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The Freezing Points of Aqueous Solutions. V. Potassium, Sodium and Lithium Chlorates and Perchlorates[1]

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

The freezing points of these substances were studied with the hope of gaining further insight into the effect of the shape and size of ions upon their chemical potentials or activity coefficients. The great difference between the behavior of the alkali nitrates and that of the alkali halides aroused our interest in the chlorates and perchlorates. x-Ray studies on salt crystals[2] indicate that the nitrate ion is planar and triangular, that the perchlorate ion is a regular tetrahedron, and that in the chlorate ion one of the oxygens of the perchlorate ion is removed without much change in the relative positions of the other atoms. There is thus a graded change in shape from the nitrate to the perchlorate ion, accompanied of course by a change in size.

Potassium and sodium chlorates were prepared by three crystallizations of C. P. salts from conductivity water. Lithium chlorate was prepared by adding a solution of C. P. barium chlorate to one of C. P. lithium sulfate. Reagent potassium perchlorate was crystallized once. Sodium and lithium perchlorates were prepared from the corresponding C. P. carbonates and C. P. perchloric acid solution. In all cases the concentration of the stock solution was determined by evaporating the solution with sulfuric acid, igniting (with the addition of ammonium carbonate for the potassium salts), and weighing as the sulfate. The potassium perchlorate was also evaporated and weighed as such. The water and ice were as described in paper I.

The results of the conductance measurements are given in Table I. M is the concentration in moles per kilogram of water, and L is the specific conductance. The results of the freezing point measurements (calculated by the thermocouple equation of paper IV) are given in Table II. j is the Lewis and Randall function previously used. The smoothed values of M/L and of j were obtained as in the previous papers. Those of j at rounded concentrations are given in Table III and the corresponding values of $-\log \gamma'$ in Table IV. The measurements on the two potassium salts are carried to the eutectic point. The small solubilities of these salts make the measurements on them slightly less consistent than those with the other salts. For the others the average deviations of the experimental points from the smooth curves is between one and two in the last place given for M/L, about 0.05% in j for solutions more concentrated than 0.01 M, and

TABLE I

CONDUCTANCE AT 10°

M	M/L	M	M/L	M	M/L
$KClO_3$		$NaClO_3$		$LiClO_3$	
0.29063	13.337	1.44454	21.728	1.2863	23.392
.20166	12.846	1.10817	20.292	1.1451	22.734
.17290	12.662	0.78319	18.919	0.97723	21.952
.12511	12.308	.65420	18.302	.74704	20.843
.098294	12.073	.64351	18.252	.57624	19.982
.092694	12.018	.54072	17.770	.38015	18.874
.062568	11.689	.36057	16.828	.33437	18.586
.041891	11.402	.17985	15.642	.20029	17.625
.036680	11.317	.14552	15.353	.12325	16.908
.028279	11.167	.064643	14.463	.086817	16.474
.021112	11.014	.059483	14.385	.047568	15.866
.015595	10.876	.058347	14.588	.036491	15.639
.008954	10.668	.022018	13.662	.012000	14.909
.008352	10.648	.021614	13.642	.008834	14.756
.006308	10.561	.007308	13.130	.004151	14.453
.002355	10.366	.007279	13.130	.003545	14.411
.002082	10.315	.006598	13.099	.001046	14.071
.000678	10.152	.002631	12.814	.000845	14.040
.000539	10.133	.002437	12.807		
		.002418	12.803		
		.001248	12.648		
		.000808	12.578		
		.000666	12.513		
$KClO_4$		$NaClO_4$		$LiClO_4$	
0.070501	11.794	1.8055	21.847	1.5038	22.052
.035755	11.250	1.2453	19.651	1.2498	21.137
.017094	10.823	1.1091	19.133	1.0264	20.328
.009189	10.571	0.86690	18.199	0.93887	20.004
.004191	10.346	.72723	17.657	.76590	19.360
.002069	10.212	.64741	17.329	.66094	18.951
.000665	10.082	.45132	16.496	.44918	18.064
		.26736	15.571	.39705	17.823
		.20308	15.185	.35768	17.637
		.12385	14.588	.28531	17.268
		.11134	14.477	.17622	16.584
		.046884	13.722	.095886	15.894
		.029136	13.402	.061488	15.485
		.012824	12.977	.031405	14.975
		.005025	12.638	.017236	14.617
		.003374	12.529	.006914	14.203
		.001575	12.379	.002568	13.906
		.001102	12.310	.001507	13.797
		.000746	12.267	.000811	13.683

