

the solutions are kept saturated with nitrogen at atmospheric pressure, the concentrations are determined from the conductance and the temperatures with a multiple-junction thermocouple.

The method combines many of what seem to us the best features of previous methods with the following new features: the stirring is done by two low-friction valve pumps in each vessel combined with hand stirring of the ice; the thermocouples are constructed so as to give the smallest possible difference between the temperature of the solution and that of the thermal junctions; the thermocouples are calibrated against a platinum resistance thermometer under conditions as nearly as possible the same as those under which they are used.

It is shown that the effect of dissolved gas is approximately proportional to the square of the salt concentration, and is much smaller than had previously been supposed.

A method of smoothing and computing by use of deviation curves is also described.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 288]

THE FREEZING POINTS OF AQUEOUS SOLUTIONS. II. POTASSIUM, SODIUM AND LITHIUM NITRATES

BY GEORGE SCATCHARD, S. S. PRENTISS AND P. T. JONES

RECEIVED MARCH 2, 1932

PUBLISHED JULY 6, 1932

It has long been known that the charge and "collision diameter" of the ions are not sufficient to explain quantitatively the properties of electrolyte solutions. One of us¹ has discussed the other factors which must enter, and was able to calculate the properties of aqueous solutions of the alkali halides on the assumption that for noble gas type ions the size of each is the only factor which need be taken into account, though this enters in several ways. To extend and test the theory further it is necessary to have accurate data on more complicated ions. For this reason we have measured the freezing point depressions of potassium, sodium and lithium nitrates in the apparatus and with the procedure described in the previous paper.²

Lithium nitrate was prepared from lithium carbonate and nitric acid. The potassium and sodium salts were manufacturer's c. p. products. All were crystallized three times from doubly distilled water. The concentrated solutions were analyzed by evaporating to dryness in a platinum crucible, adding sulfuric acid, and igniting to constant weight at dull red

¹ Scatchard, *Physik. Z.*, **33**, 22 (1932).

² Scatchard, Jones and Prentiss, Paper I, *THIS JOURNAL*, **54**, 2676 (1932).

heat. A small piece of ammonium carbonate was added to the potassium sulfate before each ignition to convert any acid sulfate to sulfate. All weights were corrected to vacuum. Except for some results obviously in error due to spattering of acid, the mean deviation from the average of three or four determinations was 0.03–0.04%.

The results of the conductance measurements are given in Table I. The first column gives M , the molality (moles per kilogram of water), the second the ratio of M to the specific conductance L , and the third column this ratio minus the smoothed value at the same L . The freezing point results are given in Table II. The first column is the molality, the second j (= one minus the ratio of the freezing point depression to 3.716 M), and the third the measured j minus the smoothed value. The note gives the temperature difference which corresponds to the third

TABLE I
CONDUCTANCE AT 10°

M	M/L	Diff.	M	M/L	Diff.
KNO ₃					
1.4615	16.619	0.000	0.081233	11.308	+0.016
1.0995	15.582	– .003	.081233	11.307	+ .013
0.93028	15.076	.000	.033518	10.670	– .005
.67706	14.263	– .001	.024071	10.501	– .003
.35013	13.000	.000	.006859	10.037	– .007
.35013	13.074	+ .084	.003544	9.880	– .010
.25008	12.507	– .002	.002268	9.818	+ .006
.18253	12.135	+ .034	.000870	9.688	+ .007
.10552	11.531	+ .007			
NaNO ₃					
1.6137	21.184	0.000	0.062877	13.427	0.000
1.2112	19.528	.000	.038031	12.949	– .085
0.91261	18.289	.000	.010775	12.354	+ .003
.70501	17.394	.000	.007714	12.161	– .065
.47661	16.335	– .001	.006852	12.181	– .004
.27393	15.222	.000	.005475	12.026	– .090
.13193	14.196	+ .010	.001002	11.772	.000
.099228	13.854	– .004	.000693	11.709	– .015
.097029	13.845	.000	.000658	11.628	– .090
.083549	13.619	– .075			
LiNO ₃					
1.3051	21.462	0.000	0.12327	15.537	–0.002
1.1218	20.679	.000	.077288	15.040	+ .006
0.90837	19.772	.000	.077288	15.033	– .002
.70208	18.858	.000	.042898	14.525	.000
.66323	18.680	.000	.011206	13.724	+ .002
.44114	17.614	.000	.007578	13.559	– .002
.44114	17.652	+ .024	.004482	13.386	+ .001
.32943	17.010	.000	.000899	13.032	– .022
.12327	15.550	+ .012	.000663	12.971	– .047

