trolytes). The aging of lead chromate is greatly enhanced by the addition of acids which increase the solubility. With increasing solubility part of the aging may be attributed to Ostwald ripening.

6. No aging was found in 95% ethanol. The solubility of lead chromate in this medium is extremely small.

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

Specific Gravities and Electrical Conductances of Some Calcium Sulfate Solutions and Mixtures of Sodium Chloride and Calcium Sulfate

BY RANDALL E. HAMM WITH THOMAS G. THOMPSON

In previous papers[1,2] were reported specific gravities and electrical conductances of pure salt solutions of sodium chloride, potassium chloride, and magnesium sulfate, and the mixtures, sodium chloride–potassium chloride and sodium chloride–magnesium sulfate. These papers were the beginning of a study of the conductances and specific gravities of salt solutions in concentrations as found in sea water and were made to further the understanding of solutions of mixed electrolytes and the physical chemistry of ocean water. This paper is a continuation of the work and reports specific gravities and electrical conductances of calcium sulfate solutions and mixtures of sodium chloride and calcium sulfate. While previous papers report only the values for mixtures having a constant ionic ratio, this paper also reports electrical conductances of solutions containing varying amounts of calcium sulfate at constant concentrations of sodium chloride.

Experimental Methods

The apparatus used has been described previously.[2,3] The bridge and the thermometers were again calibrated and the cell constants were determined using the data reported by Jones and Bradshaw[4] and Bremner and Thompson.[3]

The sodium chloride used was purified by the method described by Shedlovsky.[5]

The calcium sulfate was prepared and purified by treating the purest Baker Analyzed calcium carbonate with C. P. sulfuric acid slowly until effervescence ceased, bringing to a boil, filtering, and collecting the crystals that formed upon cooling. Successive batches were prepared by treating the original precipitate with boiling dilute sulfuric acid. The crystals were heated to about 200° until all of the sulfuric acid was driven off. Immediately before using, this calcium sulfate was heated to about 500° for eight to twelve hours in a glass-stoppered weighing bottle, the weighing bottle was transferred to a vacuum desiccator, and the desiccator evacuated. Well desiccated air was passed into the desiccator when ready for weighing the calcium sulfate.

The calcium sulfate was weighed using a tare bottle of the same size and shape which had gone through the same previous treatment. All solutions were prepared by weight. Corrections to vacuum conditions were made.

Results

Solutions were prepared which contained quantities of calcium sulfate and of sodium chloride–calcium sulfate comparable to sea water of the chlorinities of 19, 14, 8, and 4 parts per thousand. Table I gives a summary of the weights of the two salts added to one thousand grams of water.

TABLE I

GRAMS OF SALTS ADDED TO ONE THOUSAND GRAMS OF WATER

Approx. chlorinity, ‰	19	14	8	4
	Calcium Sulfate Solutions			
$CaSO_4$, g.	1.51754	1.11022	0.62904	0.31275
	Sodium Chloride–Calcium Sulfate Solutions			
NaCl, g.	27.26159	19.94439	11.30020	5.61836
$CaSO_4$, g.	1.51754	1.11022	0.62904	0.31275

Duplicate or triplicate solutions were prepared in all cases and the specific gravities and electrical conductances were determined at the temperatures 0, 5, 10, 15, 20 and 25°.

The specific gravities of calcium sulfate solutions are listed in Table II. The values calculated from the Root equation are also listed with the difference being given in the last column. The constants of the Root equation were determined by the method of least squares and are given in Table III. The specific gravities of calcium sulfate solutions have been reported by Harkins and Paine[6] and Cameron and Robinson.[7]

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[1] Bremner, Thompson and Utterback, THIS JOURNAL, **60**, 2616 (1938).

[2] Bremner, Thompson and Utterback, *ibid.*, **61**, 1219 (1939).

[3] Bremner and Thompson, *ibid.*, **59**, 2372 (1937).

[4] Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

[5] Shedlovsky, *ibid.*, **54**, 1411 (1932).

[6] Harkins and Paine, *ibid.*, **41**, 1155 (1919).

[7] Cameron and Robinson, *J. Phys. Chem.*, **14**, 569 (1910).

These values have been reported to only five decimals while the figures reported here are accurate to the fifth figure and the sixth figure is a good approximation.

