[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Electrolytic Conductivity of Alkaline Earth Chlorides in Water at 25°

BY THEODORE SHEDLOVSKY AND ALFRED SEELY BROWN[1]

Accurate measurements on the electrolytic conductivity of some uni-univalent electrolytes in water at 25° were reported in a previous paper,[2] and it was shown that they confirmed the Onsager conductance formula[3] as a limiting equation.

In this paper measurements are reported on the conductivity of alkaline earth chlorides in water at 25°, covering a concentration range from about 10^{-4} to 0.1 normal. To establish accurate conductance curves extending through a concentration of 0.1 normal for each salt about thirty-five solutions of different concentrations have been measured in this range. These data should be useful for accurate interpolation purposes, for testing further developments in conductivity theory and for obtaining the limiting mobilities of the alkaline earth ions.

Experimental

Conductivity Measurements.—The apparatus and technique used in this work were essentially the same as had been used by Shedlovsky[2] in measuring the conductivity of the more dilute solutions. Three one-liter "flask cells" of the type already described[2] were employed. One cell, for covering the range from the most dilute solutions to concentrations of several thousandths normal, had a flask of clear quartz. The other two cells had flasks of Pyrex glass and were used to cover concentration ranges from about 0.001 to 0.03 N and 0.01 to 0.1 N, respectively.

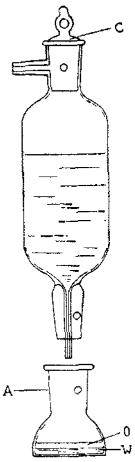

Fig. 1.—Weight buret.

Solutions of progressively increasing concentrations were made up in the cells, containing a known weight of conductivity water, by adding successive increments of stock solution of known strength from weight burets. To avoid contamination of the solution from grease, the conventional stopcock at the bottom of the weight burets was omitted and the flow of solution was controlled by means of a ground cock (C) at the top, as shown in Fig. 1. The burets, which had a capacity of about 75 cc., were constructed from Pyrex glass or quartz, the latter being used in the work with the most dilute solutions. A little mineral oil (o) was put into the ground cup (A) in order to guard against evaporation losses from accidental drops (W) falling from the tip of the buret.

Since it was not feasible to weigh the burets reproducibly closer than to a tenth of a milligram, the increments added were never under one gram.

Materials.—Calcium chloride, strontium chloride and barium chloride were each prepared by two methods. For one method the best obtainable C. P. grade nitrates were converted to carbonates with redistilled ammonium carbonate. After careful washing the carbonates were dissolved in redistilled C. P. hydrochloric acid, and the chlorides were crystallized. The other method was to recrystallize twice the best C. P. chlorides. Conductivity water was used throughout. The hydrated salts were dried in an Abderhalden vacuum drier at 100°, using "Desicchlora" (barium perchlorate) as the drying agent. With the aid of the Richards bottling apparatus the product was fused in platinum in a stream of dry hydrogen chloride, which was replaced by dry nitrogen after cooling. Stock solutions of accurately known concentrations were made up by weight, using conductivity water in well-steamed glass-stoppered Pyrex flasks. In this manner, thanks to the Richards bottling apparatus, it was possible to attain with comparative ease and rapidity a precision for the concentration values of the solutions of these very hygroscopic salts, which would be quite difficult to attain by analytical means. The neutrality of the solutions was tested with brom thymol blue. No difference was observed between the conductances of solutions made up from the salts prepared in the two different ways.

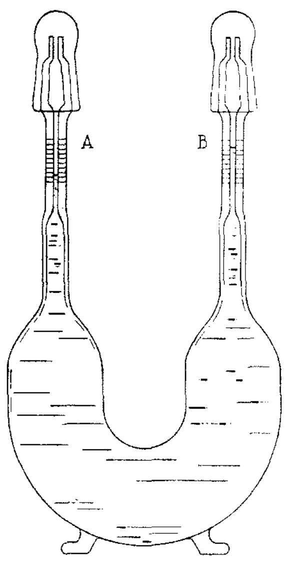

Fig. 2.—Quartz pycnometer.

It was not possible to obtain a neutral solution from magnesium chloride which had been fused in an atmosphere of hydrogen chloride. The resulting solutions were always distinctly alkaline. This difficulty was overcome by preparing the double magnesium chloride–ammonium chloride salt from purified magnesium chloride and ammonium chloride. The mixed salt was crystallized from conductivity water and dried in an electric oven at 120°. It was subsequently fused in a stream of dry hydrogen chloride in the Richards bottling apparatus, the ammonium chloride being volatilized in the process. The resulting product gave solutions which were found to be neutral.