(1) Paper IV in this series is in THIS JOURNAL, **55**, 4355 (1933).

(2) W. H. Zachariasen, *ibid.*, **53**, 2123 (1931); *Z. Krist.*, **73**, 141 (1930); H. Bräkken and L. Harang, *ibid.*, **75**, 538 (1930); K. Herrmann, O. Gerngross and W. Abitz, *ibid.*, **75**, 41 (1930).

TABLE II

FREEZING POINTS

	M	j		M	j		M	j		M	j
					$KClO_3$						
A	0.000485	0.0623	B	0.010584	0.0315	D	0.037653	0.0591	A	0.10623	0.0990
B	.000581	.0134	D	.012380	.0318	D	.039814	.0605	B	.13536	.1105
C	.001281	.0105	C	.012469	.0319	B	.043067	.0637	A	.15811	.1186
A	.001627	.0208	A	.017878	.0413	C	.055946	.0727	A	.19201	.1302
D	.002998	.0128	B	.029782	.0527	A	.062245	.0782	B	.21981	.1379
B	.004560	.0233	C	.034003	.0637	B	.079393	.0863	B	.25148	.1484
A	.005520	.0235	A	.036929	.0656						
					$NaClO_3$						
A	0.000889	0.0162	B	0.054084	0.0604	F	0.30222	0.1091	F	0.75732	0.1487
B	.001029	.0193	A	.073388	.0691	A	.35453	.1155	G	.76747	.1497
A	.001825	.0179	B	.089482	.0728	F	.37378	.1173	E	.84101	.1541
B	.003726	.0192	A	.12131	.0822	E	.42233	.1216	G	.92266	.1597
A	.005256	.0246	B	.16179	.0894	F	.48057	.1271	F	.93784	.1601
B	.011793	.0333	E	.17671	.0923	E	.54821	.1322	E	1.0406	.1635
A	.015730	.0381	F	.22034	.0989	G	.56733	.1344	G	1.0531	.1649
B	.024412	.0443	A	.24523	.1022	F	.61804	.1377	F	1.1684	.1688
A	.034813	.0537	E	.26064	.1036	E	.67554	.1415	E	1.2852	.1719
G	.046961	.0595	B	.28383	.1067						
					$LiClO_3$						
A	0.000627	0.0300	C	0.018748	0.0353	A	0.19519	0.0518	E	0.55073	0.0241
C	.000753	− .0006	B	.021459	.0383	E	.23184	.0495	F	.63822	.0155
B	.001109	+ .0053	A	.029040	.0403	F	.23585	.0498	G	.64964	.0149
C	.001396	.0072	B	.038551	.0439	B	.26641	.0482	E	.67931	.0111
B	.002100	.0274	A	.057068	.0472	E	.29786	.0452	F	.83835	− .0062
A	.002192	.0202	B	.086081	.0513	F	.31259	.0447	E	.83324	− .0060
C	.002983	.0185	A	.11738	.0522	E	.36510	.0407	G	.84784	− .0071
A	.003849	.0261	E	.15190	.0526	F	.38856	.0392	F	.95788	− .0188
B	.005650	.0236	B	.15944	.0533	E	.44750	.0342	G	1.0338	− .0266
C	.009870	.0282	F	.18045	.0526	F	.48569	.0308	G	1.2777	− .0550
A	.013646	.0328									
					$KClO_4$						
A	0.001776	0.0333	E	0.008928	0.0411	A	0.022542	0.0577	A	0.044821	0.0816
F	.003612	.0195	A	.009872	.0435	F	.022927	.0575	E	.045841	.0823
E	.004936	.0377	F	.012492	.0414	E	.029631	.0676	A	.048335	.0892
F	.006690	.0262	E	.016215	.0521	F	.030369	.0659			
					$NaClO_4$						
B	0.001049	0.0136	C	0.030269	0.0479	A	0.21433	0.0916	F	0.59212	0.1188
A	.001339	.0132	A	.036284	.0537	F	.24548	.0908	E	.67661	.1228
B	.002648	.0183	B	.061426	.0633	C	.25367	.0950	F	.73039	.1256
A	.003335	.0228	A	.078021	.0670	E	.30491	.1000	E	.83302	.1295
C	.007050	.0262	C	.093410	.0698	B	.35662	.1040	F	.88450	.1307
A	.010984	.0334	B	.11620	.0762	E	.38875	.1068	E	1.0033	.1342
B	.012620	.0343	A	.15672	.0833	F	.45140	.1111	F	1.0799	.1367
B	.023918	.0431	F	.16714	.0848	E	.52906	.1160	E	1.2075	.1398
					$LiClO_4$						
A	0.000616	−0.0056	B	0.028497	0.0368	F	0.20093	0.0394	F	0.55886	−0.0093
C	.001014	+ .0101	A	.040513	.0396	A	.22600	.0361	E	.64475	− .0226
B	.001941	.0226	B	.056796	.0431	F	.27916	.0305	F	.72178	− .0344
C	.002265	.0222	A	.078687	.0437	E	.31937	.0255	E	.78603	− .0450
A	.003267	.0140	B	.10871	.0439	B	.35680	.0190	F	.88417	− .0608
C	.007050	.0244	A	.13421	.0426	E	.40812	.0127	E	.98327	− .0771
B	.011698	.0275	C	.16828	.0419	F	.45492	.0061	F	1.0828	− .0924
A	.014363	.0292	B	.16864	.0391	E	.49946	− .0008	E	1.2054	− .1136
C	.023604	.0359									