TABLE II

SPECIFIC GRAVITY OF CALCIUM SULFATE SOLUTIONS IN THE TEMPERATURE RANGE 0 TO 25°

Mg. equivalents per Kg. water	Mg. equivalents per Liter	Sp. gr. obsd.	Sp. gr. calcd.	Calcd. − obsd. × 10^6
		25°		
4.5945	4.5811	0.997390	0.997389	−1
9.2411	9.2141	.997708	.997707	−1
16.3100	16.2624	.998188	.998190	+2
22.2938	22.2289	.998598	.998597	−1
		20°		
4.5945	4.5864	0.998548	0.998549	+1
9.2411	9.2248	.998867	.998866	−1
16.3100	16.2812	.999345	.999345	0
22.2938	22.2544	.999749	.999749	0
		15°		
4.5945	4.5906	0.999447	0.999448	+1
9.2411	9.2332	.999767	.999768	+1
16.3100	16.2960	1.000253	1.000251	−2
22.2938	22.2746	1.000656	1.000657	+1
		10°		
4.5945	4.5933	1.000047	1.000049	+2
9.2411	9.2387	1.000371	1.000372	+1
16.3100	16.3059	1.000861	1.000858	−3
22.2938	22.2882	1.001265	1.001267	+2
		5°		
4.5945	4.5945	1.000312	1.000314	+2
9.2411	9.2412	1.000643	1.000640	−3
16.3100	16.3103	1.001134	1.001132	−2
22.2938	22.2945	1.001546	1.001548	+2
		0°		
4.5945	4.5940	1.000194	1.000196	+2
9.2411	9.2402	1.000530	1.000527	−3
16.3100	16.3087	1.001029	1.001029	0
22.2938	22.2923	1.001451	1.001452	+1

TABLE III

CONSTANTS FOR THE ROOT EQUATION

Temp., °C.	p	q
	Calcium Sulfate Solutions	
0	0.07190	−0.00580
5	.07070	− .00615
10	.07076	− .01153
15	.07074	− .01382
20	.06978	− .01089
25	.06910	− .00387
	Sodium Chloride–Calcium Sulfate Solutions	
0	0.047112	−0.003023
5	.045929	− .002716
10	.045107	− .002658
15	.044190	− .002248
20	.043643	− .002198
25	.043117	− .001925

The specific gravities of mixtures of sodium chloride and calcium sulfate were determined and the constants for the Root equation determined by the method of least squares. These constants are included in Table III. The deviations between the calculated specific gravities and the determined specific gravities were of the same order as those in the case of the calcium sulfate solutions shown in Table II.

The specific conductances of calcium sulfate solutions and mixtures of sodium chloride and calcium sulfate are listed in Tables IV and V. Values of the temperature coefficients of equivalent conductance are also included. The conductances of calcium sulfate solutions have been determined by Harkins and Paine.[6] The results of Harkins and Paine, data from the "International Critical Tables," converted to the same basis (Jones and Bradshaw[4]) and the results of the

TABLE IV

CONDUCTANCE OF $CaSO_4$ SOLUTIONS IN THE TEMPERATURE RANGE 0 TO 25°

Mg. equivalents per Kg. water	Mg. equivalents per Liter	Sp. cond. 10^6	Equiv. cond.	Temp. coeff. of equiv. cond.
		25°		
4.5945	4.5811	470.12	102.62	0.0203
9.2411	9.2141	843.83	91.930	199
16.3100	16.2624	1345.2	82.718	197
22.2938	22.2289	1723.2	77.521	194
		20°		
4.5945	4.5864	423.44	92.325	0.0222
9.2411	9.2248	764.10	82.833	218
16.3100	16.2812	1214.6	74.601	216
22.2938	22.2542	1558.5	70.032	213
		15°		
4.5945	4.5906	377.41	82.214	0.0241
9.2411	9.2331	682.31	73.899	239
16.3100	16.2960	1086.0	66.642	237
22.2938	22.2746	1394.2	62.623	235
		10°		
4.5945	4.5933	332.91	72.479	0.0263
9.2411	9.2387	602.28	65.192	262
16.3100	16.3059	959.38	58.837	260
22.2938	22.2882	1233.5	55.344	259
		5°		
4.5945	4.5945	290.02	63.122	0.0288
9.2411	9.2412	524.99	56.810	286
16.3100	16.3103	836.91	51.314	285
22.2938	22.2945	1076.9	48.302	284
		0°		
4.5945	4.5940	249.63	54.338	0.0314
9.2411	9.2402	452.05	48.922	310
16.3100	16.3087	720.41	44.174	310
22.2938	22.2923	927.99	41.629	309