Density Measurements.—Since the solutions on which the conductance measurements were made were prepared by weight, it was, of course, necessary to have density

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[1] National Research Council Fellow.

[2] Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

[3] Onsager, *Physik. Z.*, **28**, 277 (1927).

data for computing the corresponding volume concentrations. The density measurements were made on solutions of the various salts with a new type of quartz pycnometer, shown in Fig. 2. The capillaries A and B, of uniform bore, about 1 mm. in diameter, were graduated in 1-mm. intervals, and the corresponding volumes were carefully determined by calibration with mercury before assembling the completed pycnometer, which has a capacity of about 25 ml. With this instrument it is possible to make precise density determinations comparatively quickly since once the pycnometer is accurately calibrated the volume of the solution to be measured need only be adjusted sufficiently closely to bring the liquid levels somewhere within the graduated regions of the capillaries at the temperature in question. After weighing, the pycnometer is immersed in a thermostat provided with a window through which the meniscus levels can be read easily to a fraction of a millimeter with the aid of a lens. The volume of the solution corresponding to the known weight is thus determined. The pycnometer described above has several obvious advantages over the Sprengel type which is commonly used. Besides being more rapid and simpler to use, it avoids two likely sources of error in the Sprengel instrument, namely, possible variations in the liquid level at the tip and of the temperature in the process of withdrawing the liquid when bringing the meniscus to the reference mark.

Results and Discussion

The density data, for solutions of the alkaline earth chlorides at 25°, are given in Table I. To express the densities as a function of the concentration for solutions of magnesium, calcium and strontium chlorides at this temperature, we have used the equation

$$d = 0.99707 + ac - bc^{3/2}$$

which has been proposed recently by Root.[4] In this equation d is the density, c the concentration (equivalents per liter of solution) and a and b are constants, whose values for the various salts are given in Table I. For the solutions of barium chloride we have used the equation

$$d = 0.99707 + 0.09112C - 0.00105C^2$$

given by Jones and Dole[5] for their measurements on solutions of this salt at 25°.

The molecular weight values we have used for computing our concentrations have been taken from the "International Critical Tables." These values, also, are given in Table I. The last column in the table gives the densities computed from the equations mentioned above. The maximum deviation between the calculated and observed density values is 0.004%, whereas the average deviation is less than 0.002%.

TABLE I

DENSITIES AT 25°

	$C = \frac{\text{Equivalents}}{\text{Liter solution}}$	Density Observed	Density Calculated
Magnesium chloride	0.076747	1.00014	1.00011
mol. wt. = 95.236	.099538	1.00100	1.00100
a = 0.0400	.163950	1.00353	1.00353
b = −0.0015	.456647	1.01486	1.01487
Calcium chloride	.079529	1.00070	1.00071
mol. wt. = 110.986	.098986	1.00161	1.00159
a = 0.0462	.239116	1.00791	1.00794
b = −0.0015	.254595	1.00868	1.00864
Strontium chloride	.098870	1.00393	1.00392
mol. wt. = 158.536	.119054	1.00532	1.00531
a = 0.0700	.181723	1.00961	1.00962
b = −0.0022	.446675	1.02771	1.02768
	.522641	1.03283	1.03283
Barium chloride	.977813	1.00600	1.00597
mol. wt. = 206.286			

