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

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

BY RAYMOND W. BREMNER WITH THOMAS G. THOMPSON AND C. L. UTTERBACK

The specific conductances of certain solutions of pure and mixed salts in the concentrations occurring in sea water have been measured. The compositions of the solutions, the methods of preparation, and the values of specific gravity used in calculating the equivalent conductances have been discussed by the authors.[2] The measurements were made at 0, 5, 10, 15, 20, and 25°, using the apparatus and employing the technique previously described.[3]

Observed deviations in measurements did not exceed 0.02%. Duplicate solutions were prepared and run in almost all instances. No discrepancies were found between duplicate samples since the experimental data and the calculations were checked repeatedly. The principal sources of error were in filling the cells rather than in preparing the solutions or in measuring the resistances. Uncertainties due to small temperature fluctuations were reduced to low values by taking several independent readings of the resistance of each cell at each temperature. Duplicate determinations usually were made in different cells at different times. This served as a check on the cell constants as well as a means of reducing experimental errors.

Results

Data.—The specific conductance and equivalent conductance data are listed in Tables I to V. Values of temperature coefficients of equivalent conductance are also included.

The conductances of sodium chloride solutions and of potassium chloride solutions at 25° have been determined by Shedlovsky[4] whose measurements were based on the standard recommended by Jones and Bradshaw.[5] The results of Shedlovsky, data from the "International Critical Tables" converted to the same basis, and the results of the present work on these solutions are shown in Fig. 1. The agreement between the results of Shedlovsky and those reported here indicates the reproducibility and consistency which can be obtained with the apparatus and technique now available.

Temperature Coefficients.—Average values of the temperature coefficients were computed for each 5° interval by means of the equation

$$\text{Temperature coefficient} = \frac{2(\Lambda_{t_1} - \Lambda_{t_2})}{5(\Lambda_{t_1} + \Lambda_{t_2})}$$

where Λ_t is the equivalent conductance at a given temperature. These results were plotted against temperature, and the values of the coefficients at

TABLE I

ELECTRICAL CONDUCTANCES AND TEMPERATURE COEFFICIENTS OF EQUIVALENT CONDUCTANCE FOR SODIUM CHLORIDE SOLUTIONS

Mg. eq. per Kg. water	Mg. eq. per Liter soln.	Specific cond. (10^6)	Equiv. cond.	Temp. coeff. of eq. cond.
		25°		
466.377	461.184	43537	94.403	0.0201
341.198	338.168	32902	97.301	202
193.318	192.109	19595	102.00	203
96.116	95.678	10247	107.09	205
		20°		
466.377	461.810	39291	85.081	0.0215
341.198	338.611	29678	87.646	216
193.318	192.348	17659	91.809	218
96.116	95.793	9225.9	96.311	220
		15°		
466.377	462.335	35187	76.059	0.0231
341.198	338.976	26558	78.349	233
193.318	192.540	15787	81.993	235
96.116	95.884	8238.9	85.926	237
		10°		
466.377	462.750	31230	67.487	0.0250
341.198	339.256	23549	69.412	251
193.318	192.682	13980	72.555	253
96.116	95.948	7286.7	75.944	257
		5°		
466.377	463.042	27423	59.217	0.0271
341.198	339.439	20659	60.862	273
193.318	192.763	12246	63.528	277
96.116	95.981	6373.1	66.400	280
		0°		
466.377	463.196	23789	51.358	0.0298
341.198	339.514	17906	52.740	300
193.318	192.779	10592	54.945	303
96.116	95.979	5502.7	57.332	307

(1) Paper read at the Ninety-sixth Meeting of the American Chemical Society at Milwaukee, Wis., September, 1938.

(2) Bremner, Thompson and Utterback, THIS JOURNAL, **60**, 2616–2618 (1938).

(3) Bremner and Thompson, *ibid.*, **59**, 2372–2374 (1937).

(4) Theodore Shedlovsky, Alfred S. Brown and Duncan A. MacInnes, *Trans. Am. Electrochem. Soc.*, **66**, 165–178 (1934).