column for concentrations less than 0.01 *M*, for which 0.00002° is more than 0.05% of the depression. It will be seen that few of the points lie farther from the smooth curve than the larger of these two quantities.

TABLE II
FREEZING POINTS

<i>M</i>		Diff. ^a	<i>M</i>	<i>f</i>	Diff.
KNO ₃ , Series A					
0.001015	0.0217	+0.0103	0.29836	0.1725	0.0000
.001893	.0191	+ .0036	.43511	.2068	- .0002
.006230	.0285	+ .0008	.55577	.2327	- .0005
.016415	.0439	- .0001	.65243	.2521	- .0001
.036379	.0669	+ .0025	.75733	.2711	- .0003
.063274	.0832	- .0003	.88145	.2911	- .0011
.11351	.1097	.0000	1.0010	.3110	.0000
.17737	.1356	+ .0005			
Series B					
0.90419	0.2974	+0.0014	0.41571	0.2015	-0.0009
.79342	.2780	+ .0003	.28564	.1687	- .0004
.62040	.2452	- .0009	.19567	.1416	+ .0001
Series C					
0.001081	0.0167	+0.0049	0.058966	0.0812	+0.0004
.003115	.0195	- .0004	.19181	.1399	- .0003
.008291	.0295	- .0023	.36331	.1898	+ .0002
.022811	.0516	.0000			
NaNO ₃ , Series A					
0.66338	0.1624	0.0000	0.31821	0.1232	-0.0003
.57485	.1539	+ .0001	.22017	.1078	- .0001
.51289	.1476	+ .0002	.15359	.0952	+ .0008
.40414	.1350	.0000			
Series B					
0.000803	0.0248	+0.0149	0.14163	0.0917	+0.0002
.002096	.0217	+ .0061	.22384	.1083	- .0001
.006389	.0262	+ .0006	1.0742	.1969	+ .0006
.017605	.0394	- .0003	1.1662	.2030	+ .0004
.055233	.0637	+ .0001	0.79637	.1741	- .0001
Series C					
0.000985	0.0165	+0.0056	0.073695	0.0718	+0.0005
.003101	.0220	+ .0036	.093962	.0788	- .0005
.010875	.0315	- .0008	.19565	.1038	+ .0006
.021100	.0428	- .0001	.24941	.1128	- .0002
.036711	.0539	.0000			
Series D					
1.6765	0.2314	0.0000	0.73521	0.1684	0.0000
1.3514	.2138	- .0001	.47385	.1432	.0000
0.94282	.1861	- .0003	.36880	.1306	.0002
.84371	.1776	- .0006			

TABLE II (Concluded)

<i>M</i>	Diff.*		<i>M</i>	<i>j</i>	Diff.
LiNO ₃ , Series A					
0.003253	0.0230	+0.0045	0.093540	0.0545	-0.0004
.007473	.0266	+ .0007	.15119	.0573	.0000
.021140	.0377	+ .0003	.22920	.0560	- .0005
.048107	.0488	+ .0012			
Series B					
0.000632	0.0207	+0.0120	0.037397	0.0450	+0.0004
.001200	.0267	+ .0150	.062754	.0500	- .0006
.002669	.0230	+ .0062	.11718	.0561	- .0001
.007210	.0251	- .0003	.17737	.0574	- .0002
.013703	.0318	- .0005			
Series C					
1.0501	-0.0066	+0.0006	0.53896	0.0367	+0.0002
0.91557	+ .0051	- .0001	.45022	.0436	+ .0002
.81478	.0141	+ .0003	.37662	.0487	+ .0002
.72572	.0211	- .0002	.29727	.0537	+ .0002
.64424	.0270	- .0011	.20538	.0582	+ .0010
Series D					
1.1906	-0.0203	-0.0013	0.37301	0.0488	-0.0001
0.92448	+ .0043	- .0002	.25647	.0552	- .0003
.70615	.0229	.0000	.17598	.0579	+ .0003
.55171	.0357	+ .0002			