TABLE II

EQUIVALENT CONDUCTANCE OF MAGNESIUM CHLORIDE IN WATER AT 25°

Series	$C = \frac{\text{Equivalents}}{\text{Liter}}$	Λ
Q 1	0.150549×10^{-3}	127.301
$\kappa_{H_2O} = 2.054 \times 10^{-7}$	$.339515 \times 10^{-3}$	126.273
	$.558398 \times 10^{-3}$	125.398
	1.06756×10^{-3}	123.928
	2.03494×10^{-3}	121.972
	2.83765×10^{-3}	120.649
P 1	0.045881×10^{-2}	125.725
$\kappa_{H_2O} = 6.344 \times 10^{-7}$	$.131600 \times 10^{-2}$	123.375
	$.226604 \times 10^{-2}$	121.610
	$.321788 \times 10^{-2}$	120.257
	$.417773 \times 10^{-2}$	119.135
	$.523298 \times 10^{-2}$	117.992
	$.631008 \times 10^{-2}$	117.138
	$.732879 \times 10^{-2}$	116.325
	$.838699 \times 10^{-2}$	115.588
	$.939470 \times 10^{-2}$	114.924
	1.05755×10^{-2}	114.215
	1.52811×10^{-2}	111.886
	1.98807×10^{-2}	110.098
R 1	0.0049158	118.379
$\kappa_{H_2O} = 5.83 \times 10^{-7}$	.0119500	113.484
	.0225992	109.203
	.0307789	106.914
	.0411325	104.654
	.0499386	103.082
	.0601106	101.547
	.0689573	100.378
	.0769359	99.425
	.085500	98.497
	.094515	97.610
	.103997	96.752
B 1	0.099540	97.118
$\kappa_{H_2O} = 3 \times 10^{-7}$		

The conductance measurements on solutions of magnesium chloride, calcium chloride, stron-

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(4) Root, THIS JOURNAL, **55**, 850 (1933).

(5) Jones and Dole, *ibid.*, **52**, 2247 (1930).

TABLE III

EQUIVALENT CONDUCTANCE OF CALCIUM CHLORIDE IN WATER AT 25°

Series	$C = \frac{\text{Equivalents}}{\text{Liter}}$	Λ
Q 1	0.463621×10^{-3}	132.096
$\kappa_{H_2O} = 3.207 \times 10^{-7}$	$.600817 \times 10^{-3}$	131.568
	$.96043 \times 10^{-3}$	130.436
	1.70903×10^{-3}	128.714
Q 2	0.241972×10^{-3}	133.089
$\kappa_{H_2O} = 2.613 \times 10^{-7}$	$.498239 \times 10^{-3}$	131.972
	$.89470 \times 10^{-3}$	130.689
	2.05142×10^{-3}	128.137
Q 3	0.156105×10^{-3}	133.657
$\kappa_{H_2O} = 2.450 \times 10^{-7}$	$.352358 \times 10^{-3}$	132.594
	$.81169 \times 10^{-3}$	130.926
	1.64435×10^{-3}	128.909
	2.54870×10^{-3}	127.317
	3.63560×10^{-3}	125.812
	4.36932×10^{-3}	124.948
Q 4	0.123383×10^{-3}	133.853
$\kappa_{H_2O} = 1.813 \times 10^{-7}$	$.265261 \times 10^{-3}$	132.998
	$.532804 \times 10^{-3}$	131.822
	$.90105 \times 10^{-3}$	130.632
	1.39603×10^{-3}	129.404
	2.23892×10^{-3}	127.797
	3.12945×10^{-3}	126.442
P 1	0.102737×10^{-2}	130.213
$\kappa_{H_2O} = 2.784 \times 10^{-7}$	$.383045 \times 10^{-2}$	125.525
	$.529940 \times 10^{-2}$	123.962
	$.82662 \times 10^{-2}$	121.515
	$.99234 \times 10^{-2}$	120.416
	1.57235×10^{-2}	117.404
P 2	0.096477×10^{-2}	130.407
$\kappa_{H_2O} = 2.98 \times 10^{-7}$	$.213248 \times 10^{-2}$	127.892
	$.331593 \times 10^{-2}$	126.136
	$.472634 \times 10^{-2}$	124.499
	$.645809 \times 10^{-2}$	122.885
	$.829696 \times 10^{-2}$	121.472
	1.01330×10^{-2}	120.281
	1.44026×10^{-2}	117.983
	1.86026×10^{-2}	116.197
	2.33099×10^{-2}	114.534
P 3	0.187041×10^{-2}	128.395
$\kappa_{H_2O} = 3.24 \times 10^{-7}$	$.353637 \times 10^{-2}$	125.886
	$.500125 \times 10^{-2}$	124.239
	$.653600 \times 10^{-2}$	122.835
	$.81556 \times 10^{-2}$	121.585
R 1	0.0080379	121.659
$\kappa_{H_2O} = 3.50 \times 10^{-7}$	.0286981	112.958
	.0418740	109.942
	.0525154	108.062
	.064060	106.370
	.076637	104.818
	.086602	103.743
	.096465	102.781
	.108542	101.721
B 1	0.098987	102.543
B 2 $\kappa_{H_2O} = 4 \times 10^{-7}$	.079531	104.484
B 3	.097125	102.700