(5) Grinnell Jones and Benjamin C. Bradshaw, THIS JOURNAL, **55**, 1780–1800 (1933).

TABLE II

ELECTRICAL CONDUCTANCES AND TEMPERATURE COEFFICIENTS OF EQUIVALENT CONDUCTANCE FOR POTASSIUM CHLORIDE SOLUTIONS

Mg. eq. per Kg. water	Mg. eq. per Liter soln	Specific cond. (10^6)	Equiv. cond.	Temp. coeff. of eq. cond.
		25°		
9.6069$_0$	9.5763$_0$	1354.8	141.48	0.0196
7.2147$_3$	7.1922$_6$	1024.1	142.39	196
4.0433$_2$	4.0310$_3$	580.8$_7$	144.10	197
2.0213$_7$	2.0153$_4$	293.8$_9$	145.83	197
		20°		
9.6069$_0$	9.5874$_6$	1224.8	127.75	0.0211
7.2147$_3$	7.2006$_0$	925.8$_9$	128.59	212
4.0433$_2$	4.0357$_3$	525.0$_4$	130.10	212
2.0213$_7$	2.0176$_8$	265.6$_1$	131.64	212
		15°		
9.6069$_0$	9.5961$_0$	1098.4	114.46	0.0228
7.2147$_3$	7.2070$_5$	830.2$_5$	115.20	228
4.0433$_2$	4.0393$_7$	470.6$_8$	116.52	228
2.0213$_7$	2.0194$_9$	238.0$_9$	117.89	229
		10°		
9.6069$_0$	9.6019$_0$	975.6$_1$	101.61	0.0248
7.2147$_3$	7.2114$_3$	737.5$_4$	102.27	249
4.0433$_2$	4.0418$_0$	418.0$_0$	103.42	249
2.0213$_7$	2.0207$_1$	211.37	104.60	250
		5°		
9.6069$_0$	9.6045$_0$	857.0$_5$	89.23$_4$	0.0270
7.2147$_3$	7.2133$_7$	637.7$_6$	89.80$_0$	271
4.0433$_2$	4.0428$_8$	367.0$_4$	90.78$_7$	272
2.0213$_7$	2.0212$_5$	185.54	91.79$_4$	
		0°		
9.6069$_0$	9.6034$_2$	743.7$_7$	77.44$_8$	0.0296
7.2147$_3$	7.2125$_0$	561.9$_5$	77.91$_3$	298
4.0433$_2$	4.0424$_0$	318.4$_1$	78.76$_8$	298
2.0213$_7$	2.0210$_1$	160.8$_8$	79.60$_4$	299

TABLE III

ELECTRICAL CONDUCTANCES AND TEMPERATURE COEFFICIENTS OF EQUIVALENT CONDUCTANCE FOR MAGNESIUM SULFATE SOLUTIONS

Mg. eq. per Kg. water	Mg. eq. per Liter soln.	Specific cond. (10^6)	Equiv. cond.	Temp. coeff. of eq. cond.
		25°		
56.766	56.605	3643.$_6$	64.36$_6$	0.0201
41.530	41.411	2831.$_5$	68.37$_6$	203
23.530	23.463	1788.$_2$	76.21$_4$	204
11.699	11.665	1006.$_7$	86.30$_1$	206
		20°		
56.766	56.671	3284.$_8$	57.96$_3$	0.0219
41.530	41.460	2550.$_8$	61.52$_4$	220
23.530	23.490	1609.$_9$	68.53$_4$	222
11.699	11.679	905.1$_2$	77.50$_0$	224
		15°		
56.766	56.723	2932.$_0$	51.69$_0$	0.0239
41.530	41.497	2276.$_1$	54.85$_0$	239
23.530	23.511	1435.$_1$	61.04$_2$	242
11.699	11.689	806.0$_1$	68.954	243
		10°		
56.766	56.759	2587.$_9$	45.59$_5$	0.0263
41.530	41.523	2008.$_7$	48.37$_6$	263
23.530	23.526	1265.$_4$	53.78$_8$	265
11.699	11.696	710.0$_9$	60.71$_2$	266
		5°		
56.766	56.776	2254.$_3$	39.70$_5$	0.0289
41.530	41.535	1749.$_4$	42.11$_6$	289
23.530	23.532	1106.$_1$	46.81$_3$	290
11.699	11.700	617.5$_9$	52.78$_5$	292
		0°		
56.766	56.772	1936.$_3$	34.10$_7$	0.0319
41.530	41.532	1501.$_3$	36.14$_8$	320
23.530	23.530	945.2	40.17$_2$	320
11.699	11.698	529.5$_1$	45.26$_6$	321