* For concentrations below 0.01 *M* the temperatures in hundred thousandths of a degree, corresponding to the *j* differences are in order: KNO₃, A, 4, 2, 2; C, 2, 0, 7; NaNO₃, B, 4, 5, 1; C, 2, 4; LiNO₃, A, 5, 2; B, 1, 5, 7, 1.

TABLE III

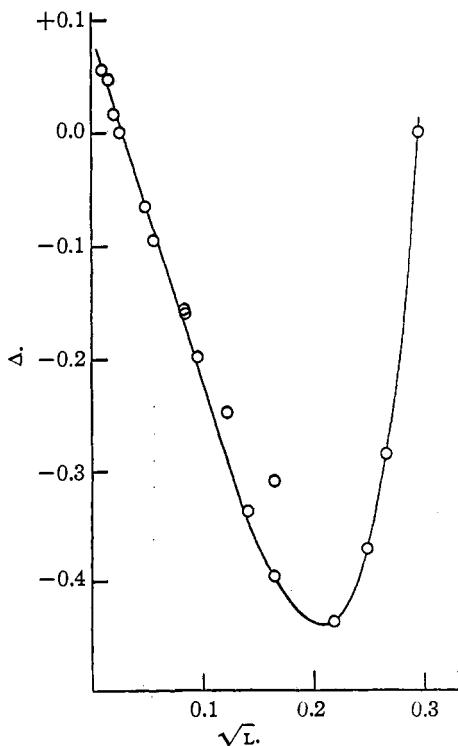
j VALUES OF THE ALKALI NITRATES

<i>M</i>	Lim. law	KNO ₃	NaNO ₃	LiNO ₃
0.001	0.0118	0.0114	0.0109	0.0109
.002	.0167	.0159	.0151	.0148
.005	.0264	.0249	.0228	.0218
.01	.0374	.0348	.0311	.0293
.02	.0529	.0485	.0419	.0368
.05	.0836	.0748	.0612	.0480
.1	.1182	.1035	.0803	.0552
.2	.1672	.1429	.1042	.0572
.3	.2047	.1731	.1209	.0533
.4	.2364	.1986	.1345	.0469
.5	.2643	.2214	.1460	.0396
.6	.2897	.2421	.1563	.0317
.7	.3127	.2612	.1656	.0234
.8	.3343	.2788	.1745	.0151
.9	.3546	.2953	.1829	.0066
1.0	.3738	.3109	.1909	- .0021
1.1	.3920	... ^a	.1981	- .0109

^a KNO₃ eutectic: *M* = 1.1396; freezing point depression = 2.8285; *j* = 0.3321 from preliminary series not otherwise used.

TABLE IV
 VALUES OF $-\log \gamma'$ FOR THE ALKALI NITRATES

M	Lim. law	KNO ₃	NaNO ₃	LiNO ₃
0.001	0.0154	0.0150	0.0146	0.0146
.002	.0218	.0210	.0204	.0201
.005	.0344	.0329	.0311	.0304
.01	.0487	.0461	.0428	.0412
.02	.0689	.0645	.0584	.0543
.05	.1089	.1001	.0870	.0760
.1	.1540	.1391	.1165	.0947
.2	.2178	.1923	.1543	.1125
.3	.2667	.2336	.1812	.1204
.4	.3080	.2677	.2030	.1238
.5	.3444	.2979	.2214	.1246
.6	.3775	.3252	.2378	.1239
.7	.4074	.3502	.2525	.12197
.8	.4356	.3734	.2661	.11931
.9	.4620	.3952	.2788	.1160
1.0	.4870	.4158	.2907	.1122
1.1	.51073018	.1079


 Fig. 1.—Conductance curve for potassium nitrate.
 $\Delta = (M/L) - 9.401 - 24.341 \sqrt{L}$.