TABLE IV

EQUIVALENT CONDUCTANCE OF STRONTIUM CHLORIDE IN WATER AT 25°

Series	$C = \frac{\text{Equivalents}}{\text{Liter}}$	Λ
Q 1	0.25179×10^{-3}	133.013
$\kappa_{H_2O} = 3.22 \times 10^{-7}$	1.10797×10^{-3}	135.943
	2.03342×10^{-3}	136.076
	3.31104×10^{-3}	136.325
Q 2	0.072920×10^{-3}	134.273
$\kappa_{H_2O} = 2.66 \times 10^{-7}$	$.26150 \times 10^{-3}$	133.002
	$.63823 \times 10^{-3}$	131.405
P 1	0.052637×10^{-2}	131.806
$\kappa_{H_2O} = 4.01 \times 10^{-7}$	$.140707 \times 10^{-2}$	129.333
	$.288343 \times 10^{-2}$	126.738
	$.581244 \times 10^{-2}$	123.434
	$.83028 \times 10^{-2}$	121.422
	1.10831×10^{-2}	119.634
	1.37603×10^{-2}	118.205
	1.60545×10^{-2}	117.137
	1.96824×10^{-2}	115.670
	2.31780×10^{-2}	114.464
	2.87616×10^{-2}	112.801
P 2	1.01426×10^{-2}	120.194
$\kappa_{H_2O} = 7.40 \times 10^{-7}$	1.97590×10^{-2}	115.654
	3.04632×10^{-2}	112.331
	3.95323×10^{-2}	110.235
	4.98367×10^{-2}	108.283
	5.73688×10^{-2}	107.089
	7.0617×10^{-2}	105.287
	7.9005×10^{-2}	104.298
	8.8455×10^{-2}	103.300
	9.8869×10^{-2}	102.283
R 1	0.0094176	120.652
$\kappa_{H_2O} = 7.4 \times 10^{-7}$	.0301510	112.417
	.0511123	108.083
	.070960	105.250
	.093749	102.770
	.099818	102.209
	.119052	100.597
B 1	0.111900	101.159
$\kappa_{H_2O} = 5.0 \times 10^{-7}$		

trium chloride and barium chloride in water at 25.000 ± 0.001° are given in Tables II to V. The equivalent conductance values listed in these tables are based on the recent redetermination in absolute units of the specific conductance of a 0.1 demal solution of potassium chloride at 25° by Jones and Bradshaw.[6] This solution contains 7.41913 g. of potassium chloride per 1000 g. of solution in vacuum (or 7.47896 g. of potassium chloride per 1000 g. of water in air) and has a specific conductance of 0.0128560 ohm^{-1} cm.$^{-1}$ at 25° according to these authors. This value is 0.028% higher than the corresponding one given by Parker and Parker,[7] which is given in the

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(6) Jones and Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

(7) Parker and Parker, *ibid.*, **46**, 333 (1924).

TABLE V

EQUIVALENT CONDUCTANCE OF BARIUM CHLORIDE IN WATER AT 25°

Series	$C = \frac{\text{Equivalents}}{\text{Liter}}$	Λ
Q 1	0.202649×10^{-3}	137.461
$\kappa_{H_2O} = 1.395 \times 10^{-7}$	$.570385 \times 10^{-3}$	135.712
	$.98548 \times 10^{-3}$	134.382
	1.45695×10^{-3}	133.217
	2.01571×10^{-3}	132.078
	2.96384×10^{-3}	130.524
	3.92017×10^{-3}	129.249
Q 2	0.133962×10^{-3}	137.873
$\kappa_{H_2O} = 1.595 \times 10^{-7}$	$.314789 \times 10^{-3}$	136.811
	$.589994 \times 10^{-3}$	135.638
	1.22595×10^{-3}	133.759
	2.35182×10^{-3}	131.482
P 1	0.155074×10^{-2}	132.998
$\kappa_{H_2O} = 2.65 \times 10^{-7}$	$.286177 \times 10^{-2}$	130.664
	$.459208 \times 10^{-2}$	128.446
	$.617871 \times 10^{-2}$	126.860
	$.776610 \times 10^{-2}$	125.526
	$.926045 \times 10^{-2}$	124.439
	1.12059×10^{-2}	123.201
	1.45571×10^{-2}	121.405
	1.75329×10^{-2}	120.051
R 1	0.0069754	126.143
$\kappa_{H_2O} = 4.20 \times 10^{-7}$	.0161828	120.638
	.0292418	116.048
	.0401556	113.395
	.0539624	110.826
	.0651817	109.132
	.0764709	107.679
	.0876067	106.430
	.103499	104.875
B 1 $\kappa_{H_2O} = 4.0 \times 10^{-7}$	0.097780	105.397
B 2	.100863	105.116