TABLE V

CONDUCTANCE OF NaCl–$CaSO_4$ MIXTURES IN THE TEMPERATURE RANGE 0 TO 25°

Mg. equivs. per kg. H_2O NaCl	$CaSO_4$	Total mg. equiv. per l. of soln.	Sp. cond. 10^6	Equiv. cond.	Temp. coeff. of equiv. cond.
		25°			
96.116	4.5945	100.251	10578	105.52	0.0205
193.318	9.2411	201.288	20171	100.21	203
341.198	16.3100	354.318	33755	95.268	202
466.377	22.2938	483.200	44575	92.249	201
		20°			
96.116	4.5945	100.371	9526.2	94.909	0.0220
193.318	9.2411	201.538	18179	90.201	218
341.198	16.3100	354.775	3045.0	85.829	216
466.377	22.2938	483.839	40229	83.145	215
		15°			
96.1167	4.5945	100.467	8560.6	84.671	0.0237
193.318	9.2411	201.740	16241	80.505	235
341.198	16.3100	355.160	27246	76.715	233
466.377	22.2938	484.393	36024	74.369	231
		10°			
96.116	4.5945	100.535	7523.2	74.832	0.0258
193.318	9.2411	201.890	14380	71.227	254
341.198	16.3100	355.459	24155	67.954	252
466.377	22.2938	484.833	31960	65.920	251
		5°			
96.116	4.5945	100.570	6574.8	65.375	0.0282
193.318	9.2411	201.977	12597	62.368	277
341.198	16.3100	355.653	21182	59.558	275
466.377	22.2938	485.144	28038	57.793	274
		0°			
96.116	4.5945	100.568	5675.0	56.429	0.0306
193.318	9.2411	201.994	10896	53.942	303
341.198	16.3100	355.725	18350	51.585	299
466.377	22.2938	485.312	24309	50.089	297

present work on these solutions are shown in Fig. 1.

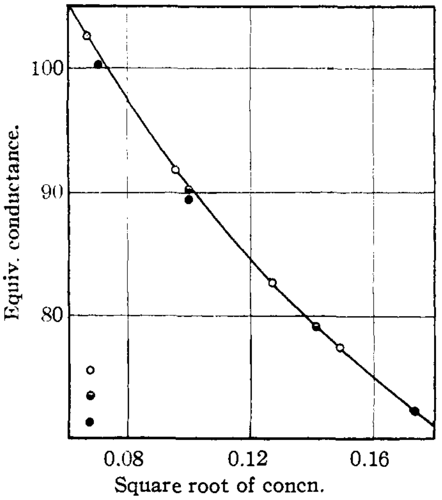

Fig. 1.—Equivalent conductance of calcium sulfate solution at 25°: ○, new data; ⊖, Harkins and Paine; ●, "International Critical Tables."

The temperature coefficients were computed as described by Bremner, Thompson and Utterback.[2] No detectable change in the coefficients of sodium chloride solutions occurs when calcium sulfate is added in the ratios used in this investigation. The coefficients of calcium sulfate solutions are slightly below those of magnesium sulfate. The divergence of the temperature coefficients for calcium sulfate decreases with increased temperature in the same manner as magnesium sulfate.

The specific and equivalent conductances of the sodium chloride solutions containing varying amounts of calcium sulfate were determined at 25°. The sodium chloride concentrations used for this investigation were 95.678, 192.109 and 338.168 milligram equivalents per liter at 25°.