TABLE IV

ELECTRICAL CONDUCTANCES AND TEMPERATURE COEFFICIENTS OF EQUIVALENT CONDUCTANCE FOR MIXED SOLUTIONS OF SODIUM CHLORIDE AND POTASSIUM CHLORIDE

Mg. eq. per kg. water NaCl	Mg. eq. per kg. water KCl	Total mg. eq. per liter soln.	Specific cond. (10^6)	Equiv. cond.	Temp. coeff. of eq. cond.
		25°			
466.377	9.8617$_2$	470.80$_5$	4456$_4$	94.65$_5$	0.0201
341.198	7.2147$_3$	345.24$_7$	3367$_9$	97.55$_5$	202
193.318	4.0877$_5$	196.14$_7$	2005$_6$	102.25	203
96.116	2.0324$_1$	97.69$_5$	10486	107.33	204
		20°			
466.377	9.8617$_2$	471.44$_5$	4023$_2$	85.33$_7$	0.0214
341.198	7.2147$_3$	345.69$_8$	3038$_3$	87.89$_0$	215
193.318	4.0877$_5$	196.39$_2$	1808$_0$	92.06$_3$	218
96.116	2.0324$_1$	97.81$_2$	9444.$_7$	96.56$_0$	219
		15°			
466.377	9.8617$_2$	471.98$_2$	3603$_8$	76.35$_5$	0.0230
341.198	7.2147$_3$	346.07$_2$	2719$_8$	78.59$_0$	232
193.318	4.0877$_5$	196.58$_9$	1616$_7$	82.23$_9$	234
96.116	2.0324$_1$	97.90$_5$	8438.$_3$	86.18$_9$	236
		10°			
466.377	9.8617$_2$	472.41$_0$	3199$_0$	67.71$_6$	0.0250
341.198	7.2147$_3$	346.35$_9$	2412$_0$	69.63$_8$	252
193.318	4.0877$_5$	196.73$_3$	1432$_2$	72.79$_8$	254
96.116	2.0324$_1$	97.97$_1$	7466.$_9$	76.21$_5$	256
		5°			
466.377	9.8617$_2$	472.71$_0$	28096	59.43$_6$	0.0271
341.198	7.2147$_3$	346.54$_8$	2116$_2$	61.06$_6$	273
193.318	4.0877$_5$	196.81$_8$	12545	63.73$_8$	277
96.116	2.0324$_1$	98.00$_5$	6533.$_2$	66.66$_2$	279
		0°			
466.377	9.8617$_2$	472.87$_0$	2438$_9$	51.57$_6$	0.0297
341.198	7.2147$_3$	346.62$_7$	1834$_3$	52.91$_5$	299
193.318	4.0877$_5$	196.83$_5$	1085$_9$	55.16$_9$	302
96.116	2.0324$_1$	98.004	5643.$_3$	57.58$_2$	306

the other temperatures were obtained from these graphs.