"International Critical Tables." The conductance values previously reported in publications from this Laboratory had been all based on Parker's value, and should be raised by 0.028% to convert them to the new and more accurate basis of Jones and Bradshaw, which will doubtless be generally used in the future.

The cell constants of the "flask cells," designated, respectively, as Q, P and R in the tables, were 0.58869, 6.4755 and 23.344,[4] respectively. The pipet cell referred to as cell B, in which a few of the more concentrated solutions were measured, had a cell constant of 24.713. The values of the equivalent conductance, Λ, listed in the Tables II to V have been corrected for the conductance of the solvent, κ_{H_2O}, which was determined for each measurement.

An equation for electrolytic conductance which reduces in the limit to Onsager's theoretical equation has been used by Shedlovsky[8] in connection with strong uni-univalent electrolytes. For bi-univalent electrolytes this equation takes the form

$$\Lambda_0 = \frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} - BC \qquad (1)$$

in which, at 25° in water, $\beta = 109.80$ and $\alpha = 1.267/(1 + T^\circ_- + 0.816\sqrt{1 + T^\circ_-})$ where T°_- is the limiting value of the transference number of the univalent ion. For the alkaline earth chlorides at 25° $T^\circ_- = 76.34/\Lambda_0$, 76.34 being the limiting value of the chloride ion mobility. In the above formulations C is the concentration (equivalents per liter), Λ is the equivalent conductance, Λ_0 is the equivalent conductance at infinite dilution, and α, β and B are constants. If we designate $(\Lambda + \beta\sqrt{C})/(1 - \alpha\sqrt{C})$ by Λ_0' and plot its values against the corresponding concentrations, a straight line with a slope of B and an intercept of Λ_0 should be obtained if equation (1) is valid.

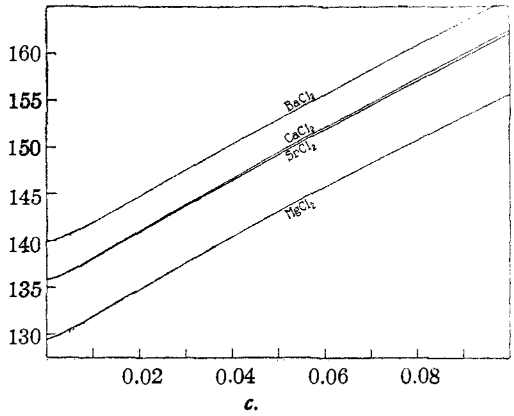

Fig. 3.—Plots of λ'_0 against concentration for alkaline earth chlorides in water at 25°.

These plots of Λ_0' against C for the data on the various salts are shown in Fig. 3. It will be noticed that there are systematic deviations from a linear relationship, though not very great ones. Although equation (1) does not represent the data quite within the precision of the measurements, we believe that a large scale plot of Λ_0' against C, which is a plot of deviations from Onsager's limiting equation, offers a perfectly satisfactory means for extrapolating to the limiting equivalent conductance Λ_0, and for purposes of interpolation. The values of Λ_0 which we have obtained by this means agree with those obtained by linear extrapolation from plots of Λ

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[8] Shedlovsky, THIS JOURNAL, 54, 1405 (1932).

