[CONTRIBUTION FROM THE CHEMICAL AND OCEANOGRAPHIC LABORATORIES OF THE UNIVERSITY OF WASHINGTON]

Specific Gravities of Pure and Mixed Salt Solutions in the Temperature Range 0 to 25°[1]

BY RAYMOND W. BREMNER, THOMAS G. THOMPSON AND CLINTON L. UTTERBACK

In this paper are presented specific gravity data for aqueous solutions. The solutions are those of some of the various salts occurring in sea water. The concentrations of the binary solutions were in the same ratios that occur in the ocean waters.

Method of Procedure and Apparatus

Using the Archimedes principle, the weight of a given volume of solution was compared with that of an equal volume of pure water, the density of which was accurately known.[2] This method is more rapid than the pycnometer method and, with the refinements used, is capable of great precision.

A cylindrical glass bulb weighted with mercury and suspended by means of a piece of fine platinized platinum wire, was weighed when immersed in water and also in the solutions. For this purpose, the water and the solutions were contained in a cylindrical copper tank of suitable design, which was suspended in a water-bath. The temperature fluctuation in the water-bath varied from 0.01° at 0° to 0.002° at 25°. The weighings were made to 0.1 mg.

Check determinations were made with two different glass bulbs and two cylindrical copper tanks, using duplicate solutions. The approximate volumes of the bulbs were 250 and 260 ml., respectively. With the copper tank in position in the water-bath and the glass bulb suitably suspended in the solution at the desired temperature, consecutive weighings of the bulb were made at five-minute intervals until the change in weight during a five-minute interval was not greater than 0.1 mg. Observations were made in this way at 0, 5, 10, 15, 20, and 25°, respectively.

Immediately after making each observation, the weight of the support for the bulb was determined. The change in the buoyancy of the solution on the portion of the support immersed was negligibly small over the temperature range.

Solutions Measured

Materials.—Very pure potassium chloride and sodium chloride were prepared by well-known methods.[3] Purified magnesium sulfate was heated in air at 360° for sixteen hours. It was cooled in a vacuum desiccator charged with anhydrous magnesium perchlorate. It was then weighed in contact with dried air in a tared ground glass-stoppered weighing bottle.[4,5] The water used was similar to the equilibrium water described by Washburn.[6] The solutions were prepared according to the composition of sea water as reported by Thompson.[7]

The ions of the salts comprising the major constituents of sea water are chloride, sulfate, sodium, magnesium, calcium, and potassium. The ratio of the number of milligram atoms of any one of these to that of any other is a constant.[8] The concentrations of the elements comprising these ions for a sea water having a chlorinity of 19.00‰[9] are as follows:

	Mg. at./kg. of sea water
Chlorine	535.0
Sodium	454.0
Magnesium	52.30
Sulfur (sulfate)	27.63
Potassium	9.6

The solutions were prepared by taking a fixed mass of pure water, 1 kg., to which were added the various salts in the proper concentrations. It should be noted that this method differs from that in which the number of grams of salt per kilogram of solution is considered.

The constituents used were salts that are comparatively easy to purify and handle quantitatively in the dry condition. The sodium and potassium ions were introduced as chlorides, the sulfate and magnesium ions as magnesium sulfate.

TABLE I

SHOWING THE WEIGHT OF SALT ADDED TO 1 KG. OF WATER

Approximate chlorinity	19‰	14‰	8‰	4‰
	Sodium Chloride Solutions			
NaCl, g.	27.26159	19.94439	11.30020	5.61836
	Potassium Chloride Solutions			
KCl, g.	0.735220	0.537882	0.304756	0.151522
	Magnesium Sulfate Solutions			
$MgSO_4$, g.	3.41676	2.49969	1.41629	0.704166
	Sodium Chloride, Potassium Chloride Solutions			
NaCl, g.	27.26159	19.94439	11.30020	5.61836
KCl, g.	0.735220	0.537882	0.304756	0.151522
	Sodium Chloride, Magnesium Sulfate Solutions			
NaCl, g.	27.26159	19.94439	11.30020	5.61836
$MgSO_4$, g.	3.41678	2.49969	1.41629	0.704166

Sodium chloride was present in all of the solutions containing two salts. In preparing such solutions the approximate amount of a stock solution of the salt, other than sodium chloride, required to prepare about a liter of the desired solution was weighed accurately in a ground glass-stoppered flask. From this, the required weight of

(1) Read before the Ninety-Fifth Meeting of the American Chemical Society at Dallas, Texas, April, 1938. For supplementary tabular data, order Document 1142, American Documentation Institute, 2101 Constitution Ave., Washington, D. C., remitting $1.00 for 6" × 8" photoprints or 28¢ for microfilm.

