 meters, 45 miles south of Kodiak Island.

All of the samples described above were analyzed carefully for calcium and magnesium ions, and for chlorinity. The latter was determined by the method previously described by one of us.[14] The results obtained, together with the ratios calculated therefrom, are given in Table III.

TABLE III

ANALYSES AND IONIC RATIOS OF THE WATERS OF THE NORTH AND NORTHEAST PACIFIC OCEAN

Samples					Ratios		
Source	Description	Chlorinity, grams/kilo	Mg, grams, per kilo	Ca, grams, per kilo	Mg/Cl	Ca/Cl	Ca/Mg
Friday Harbor	Sept. '26	16.95	1.134	0.3640	0.06690	0.02144	0.3211
Friday Harbor	Oct. '26	17.18	1.147	.3681	.06676	.02143	.3209
Friday Harbor	Nov. '26	16.98	1.136	.3646	.06690	.02147	.3210
Friday Harbor	Dec. '26	17.02	1.140	.3673	.06698	.02158	.3222
Friday Harbor	Jan. '27	16.81	1.125	.3614	.06692	.02150	.3212
Friday Harbor	Feb. '27	16.83	1.125	.3608	.06687	.02144	.3206
Friday Harbor	Mar. '27	16.78	1.124	.3598	.06698	.02144	.3201
Friday Harbor	Apr. '27	16.96	1.134	.3640	.06686	.02146	.3216
Friday Harbor	May '27	17.11	1.141	.3676	.06669	.02148	.3222
Friday Harbor	June '27	16.98	1.139	.3655	.06708	.02153	.3209
Friday Harbor	July '27	16.54	1.107	.3562	.06696	.02154	.3216
Friday Harbor	Aug. '27	16.29	1.093	.3503	.06710	.02150	.3205
Friday Harbor	Sept. '27	No sample	...	...	....	....	...
Friday Harbor	Oct. '27	16.90	1.133	.3626	.06704	.02146	.3201
Friday Harbor	Nov. '27	16.81	1.128	.3612	.06710	.02149	.3202
Friday Harbor	Dec. '27	16.37	1.097	.3502	.06701	.02139	.3192
Friday Harbor	Jan. '28	16.38	1.097	.3508	.06700	.02142	.3196
Friday Harbor	Feb. '28	16.58	1.108	.3568	.06686	.02152	.3219
Friday Harbor	Mar. '28	16.85	1.127	.3627	.06691	.02153	.3217
Friday Harbor	Apr. '28	16.86	1.132	.3633	.06711	.02155	.3209
Friday Harbor	May '28	16.65	1.115	.3589	.06697	.02156	.3219
Friday Harbor	June '28	16.25	1.085	.3504	.06675	.02156	.3229
Friday Harbor	July '28	16.38	1.097	.3528	.06697	.02154	.3216
Friday Harbor	Aug. '28	16.90	1.130	.3618	.06686	.02141	.3202
East Sound	Comp. '28	16.44	1.101	.3549	.06700	.02159	.3220
Nanaimo Bay, B. C.	Comp. '29	14.21	0.9521	.3070	.06700	.02160	.3224
Gulf of Alaska	Comp. '28	18.12	1.214	.3883	.06700	.02143	.3199
Gulf of Alaska	No. 16 '29	17.83	1.191	.3834	.06680	.02150	.3219
Gulf of Alaska	No. 370 '29	19.09	1.280	.4121	.06705	.02159	.3220
Gulf of Alaska	No. 406 '29	18.79	1.257	.4054	.06690	.02158	.3225
			Average		.06694	.02150	.3212
			Maximum		.06711	.02160	.3229
			Minimum		.06669	.02139	.3192
			Difference		.00042	.00021	.0037

Discussion

The authors claim a maximum experimental error less than 0.0015 g. of magnesium, 0.0006 g. of calcium and 0.015 g. chlorinity per kilo of water. Based on these limits, the variations in the ratios resulting from experi-

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[14] Thompson, THIS JOURNAL, 50, 681 (1928).

mental error were calculated to be 0.00011 for Ca/Cl, 0.00020 for Mg/Cl and 0.0016 for Ca/Mg. Of the 30 samples studied, only 2 showed values outside these limits of error. The errors in the method used by Matthews and Ellis, as shown by their results, are far greater than any variations in the composition of the sea waters examined by the authors. Thus, assuming Mg/Cl as 0.06692 and a chlorinity of $17.00\,^0/_{00}$, the experimental error of their method would give a variation from 0.0661 to 0.0677, or a maximum difference of 0.0016.

From the data of Johnston[15] the ionic ratios for the fresh water of the Fraser River were calculated to be 0.484 Mg/Cl, 2.719 Ca/Cl and 5.618 Ca/Mg, which is an interesting contrast for those obtained on sea water. Using Johnston's data and assuming a sea water with a chlorinity of $17.00\,^0/_{00}$ the effect of dilution by the Fraser River would produce the following very slight changes in the ionic ratios.