The temperature coefficients for potassium chloride solutions are almost the same as those for

TABLE V

ELECTRICAL CONDUCTANCES AND TEMPERATURE COEFFICIENTS OF EQUIVALENT CONDUCTANCE FOR MIXED SOLUTIONS OF SODIUM CHLORIDE AND MAGNESIUM SULFATE

Mg. eq. per kg. water NaCl	Mg. eq. per kg. water $MgSO_4$	Total mg. eq. per liter soln.	Specific cond. (10^6)	Equiv. cond.	Temp. coeff. of eq. cond.
		25°			
466.377	56.766	517.30$_0$	4574$_1$	88.42$_3$	0.0201
341.198	41.530	379.32$_7$	3475$_6$	91.62$_5$	202
193.318	23.530	215.49$_2$	2087$_1$	96.85$_4$	203
96.116	11.699	107.32$_5$	11003	102.52	205
		20°			
466.377	56.766	518.00$_6$	4127$_1$	79.67$_3$	0.0215
341.198	41.530	379.82$_5$	3133$_8$	82.50$_6$	217
193.318	23.530		1880$_5$		219
96.116	11.699	107.45$_5$	9906.$_4$	92.19$_2$	220
		15°			
466.377	56.766	518.60$_3$	3694$_6$	71.24$_1$	0.0232
341.198	41.530	380.23$_9$	2803$_5$	73.73$_0$	234
193.318	23.530	215.98$_0$	1680$_6$	77.81$_2$	236
96.116	11.699	107.55$_7$	8844.$_3$	82.22$_9$	238
		10°			
466.377	56.766	519.08$_0$	3277$_4$	63.13$_8$	0.0252
341.198	41.530	380.55$_9$	2484$_9$	65.29$_5$	253
193.318	23.530	216.14$_1$	1487$_8$	68.83$_5$	256
96.116	11.699	107.63$_0$	7822.$_4$	72.67$_9$	258
		5°			
466.377	56.766	519.42$_0$	28754	55.35$_9$	0.0274
341.198	41.530	380.77$_3$	2177$_9$	57.19$_8$	275
193.318	23.530	216.23$_5$	13024	60.22$_8$	278
96.116	11.699	107.66$_7$	6839.$_7$	63.52$_6$	280
		0°			
466.377	56.766	519.60$_9$	2494$_5$	48.00$_6$	0.0298
341.198	41.530	380.86$_5$	18867	49.53$_8$	299
193.318	23.530	216.25$_7$	11262	52.07$_8$	303
96.116	11.699	107.666	5906.$_0$	54.85$_5$	306

the most concentrated sodium chloride solution, particularly at 0°, and no detectable change in the coefficients of sodium chloride solutions occurs upon the addition of potassium chloride to sodium chloride solutions in the ratios used. The coefficients for magnesium sulfate solutions are larger than those for the alkali halides except at 25° and increase more rapidly with decrease of temperature. However, the addition of magnesium sulfate to sodium chloride solutions in the ratios used has no detectable effect upon the coefficients of sodium chloride solutions.

Temperature coefficients of equivalent conductance for the most dilute and the most concentrated solutions of each type investigated are shown in Figs. 2 and 3. Graphs of the data for

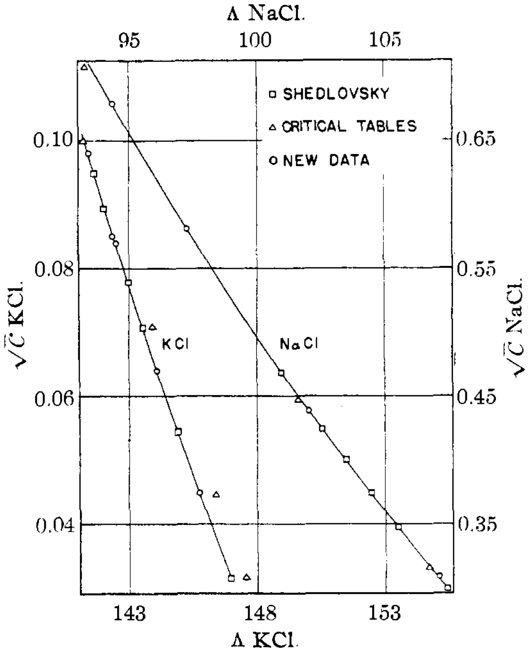

Fig. 1.—Equivalent conductance of sodium chloride and of potassium chloride solutions.

solutions of intermediate concentrations would fall between those shown in each case.