The smoothed values were obtained from deviation curves made by the methods described in the first paper.² Figures 1 and 2 give illustrative small-scale reproductions of the conductance and freezing point curves for potassium nitrate. The broken line in the latter shows the deviation from the zero line corresponding to two hundred-thousandths of a degree. The crosses give the measurements of Adams.³ The curves extrapolate naturally to a horizontal tangent at zero concentration, that is, to the theoretical limiting law, but the measurements in very dilute solutions are not accurate enough to preclude a change of a few per cent. in the limiting law.

Table III gives at round concentrations the values of j determined from the smooth curves,

³ Adams, THIS JOURNAL, 37, 481 (1915).

and Table IV the values of γ' calculated from the same curves as described in the previous paper.² Both tables give values according to the theoretical limiting law; in no case do we obtain a larger effect. For potassium nitrate the effect is never much smaller even at the highest concentrations. For lithium nitrate, on the other hand, j becomes negative in concentrated solutions.

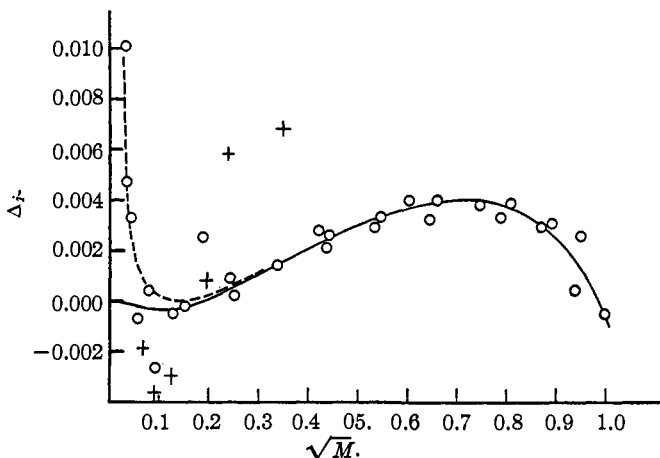


Fig. 2.— Δ_j Values for KNO_3 ; $\Delta_j = j - \frac{0.3738\sqrt{M}}{1 + \sqrt{M}} - 0.1245 M$.

○, our results; +, Adams' results. Broken line represents the deviations for 0.00002° .

The large effects for potassium nitrate have often been attributed to the smallness of the nitrate ion, or to the charge lying near the surface.⁴ The fact that sodium nitrate and lithium nitrate have so much smaller effects is enough to make this explanation highly improbable. From the point of view recently published by one of us,¹ the explanation for the difference between the nitrate and the bromide or iodide ions should lie either in a larger effect of non-ionic forces or in a smaller decrease of the dielectric constant. For the unsymmetrical nitrate ion we should expect both effects to be smaller, in which case the second effect must predominate. Uncertainty concerning the non-ionic forces in solutions containing an unsymmetrical ion make it desirable to leave further theoretical discussion until more salts have been studied. We shall limit ourselves to the fact that our measurements are quantitatively consistent with a size for the nitrate ion which should be expected from the volume of its solutions and from its salting out effects, a size between those of the bromide and iodide ions.

CAMBRIDGE, MASSACHUSETTS

⁴ N. Bjerrum, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, VII, No. 9 (1926); H. Müller, *Physik. Z.*, **28**, 324 (1927); **29**, 78 (1928); Gronwall, La Mer and Sandved, *ibid.*, **29**, 358 (1928).