The equivalent conductances are plotted against $\mu_v^{1/2} - c_2^{0\,1/2}$ in Fig. 2, where μ_v is the total volume ionic strength of the mixed solution and c_2^0 is the molar concentration of the sodium chloride solu-

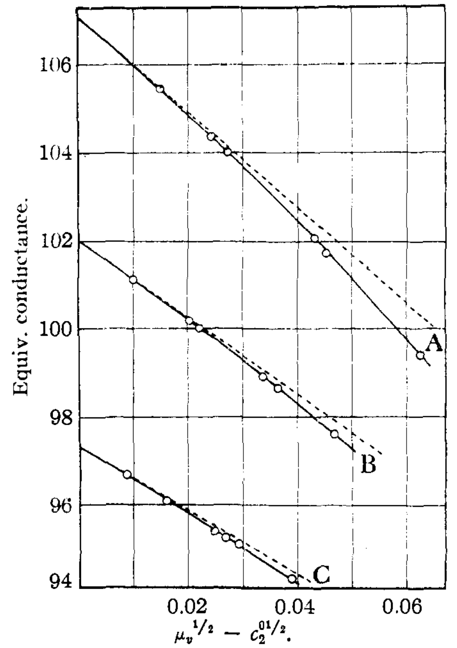

Fig. 2.—Equivalent conductance of NaCl-CaSO$_4$ mixtures *versus* increase in square root of ionic strength; milligram equivalents of NaCl per liter, A = 95.678, B = 192.109, C = 338.168.

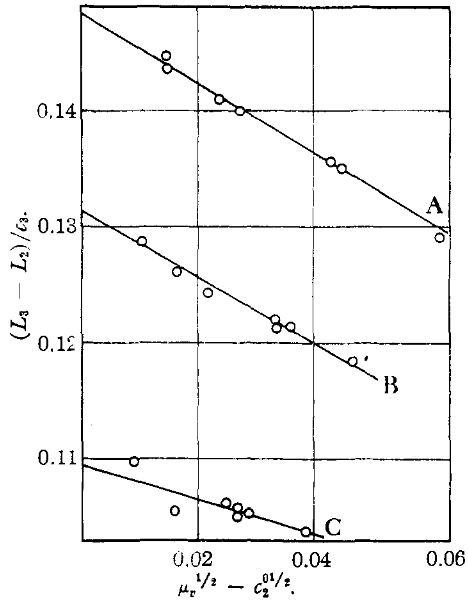

Fig. 3.—Increase in specific conductance of NaCl-CaSO$_4$ mixtures per mole of added CaSO$_4$ *versus* increase in square root of volume ionic strength; milligram equivalents of NaCl per liter, A = 95.678, B = 192.109, C = 338.168.

tion. The plot is seen to approach a limiting straight line that reaches the equivalent conductance axis at the equivalent conductance of the pure sodium chloride.

In Fig. 3 the function $(L_3 - L_2)/c_3$ is plotted against $\mu_v^{1/2} - c_2^{01/2}$ where L_3 is the specific conductance of the mixed solution, L_2 is the specific conductance of the pure sodium chloride solution and c_3 is the molar concentration of the added calcium sulfate. This plot is seen to approximate a straight line; therefore it is proposed to represent the specific conductance of the mixture by the function

$$L_3 = L_2 + ac_3 - bc_3(\mu_v^{1/2} - c_2^{01/2})$$

The constants for this equation have been determined by the method of least squares and are given in Table VI.

TABLE VI

$c_2^{01/2}$	a	b
0.581522	0.1094	0.145
.438298	.1313	.279
.309163	.1484	.298

Using the constants included in Table VI, values of the specific conductances of the mixtures were calculated. The average deviation between the calculated conductances and the determined conductances was found to be 0.01%. Since it was attempted to keep the experimental error within 0.02% this tends to show that the empirical equation chosen predicts the data within the experimental error.

By interpolation, values of constants for other sodium chloride concentrations can be obtained and the equation proposed can be used to calculate the specific conductance of any mixture of sodium chloride and calcium sulfate that comes within the limits of this investigation.

Summary

1. The electrical conductances of mixtures of sodium chloride and calcium sulfate having a constant ionic ratio are reported at the temperatures 0, 5, 10, 15, 20 and 25°.

2. The electrical conductances and specific gravities of solutions of calcium sulfate are reported at the temperatures 0, 5, 10, 15, 20 and 25°.

3. The calcium sulfate solutions and mixtures of sodium chloride and calcium sulfate were found to follow the Root equation and the constants determined by the method of least squares are reported.