The divergence of the two lines shown in each figure increases with decrease of temperature in all cases except that of magnesium sulfate, where it decreases. It would seem that the effect of this difference would be seen in the graphs of the sodium chloride + magnesium sulfate mixed solutions, where the divergence would be slightly less than for pure sodium chloride. However, such an effect is not observed.

Mixture Rules.—Electrical conductances of mixed electrolytes have been measured at 25° by Smith and Gortner,[6] Stearn,[7] Semenchenko,[8] Ruby and Kawai[9] and others. Some of these authors have postulated complex ion formation, but others have shown this explanation to be inadequate to account for the observed data. Some have applied the Debye–Hückel–Onsager equation to dilute solutions with more or less success. Still others have attempted to explain the results by means of the "mixture rule."

The mixture rule for a binary mixture is

$$\Lambda = x\Lambda^0_{ACl} + (1 - x)\Lambda^0_{BCl}$$

(6) A. Kay Smith and R. A. Gortner, *J. Phys. Chem.*, **37**, 79–86 (1933).

(7) A. E. Stearn, THIS JOURNAL, **44**, 670–678 (1922).

(8) V. K. Semenchenko and V. V. Serpinskii, *Trans. Mendeleev, Congr. Theor. Applied Chem. VI Congr. 1932*, **2**, 195 (1935).

(9) Charles E. Ruby and Juntaro Kawai, THIS JOURNAL, **48**, 1119–1128 (1926).

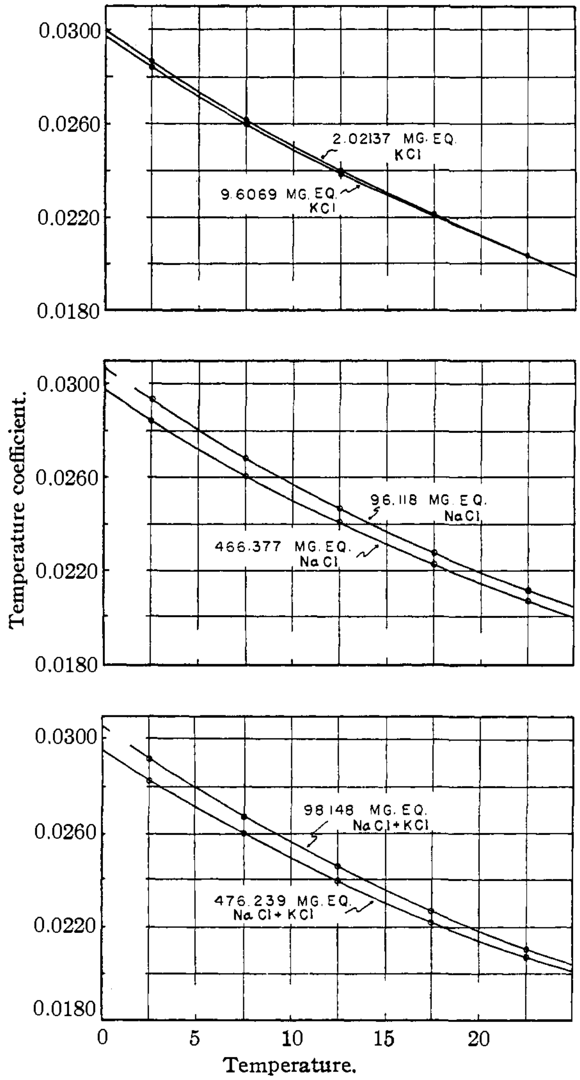

Fig. 2.—Temperature coefficients of the equivalent conductance for sodium chloride, potassium chloride and a mixture of sodium chloride and potassium chloride.

where ACl and BCl are alkali chlorides, x and $1 - x$ are mole fractions of the electrolytes present, Λ^0_{ACl} and Λ^0_{BCl} are the equivalent conductances of pure salt solutions of concentrations equal to the total electrolyte concentration.