TABLE VI

EQUIVALENT CONDUCTANCE OF ALKALINE EARTH CHLORIDES IN WATER AT 25° FOR ROUND CONCENTRATIONS

$C = \frac{\text{Equivalents}}{\text{Liter}}$	Equivalent conductances				(Jones and Dole)
	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$	
0	129.40	135.84	135.80	139.98	
0.001	124.11	130.36	130.33	134.34	(134.15)
.002	122.04	128.20	128.17	132.10	(132.11)
.003	120.56	126.62	126.60	130.48	
.004	119.33	125.34	125.32	129.15	
.005	118.31	124.25	124.24	128.02	(127.97)
.006	117.40	123.29	123.28	127.03	
.007	116.57	122.45	122.43	126.14	
.008	115.85	121.70	121.65	125.35	
.009	115.17	121.00	120.94	124.62	
.010	114.55	120.36	120.29	123.94	
.020	110.04	115.65	115.54	119.09	(118.99)
.030	107.09	112.58	112.45	115.83	
.040	104.88	110.30	110.14	113.44	
.050	103.08	108.47	108.25	111.48	(111.49)
.060	101.57	106.91	106.69	109.86	
.070	100.23	105.59	105.36	108.48	
.080	99.07	104.43	104.18	107.25	
.090	98.04	103.40	103.14	106.16	
.100	97.10	102.46	102.19	105.19	(105.20)

against $\sqrt{C}$ for measurements on the very dilute solutions. The conductance values corresponding to round concentrations, which are listed in Table VI, have also been derived from the corresponding interpolated values of Λ_0'.

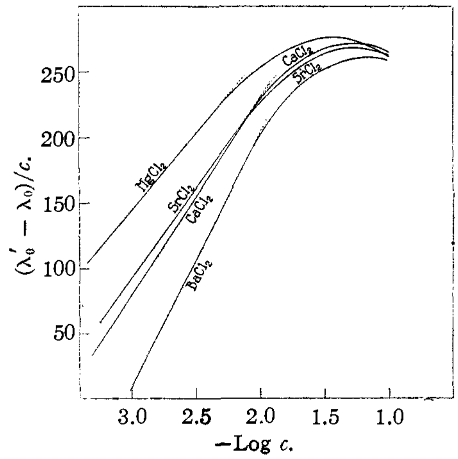

Fig. 4.—Plots of $(\lambda_0' - \lambda_0)/c$ against logarithm of concentration for alkaline earth chlorides in water at 25°.

The conductance values for barium chloride solutions reported by Jones and Dole[5] have been corrected to the new cell constant basis and are given (in parentheses) in the last column of the table for comparison with our measurements.

The small systematic deviations from equation (1) actually found can be clearly shown by plotting values of $(\Lambda_0' - \Lambda_0)/C$ against some function of the concentration. If equation (1) were accurately obeyed, we should obtain a horizontal line with an ordinate equal to B. Actually, in the case of all the alkaline earth chlorides, we obtain curves expressible analytically as the difference between a logarithmic term and a linear term. The presence of the logarithmic term is apparent from Fig. 4, which shows plots of $(\Lambda_0' - \Lambda_0)/C$ against log C. It will be noted that the curves, indicated by the solid lines, become linear as the concentration decreases. Thus, instead of equation (1) we should have $(\Lambda_0' - \Lambda_0)/C = B + D \log C - EC$ (in which B, D and E are constants) or

$$\Lambda_0' = \Lambda_0 + BC + DC \log C - EC^2 \qquad (2)$$

This result provides an interesting confirmation of Onsager's theoretical prediction[3,9] that the deviation terms from the limiting theoretical equation $(\Lambda_0' = \Lambda_0)$ should be of the form $BC + DC \log C + \ldots$

Since, in general, the magnitudes of the deviations from all the limiting equations derived from the Debye–Hückel interionic attraction theory (that is, the higher terms) are a function of the size and the charge of the ions, we may expect the $C \log C$ term to be relatively larger in salts of higher valence types and with smaller ions. The limiting conductances (Λ_0) of magnesium chloride, calcium chloride, strontium chloride and barium chloride are 129.40, 135.84, 135.80 and 139.98, respectively. Thus, on the basis of Stokes' law, the magnesium ion is the largest, the barium ion is the smallest, and the calcium and strontium ions are about equal in size. It will be observed in Fig. 4 from the slopes of the dotted lines, which are a measure of the magnitude of the corresponding $C \log C$ terms, that the prediction of larger $C \log C$ terms for smaller ions is borne out.

Summary

1. A convenient type of quartz pycnometer is described, and measurements on densities of aqueous solutions of alkaline earth chlorides at 25° are recorded.

2. Measurements are reported on the electrical conductance of solutions of magnesium chloride, calcium chloride, strontium chloride and barium chloride in water at 25,000°, at

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[9] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

numerous concentrations up to about 0.1 normal.