4. Sodium chloride solutions of three different concentrations with varying quantities of calcium sulfate were prepared and the specific con-

ductances were determined at 25°. The function $L_3 - L_2 = ac_3 - bc_3 (\mu_v^{1/2} - c_2^{0^{1/2}})$ was proposed to represent the experimental data. The constants of the equation were determined by the method of least squares and were found to predict the observed values with an average deviation of 0.01%.

SEATTLE, WASHINGTON RECEIVED DECEMBER 21, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

A Comparative Study of Surfaces of Solutions with the Film Balance and Surface Tension Equipment

BY JAMES W. MCBAIN AND EVERT R. SHARP*

When the film balance is applied to the study of uncontaminated solutions,[1] results are obtained which could not have been anticipated from studies of insoluble films or from the ordinary theory of diffusion. It is therefore very important to find out whether these complicated surface effects are paralleled by corresponding changes in surface tension as measured by other standard equipment.

The nearest instrument to the film balance is the PLAWM trough[2] which has an impermeable flexible partition between the liquids on the two sides of the floating barrier and thus actually measures surface tension on plane swept surfaces. Wilson[2,3] had already shown that this gave results closely similar to that of the Lloyd and Scarth ring method. Thus, although all experiments with the film balance can be paralleled by more complete measurements with the PLAWM trough, it is experimentally much easier to use the film balance and the duNoüy tensiometer, or ring method.

The ring method has been criticized as referring to surfaces that are not completely static or undisturbed. However, this disability may be obviated by using the ring on a very large swept surface, such as that in the film balance or PLAWM trough, for then the disturbance involves a negligible proportion of the surface. The same consideration applies to the Wilhelmy method. The remaining objection that the solution lying within the ring is more extensively disturbed and therefore may inject some doubt into the measurements, is likewise obviated if two rings of different diameter are used and yet give the same result. For our purpose only the first precaution was necessary to establish what it is that is observed in the film balance.

We have found that the changing pressures observed on compressing and expanding the superficial areas of solutions in the film balance are paralleled by changes in surface tension found with the duNoüy tensiometer on the same large surfaces.

The Film Balance

The equipment and precautions described by Spencer[1] were again employed, but the whole apparatus was placed inside a new air-tight metal cabinet of practically saturated humidity, with glass front and sliding glass doors for use during actual manipulation. The double walls were six inches thick on four sides, and were filled with water thermostated at 25°. The platinum–iridium float was provided with short platinum wires coated with dicetane to which the suspending threads were tied.

This cabinet also contained for use with the tensiometer a fused silica trough 38 cm. long and 15 cm. wide, with six coats of Bakelite lacquer. This was mounted on a disk with three levelling screws. The disk was mounted on a stand with micrometer screw to raise and lower the tray. The area available for sweeping was 450 sq. cm. The 0.25 mm. steel torsion wire was thinly coated with Bakelite lacquer. The 40 mm. platinum ring was always washed and heated to redness before use. The surface tension of pure water after calibration of the wire appeared as 72.00 dynes/cm. as compared with the standard value 71.97.

Invariably, sweeping[1] and tests for contamination[1] preceded each experiment.

The nine procedures of previous studies[4] with the film balance were simplified to four for use with the tensiometer trough. These should be briefly recorded. Force–area curves are illusory when obtained with soluble surfaces.

Procedure I_a determines the rate at which surface tension attains equilibrium, and also the maximum observable change of surface tension between a freshly swept and a completely aged surface. After repeated sweeping, *away from* the float or from the very end of the trough, the initial surface tension is taken as rapidly as possible and then at

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* Thesis (87 pages, including 21 figures and 34 tables) available in bibliofilm through the Department of Agriculture, Washington, D. C.

(1) References to eight papers by Doss, 1935–1939, and to four papers from this Laboratory, 1935–1939, are given in McBain and Spencer, THIS JOURNAL, **62**, 239 (1940).

(2) McBain, Vinograd and Wilson, *ibid.*, **62**, 244 (1940).

(3) McBain, Ford and Wilson, *Kolloid-Z.*, **78**, 1 (1937).

(4) McBain and Perry, *Ind. Eng. Chem.*, **31**, 35 (1939).