Van Rysselberghe and Nutting[10] have recently modified this equation by the introduction of transport numbers of the pure salt solutions. The resulting equation was applied with remarkable success to solutions of mixed alkali chlorides in which the total concentration ranged as high as two normal.

The equation of Van Rysselberghe and Nutting for mixtures of alkali chlorides is

(10) Pierre Van Rysselberghe and Lee Nutting, THIS JOURNAL, 56, 1435–1437 (1934).

$$\Lambda = [x\Lambda^0_{\mathrm{ACl}}\,T^0_{\mathrm{Cl,A}} + (1 - x)\,\Lambda^0_{\mathrm{BCl}}\,T^0_{\mathrm{Cl,B}}]$$
$$\left[x\,\frac{T^0_{\mathrm{A}}}{T^0_{\mathrm{Cl,A}}} + (1 - x)\,\frac{T^0_{\mathrm{B}}}{T^0_{\mathrm{Cl,B}}} + 1\right]$$

where ACl and BCl are alkali chlorides, x is a mixing ratio, xC the concentration of ACl (moles/l.), $(1 - x)C$ the concentration of BCl (moles/l.), T^0_{A}, $T^0_{\mathrm{Cl,A}}$ transport numbers of pure ACl at concentration C, Λ^0_{ACl} the equivalent conductance of pure ACl at concentration C, and Λ the equivalent conductance of the mixture at total concentration C.

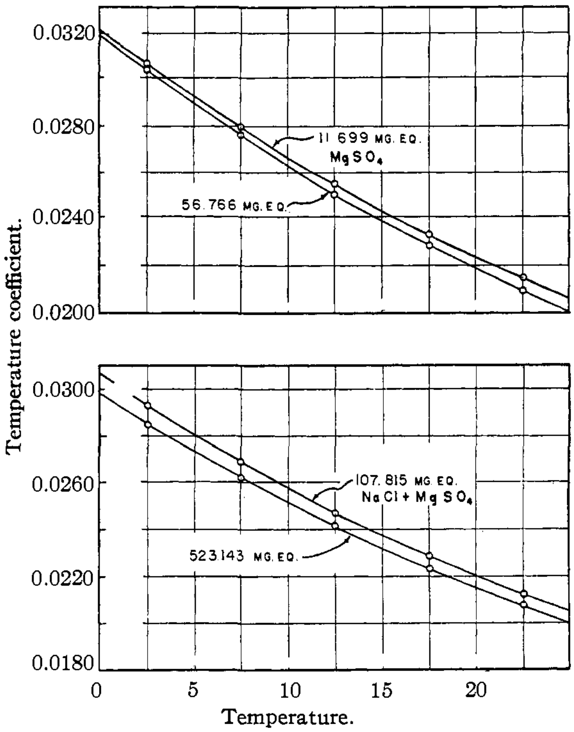

Fig. 3.—Temperature coefficients of the equivalent conductance of magnesium sulfate and a mixture of magnesium sulfate and sodium chloride.

The mixture rule and the equation proposed by Van Rysselberghe and Nutting have been applied to the data on two of the sodium chloride + potassium chloride solutions at 25° with the results shown in Table VI. The conductance values for solutions of sodium chloride and potassium chloride are those of Shedlovsky[4] and the trans-

TABLE VI

APPLICATION OF MIXTURE RULES

C	$\Lambda^0_{\mathrm{NaCl}}$	Λ^0_{KCl}	$T^0_{\mathrm{Na^+}}$	$T^0_{\mathrm{K^+}}$	x
97.69$_5$	106.90	129.11	0.3855	0.4898	0.9793$_5$
196.147	101.86	123.40	.3822	.4894	.9794$_1$
	Λ_{V}	Λ_{R}		Λ_0	%
	107.36	107.36		107.33	0.03
	102.30	102.30		102.25	.05

ference number data are from a table published by Longsworth.[11]

Λ_V is the equivalent conductance of a mixture calculated by the Van Rysselberghe and Nutting equation, Λ_R the equivalent conductance of a mixture calculated by the mixture rule, Λ_0 the equivalent conductance of a mixture observed at 25°, and % signifies the percentage deviation of the calculated from the observed equivalent conductance.