The letters denote the series. Series A–D were run with increasing concentrations and series E–H with decreasing concentrations.

TABLE III

j VALUES OF THE ALKALI CHLORATES AND PERCHLORATES

M	Lim. law	$KClO_3$	$NaClO_3$	$LiClO_3$	$KClO_4$	$NaClO_4$	$LiClO_4$
0.001	0.0118	0.0105	0.0110	0.0109	0.0118	0.0113	0.0104
.002	.0167	.0144	.0152	.0147	.0168	.0157	.0141
.005	.0264	.0221	.0233	.0216	.0266	.0237	.0204
.01	.0374	.0308	.0315	.0284	.0379	.0317	.0265
.02	.0529	.0435	.0419	.0361	.0539	.0410	.0332
.05	.0836	.0686	.0597	.0463	[b]	.0579	.0417
.1	.1182	.0960	.0761	.0518		.0724	.0448
.2	.1672	.1325	.0958	.0513		.0890	.0393
.3	.2047	[a]	.1090	.0459		.0997	.0277
.4	.2364		.1195	.0381		.1075	.0140
.5	.2643		.1285	.0292		.1140	−.0006
.6	.2897		.1367	.0195		.1195	−.0158
.7	.3127		.1445	.0092		.1241	−.0313
.8	.3343		.1517	−.0016		.1280	−.0473
.9	.3546		.1580	−.0125		.1315	−.0635
1.0	.3738		.1627	−.0235		.1344	−.0798
1.1	.3920		.1665	−.0347		.1372	−.0962

[a] Eutectic, $M = 0.25148$, $\Theta = 0.79553°$, $j = 0.1481$.
[b] Eutectic, $M = .04834$, $\Theta = .16353°$, $j = .0850$.