(2) "International Critical Tables," Vol. III, 1938, p. 25.

(3) Theodore Shedlovsky, THIS JOURNAL, **54**, 1417 (1932).

(4) G. H. J. Bailey, *J. Chem. Soc.*, **51**, 676–683 (1887).

(5) Adolph Schröder, *Ber.*, **4**, 471 (1871).

(6) Edward W. Washburn, THIS JOURNAL, **40**, 111 (1918).

(7) Thomas G. Thompson, *J. Chem. Ed.*, **13**, 203–209 (1936).

(8) Thomas G. Thompson, "Contribution to Marine Biology," Stanford University Press, 1930, p. 79.

(9) 19.00‰ means 19 parts per thousand by weight.

sodium chloride and of the desired solution was calculated. The calculated amount of dry sodium chloride was weighed out and added to the solution in the flask, which was then made up to the calculated weight by the addition of equilibrium water. All weights were corrected to vacuum for the purpose of computation and to the conditions pertaining in the laboratory for the purpose of weighing. The apparatus used for weighing has been described.[10] The solutions, as well as the equilibrium water used in their preparation, were kept in well seasoned and steamed Pyrex ground glass-stoppered bottles.

Experimental Results

The specific gravities of each of the following solutions were measured at 0, 5, 10, 15, 20, and 25°: sodium chloride, potassium chloride, magnesium sulfate, sodium chloride plus potassium chloride, and sodium chloride plus magnesium sulfate. Each of these was found by direct comparison with one of the values for water given in the "International Critical Tables." The experimentally determined data are accurate to five decimal places, the sixth being a close estimate in most cases. Duplicate values usually agreed exactly to five decimal places. A total of 120 determinations was made.

The specific gravities of the solutions were computed by the usual method. The volume of the bulb, its weight *in vacuo*, and its weight immersed in the solution at each temperature were redetermined several different times during the work, but no appreciable departure from the original values was observed.

The equation proposed by Root,[11] contains

$$D = D_0 + pN + qN^{3/2}$$

two constants p and q which are different for each type of solution and at each temperature. These constants were evaluated by the method of least squares at each of the six temperatures for each type of solution measured, and their values are listed in Table II. D and N are density and normality, respectively. Normalities were computed from the data in Table I, using the 1936 atomic weights.

After p and q were obtained for a particular type of solution, the specific gravities were calculated for the concentrations at which measurements were made and for concentrations at which specific gravity data were found in the "International Critical Tables."

Table III is illustrative of the agreement between the observed and calculated values for two mixed solutions at two of the temperatures.

TABLE II

CONSTANTS FOR THE ROOT EQUATION

Approx. no. mg. eq. wts. per 1 soln.	°C.	p	q
Sodium chloride			
100 to 500	25	0.041916	−0.001853
	20	.042432	− .001990
	15	.042995	− .002052
	10	.043740	− .002204
	5	.044660	− .002391
	0	.045846	− .002684
Potassium chloride			
2 to 10	25	.04570	.0211
	20	.04710	.0110
	15	.04802	.0050
	10	.04884	.0015
	5	.04949	.0023
	0	.05141	− .0088
Magnesium sulfate			
10 to 60	25	.06340	− .00795
	20	.06331	− .00611
	15	.06423	− .00854
	10	.06440	− .00710
	5	.06476	− .00579
	0	.06631	− .00890
Sodium chloride and potassium chloride			
100 to 500	25	.041983	− .001776
	20	.042467	− .001868
	15	.043042	− .001952
	10	.043759	− .002057
	5	.044728	− .002321
	0	.046004	− .002760
Sodium chloride and magnesium sulfate			
100 to 500	25	.044213	− .002090
	20	.044658	− .002158
	15	.045240	− .002285
	10	.045968	− .002442
	5	.046880	− .002661
	0	.048054	− .002987

The agreement between the calculated and observed values, not given in Table III, is also in every instance within 5 in the sixth decimal place. Thus the equation proposed by Root is shown to reproduce the experimental results within the limit of experimental error in the case of mixed salt solutions as well as pure salt solutions in all the concentrations and at all the temperatures measured.