The results show that the mixture rule and the equation of Van Rysselberghe and Nutting give the same results when applied to these solutions. The deviation of the calculated from the experimental equivalent conductance of the mixture is in each case within the aggregate experimental error involved in the measurements of electrical conductances and transference numbers.

Lack of reliable electrical conductance and transference number data for appropriate pure salt solutions prevents further application of these rules to the data on mixed salt solutions.

Summary

1. The specific and equivalent conductances of various solutions of salts occurring in sea water have been measured at 5° intervals from 0 to 25° inclusive. The data for pure sodium chloride and pure potassium chloride solutions at 25° have been shown to be in close agreement with the measurements of Shedlovsky.

2. Certain electrical conductance data in the "International Critical Tables" are not in good agreement.

3. Temperature coefficients of equivalent conductance have been calculated for the twenty solutions at each of the six temperatures used. Although the coefficients for magnesium sulfate solutions are quite different from those of sodium chloride, the addition of magnesium sulfate to sodium chloride solutions in the ratio used has no detectable effect upon the coefficients of sodium chloride. The addition of potassium chloride to sodium chloride solutions in the ratio used has no detectable effect upon the temperature coefficients of sodium chloride.

4. The mixture rule and the equation proposed by Van Rysselberghe and Nutting give the same results when applied to part of the data on sodium chloride + potassium chloride solutions at 25°. These results agree with the measured values within the experimental error.

(11) L. G. Longsworth, THIS JOURNAL, **57**, 1185–1191 (1935).

SEATTLE, WASH. RECEIVED JANUARY 24, 1939

[CONTRIBUTION FROM THE DIVISION OF PLANT NUTRITION, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

A Water-Soluble Glucosan from Barley Roots

BY W. Z. HASSID

In the study of respiration of excised barley roots by Hoagland and Broyer[1] it was necessary to identify and determine the soluble carbohydrates. Since Yemm[2] and later Archbold and Barter[3] reported fructose anhydrides in barley leaves the identification of this polysaccharide was attempted in the roots. Upon investigation, however, no fructose anhydride could be found in any considerable quantity but instead a water-soluble glucose anhydride was isolated.

Fructosans have been known to be distributed widely in the Gramineae.[4] Their constitution was studied by Challinor, Haworth and Hirst,[5] Haworth, Hirst and Lyne[6] and also by Schlubach and his co-workers.[7] A water-soluble glucosan or glucose anhydride such as that which is now shown to exist in barley roots has not previously been reported in any plant.

Experimental

The glucosan was isolated as follows from barley roots grown in Hoagland's culture solution for about three weeks. The roots were placed into boiling 95% alcohol in such quantity that the final alcohol concentration was 75 to 80%. After extracting under a reflux condenser for six hours the alcoholic extract was poured off and the

(1) D. R. Hoagland and T. C. Broyer, *Plant Physiol.*, **11**, 471 (1936).

(2) E. W. Yemm, *Proc. Roy. Soc.* (London), **B117**, 483 (1935).

(3) H. K. Archbold and A. M. Barter, *Biochem. J.*, **29**, 2689 (1935).

(4) A. de Cugnac, *Bull. soc. chim. biol.*, **13**, 125 (1931).

(5) S. W. Challinor, W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, 1560 (1934).

(6) W. N. Haworth, E. L. Hirst and R. R. Lyne, *Biochem. J.*, **31**, 786 (1937).

(7) H. H. Schlubach, H. Knoop and M. Y. Liu, *Ann.*, **504**, 30 (1933), also **511**, 140 (1934); H. H. Schlubach and K. Koenig, *ibid.*, **514**, 182 (1934); H. H. Schlubach, *ibid.*, **523**, 130 (1936); H. H. Schlubach and H. Peitzner, *ibid.*, **530**, 120 (1937); H. H. Schlubach and H. Böe, *ibid.*, **532**, 191 (1937); H. H. Schlubach and H. Lendzian, *ibid.*, **532**, 200 (1937).