3. The measurements confirm Onsager's limiting conductance equation and his prediction of the presence of C (concentration) and a $C \log C$ term at increasing concentrations.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Ternary Systems. XIX. Calcium Sulfate, Potassium Sulfate and Water

BY ARTHUR E. HILL

The finding of deposits of polyhalite, $(CaSO_4)_2 \cdot K_2SO_4 \cdot MgSO_4 \cdot 2H_2O$, in the southwest of this country, has in it possibility of value as a commercial source of potash. It was suggested to me by Dr. Everett P. Partridge, of the U. S. Bureau of Mines, New Brunswick, N. J., that information on the ternary system consisting of calcium sulfate, potassium sulfate and water would be helpful in attacking the problem. I am indebted not only to Dr. Partridge for the suggestion, but to him, Mr. John E. Conley and Mr. Loyal Clarke of the same station for much valuable help during the course of the work, and particularly to Dr. Alton Gabriel for the petrographic examination of solid phases in nearly all the experiments reported, without which the work would have dragged and might easily have gone astray.

The system in question has been studied in part by a number of investigators, who have laid out its general outline from 0 to 83°, but with considerable omission and occasional error. It was first studied as part of the work on the Stassfurt salts, by van't Hoff and his co-workers,[1] later by Cameron and Breazeale,[2] by Barre[3] and by Anderson and Nestell.[4] This large amount of work however includes no isotherms at any temperature except the 25° isotherm of Cameron and Breazeale, all other points given being for saturation with two or with three solid phases; there is no guide as to which equilibria are stable and which are metastable; there are some erroneous points given, doubtless because of lack of information as to the phases present; and, finally, there has been no attention paid to the occurrence of anhydrite, $CaSO_4$, which is the dominating stable phase at all the higher temperatures. The present work gives complete isotherms at 40, 60 and 100°, and makes it possible to determine the stability or metastability of the various phase-complexes.

Between 0 and 100°, the solid phases which were found by the earlier workers, and to which no new compounds have been added, are the following

Gypsum, $CaSO_4 \cdot 2H_2O$
Hemihydrate, $CaSO_4 \cdot 0.5H_2O$
Anhydrite, $CaSO_4$
Syngenite, $CaSO_4 \cdot K_2SO_4 \cdot H_2O$
Pentacalcium potassium sulfate, $(CaSO_4)_5 \cdot K_2SO_4 \cdot H_2O$

The last-named salt, first found by van't Hoff and Geiger,[1] has been commonly called the "pentasalt." In dealing with aqueous systems containing any of the complex salts, one finds the solubility always very low with respect to calcium ion, as is well known for calcium sulfate in all its forms; there is also met with the problem of slow attainment of equilibrium. Successful work has been possible only with knowledge of and consistent use of the principle laid down by van't Hoff,[5] as the "Verzögerungs-regal," which, though entirely empirical as far as I have been able to find, is a rule of the greatest usefulness in solubility determinations, and very rarely has been quoted. It is to the effect that the retardation of salts in attaining equilibrium, presumably not only external equilibrium with solution but also internal equilibrium as to the stable phases, is expressed by the mean valence, which is calculated by dividing the total valence representing all ions in the formula by the total number of such ions. In this calculation, water of hydration is regarded as hydrogen oxide and given arbitrarily a mean valence of 4/3. By this treatment uni-univalent salts, which usually attain equilibrium

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[1] Van't Hoff and Wilson, *Sitzungsberichte der Preuss. Akad.*, 1142 (1900); van't Hoff and Geiger, *ibid.*, 935 (1904); van't Hoff, Voerman and Blasdale, *ibid.*, 305 (1905); D'Ans, *Z. anorg. Chem.*, **62**, 129 (1909). For a complete tabulation, see D'Ans, "Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen," Verlagsgesellschaft für Ackerbau, Berlin, 1933.

[2] Cameron and Breazeale, *J. Phys. Chem.*, **8**, 335 (1904).

[3] Barre, *Compt. rend.*, **148**, 1604 (1909); *Ann. chim. phys.*, (VIII) **24**, 145, 1911.

[4] Anderson and Nestell, *J. Ind. Eng. Chem.*, **12**, 243 (1920); Anderson, *ibid.*, **11**, 327 (1919).

[5] Van't Hoff, "Zur Bildung der ozeanischen Salzablagerungen," Braunschweig, 1905, Vol. 1, p. 32; Vol. II, p. 17.