The most exact applicable data found in the "International Critical Tables" are for potassium chloride at 20°. They are reported to eight decimal places. These data and the values calculated from the constants given in Table II are consistent within the limits of experimental error.

(10) Raymond W. Bremner and Thomas G. Thompson, THIS JOURNAL, **59**, 2372 (1937).

(11) William C. Root, *ibid.*, **55**, 850–851 (1933).

TABLE III

SPECIFIC GRAVITIES OF MIXED SOLUTIONS

Mg. eq. wts. per kg. water		Mg. eq. wts. per 1 soln.	Sp. gr. obsd.	Sp. gr. calcd.	Difference (10^6)
SODIUM CHLORIDE AND POTASSIUM CHLORIDE					
Temperature 25°					
NaCl	KCl				
466.377	9.86172	470.805	1.016267	1.016266	1
341.198	7.21473	345.247	1.011206	1.011209	3
193.318	4.08775	196.147	1.005156	1.005155	1
96.116	2.03241	97.695	1.001123	1.001122	1
Temperature 0°					
466.377	9.86172	472.870	1.020725	1.020725	0
341.198	7.21473	346.627	1.015252	1.015251	1
193.318	4.08775	196.835	1.008679	1.008682	3
96.116	2.03241	98.004	1.004290	1.004292	2
SODIUM CHLORIDE AND MAGNESIUM SULFATE					
Temperature 25°					
NaCl	$MgSO_4$				
466.377	56.766	517.300	1.019167	1.019167	0
341.198	41.530	379.327	1.013359	1.013357	2
193.318	23.530	215.492	1.006391	1.006393	2
96.116	11.699	107.325	1.001746	1.001746	0
Temperature 0°					
466.377	56.766	519.609	1.023716	1.023718	2
341.198	41.530	380.865	1.017472	1.017468	4
193.318	23.530	216.257	1.009960	1.009960	0
96.116	11.699	107.666	1.004932	1.004936	4

Specific gravity values for sodium chloride solutions at 0, 10 and 25° are reported in the "International Critical Tables" to five decimal places. Using the concentrations listed and the above constants, these specific gravities were calculated by means of the equation proposed by Root. The deviations of the calculated values from those given in the "International Critical Tables" range from 0.00002 to 0.00023. These deviations are large considering that the data are reported to five decimal places. They are all negative but are considerably larger at 25 and 0° than they are at 10°. In some instances they increase with concentration while in others they decrease. It is evident that the "International Critical Tables" data for sodium chloride do not conform to the Root equation as well as those for potassium chloride.

Summary

1. The specific gravities of various solutions of salts occurring in sea water have been measured at 5° intervals from 0 to 25° inclusive.

2. The solutions were prepared to contain the pure and mixed salts in concentrations covering the range found in nature.

3. The specific gravity measurements, which are accurate to five decimal places and closely estimated to the sixth, were made by the method of weighing a weighted glass bulb suspended in the solutions.

4. Some of the data on the specific gravity of sodium chloride solutions reported to five decimal places in the "International Critical Tables" can be represented by the equation proposed by Root to only four decimal places. Certain more accurate data on potassium chloride solutions have been shown to be entirely consistent with the data reported in this paper.

5. The equation proposed by Root has been shown to reproduce the experimental results, within the limits of experimental error, at each of the six temperatures used. It applies equally well to solutions containing one solute and to those containing sodium chloride plus potassium chloride and sodium chloride plus magnesium sulfate. The constants for this equation have been calculated at six temperatures for each of the five types of solutions studied.

SEATTLE, WASHINGTON RECEIVED JULY 5, 1938