TABLE IV

VALUES FOR $-\text{LOG}\ \gamma'$ FOR THE ALKALI CHLORATES AND PERCHLORATES

M	Lim. law	$KClO_3$	$NaClO_3$	$LiClO_3$	$KClO_4$	$NaClO_4$	$LiClO_4$
0.001	0.0154	0.0142	0.0148	0.0145	0.0154	0.0149	0.0141
.002	.0218	.0196	.0205	.0201	.0218	.0209	.0194
.005	.0344	.0301	.0316	.0302	.0347	.0321	.0290
.01	.0487	.0418	.0433	.0406	.0492	.0439	.0386
.02	.0689	.0583	.0588	.0537	.0697	.0588	.0506
.05	.1089	.0913	.0865	.0745	[b]	.0857	.0692
.1	.1540	.1277	.1139	.0915		.1116	.0835
.2	.2178	.1771	.1482	.1070		.1429	.0940
.3	.2667	[a]	.1718	.1131		.1640	.0948
.4	.3080		.1905	.1149		.1801	.0914
.5	.3444		.2066	.1141		.1936	.0856
.6	.3775		.2203	.1117		.2052	.0782
.7	.4074		.2330	.1080		.2151	.0697
.8	.4356		.2445	.1034		.2241	.0601
.9	.4620		.2551	.0981		.2321	.0502
1.0	.4870		.2644	.0923		.2393	.0396
1.1	.5107		.2727	.0860		.2461	.0287

[a] Eutectic, $M = 0.25148$, $-\log \gamma' = 0.1984$.
[b] Eutectic, $M = .04834$, $-\log \gamma' = .1094$.

about three hundred-thousandths of a degree for more dilute solutions.[3]

The *j* values for the chlorates are more negative, that is, the activity coefficients are larger, than those for the corresponding nitrates. Those for lithium and sodium perchlorates are still more negative, so that lithium perchlorate has the most negative *j* function of any of the twenty-five uni-univalent salts we have studied. The *j* value for potassium perchlorate is, on the other hand, more positive than those of the chlorate and nitrate, and even more positive than the Debye–Hückel limiting law. The difference from the latter is, however, less than 0.3% at the eutectic, and therefore not much more than the error of measurement on this difficultly soluble salt. Except for the "humps" in the curves for the ammonium salts, and the smaller one for lithium chloride, all the uni-univalent salts we have studied fall in the spread of lithium and potassium perchlorates. Their relations will be discussed more fully in paper VI.

(3) Earlier measurements are reported only on dilute solutions of sodium and potassium chlorates, and on concentrated solutions of lithium chlorate. The references are given in "International Critical Tables," Vol. IV, pp. 258–259.

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The Freezing Points of Aqueous Solutions. VI. Potassium, Sodium and Lithium Formates and Acetates[1]

BY GEORGE SCATCHARD AND S. S. PRENTISS

The freezing point depressions of the potassium, sodium and lithium formates and acetates were measured since salts of the lower aliphatic acids are of considerable practical importance, and because of the information the study of them can give as to the effect of the shape of ions on the properties of their solutions. Aside from the difference between the carbon and nitrogen nuclei, the formate ion differs from the nitrate ion in the replacement of one oxygen by a hydrogen, which decreases greatly the symmetry of the ion, particularly since the ionic charge is doubtless associated with the oxygens. The acetate ion has the additional difference of a CH_2 group inserted very unsymmetrically between the carbon and the hydrogen of the formate ion.

The lithium formate was prepared from C. P. formic acid and washed lithium carbonate. It was crystallized three times from conductivity water. The starting materials for the other salts were the C. P. or reagent salts. The potassium salts were made neutral to phenolphthalein with C. P. potassium hydroxide. So-

(1) Paper V in this series is in THIS JOURNAL, **56**, 805 (1934).