	Ca/Cl	Mg/Cl	Ca/Mg
Sea water, $17.00\,^0/_{00}$ Cl	0.02150	0.06692	0.3211
Sea water diluted by Fraser River to $14.00\,^0/_{00}$ Cl	.02165	.06694	.3234

TABLE IV

IONIC RATIOS OF OTHER INVESTIGATIONS

Worker	Source	Date	Number of samples	Ca/Mg = K	Ca/Cl = K	Mg/Cl = K
Thorpe	Irish Sea	1871	1	0.3351	0.02183	0.06528
Schmidt[a]	White Sea	1878	3	.3185	.02189	.06873
Schmidt[a]	Arctic Ocean	1878	2	.3103	.02095	.06753
Schmidt[a]	Straits of Malacca	1878	1	.2915	.02143	.07259
Schmidt[a]	China Sea	1878	1	.3132	.02145	.06758
Schmidt[a]	Indian Ocean	1878	2	.3120	.02091	.06685
Schmelck[a]	North Atlantic	1882	51	.3151	.02182	.06926
Forsberg	Siberian Ocean	1883	4	.3089	.02128	.06889
Dittmar[a]	All oceans	1884	77	.3171	.02162	.06815
Natterer[a]	Mediterranean Sea	1892	42	.3183	.02152	.06971
Natterer[a]	Sea of Marmora	1895	44	....	.02197	.....
Natterer[a]	Red Sea	1896	15	.3167	.....	.....
Kolotoff	Black Sea	1896	4	.3348	.02177	.06512
Schloesing	Mediterranean Sea	1906	1	.3370	.02228	.06612
Schloesing	Mediterranean Sea	1906	1	.3462	.02266	.06546
Schloesing	Atlantic Ocean	1906	1	.3441	.02303	.06693
Steiger	Gulf of Mexico	1910	1	.3348	.02205	.06490
Wheeler	West Atlantic	1910	5	.3297	.02208	.06697
Bertrand	Atlantic Ocean	1922	1	.3319	.02092	.06302
Bertrand	Mediterranean Sea	1922	1	.3299	.02133	.06465
	Mean average			.3243	.02177	.06713
	Weighted average		258	.3178	.02172	.06859
	Thompson and Wright			.3212	.02150	.06694

[a] Corrected for gravimetric factors used due to change in atomic weight.

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[15] Johnston, "Canada Dept. of Mines, Geol. Sur., Memoir, 125," No. 107, p. 25 (1921).

In Table IV are shown the results obtained for the ionic ratios calculated from the data of other investigators. A comparison of either of the ratios involving magnesium is hardly justifiable, since the methods of analysis are open to criticism in the light of Epperson's work. For the Ca/Cl, however, several workers, with samples from widely scattered sources, obtained values agreeing with those found by the authors.

Conclusions

1. A study of the methods of analysis for calcium and magnesium in sea water has been made. The gravimetric calcium oxalate method and Epperson's modification of the magnesium ammonium phosphate method are the most accurate. Because of the large quantities of interfering ions, three precipitations are necessary for both the calcium and magnesium determinations.
2. The constancy of composition of the waters of the North and Northeast Pacific with reference to the calcium and magnesium ions and the chlorinity has been demonstrated.
3. The ratio for calcium chlorinity is 0.02150, for magnesium chlorinity 0.06694 and for calcium–magnesium 0.3212. The amounts of calcium and magnesium per kilo of sea water may be very closely estimated by multiplying the chlorinity by these factors.

Seattle, Washington

[Contribution from the Chemical Laboratory of Purdue University]

THE DISSOCIATION CONSTANT OF WATER FROM AN EQUILIBRIUM INVOLVING MERCURIC OXIDE AND MERCUROUS BROMIDE[1]

By Roy F. Newton and M. G. Bolinger

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Introduction

The dissociation constant of water has usually been determined by one of three methods: by measurement of the conductivity of water, by determining the hydrolysis of salt solutions, or by finding the e.m.f. of cells. Possibly the best determination by conductivity measurements is that of Kohlrausch and Heydweiller[2] on the conductivity of water. It is rather difficult to estimate the magnitude of the uncertainty of their result, but their method of extrapolation from their best water to the conductivity of pure water would seem to introduce an uncertainty of 5% or more in

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[1] From a thesis submitted by M. G. Bolinger to the Graduate School of Purdue University in partial fulfilment of the requirements for the Degree of Master of Science.

[2] Kohlrausch and Heydweiller, *Z. physik. Chem.*, **14**, 330 (1894); *Ann. Physik*, [4] **28**, 503 (1909).