

TABLE III

j VALUES OF THE ALKALI CHLORATES AND PERCHLORATES

<i>M</i>	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, $M = 0.25148$, $\Theta = 0.79553^\circ$, $j = 0.1481$.^b Eutectic, $M = .04834$, $\Theta = .16353^\circ$, $j = .0850$.

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,

(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.

TABLE IV

VALUES FOR $-\log \gamma'$ FOR THE ALKALI CHLORATES AND PERCHLORATES

<i>M</i>	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, $M = .04834$, $-\log \gamma' = .1094$.

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.

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The Freezing Points of Aqueous Solutions. VI. Potassium, Sodium and Lithium Formates and Acetates¹

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, par-

ticularly since the ionic charge is doubtless associated with the oxygens. The acetate ion has the additional difference of a CH₂ 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).

dium acetate was crystallized once, potassium acetate twice, and sodium formate and lithium acetate three times. The stock solutions were all titrated to neutrality with phenolphthalein. The sodium formate was found to contain 0.01% formic acid, a negligible amount, and the others were all neutral. The concentrations were determined by evaporating to dryness with sulfuric acid, igniting (with the addition of ammonium carbonate for each heating of the potassium salts), and weighing as the sulfate. The water and ice were the same 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 work. Those of j at round concentrations are given in Table III and the corresponding values of $-\log \gamma'$ in Table IV. The average deviation of the experimental points from the smooth curves is about one in the last

place given for M/L , about 0.06% for j in solutions more concentrated than 0.01 M , and about four hundred-thousandths of a degree for the more dilute solutions.²

The acid dissociation constant of acetic acid is almost exactly equal to the basic dissociation constant of ammonia. Therefore the calculation of the effect of hydrolysis on the freezing points given in paper III³ may be applied equally well to the acetates. The effect is negligible in the range of our experiments for the salts of acetic acid, and is even smaller for the salts of the stronger formic acid.

Discussion

The behavior of the formates and acetates is quite different from that of the halides or that of the nitrates, chlorates and perchlorates. For the acetates the osmotic coefficient ($1 - j$) increases in the order: lithium, sodium, potassium, while for the salts previously studied the osmotic coefficients decrease in that order. The spread of the formates is not very great but the order is the same as for the acetates below 0.4 M . Above that concentration the coefficient of sodium formate is smaller than that of the lithium salt.

We have completed measurements of the freezing point depressions of twenty-five uni-univalent salts, and shall now attempt to correlate the results with the size and structure of the ions. The mass of data is too large to make comparisons at all concentrations, and it is necessary to make some arbitrary choice. If we were to limit the discussion to our own measurements we should choose the term proportional to the concentration determined from dilute solutions in a previous paper.⁴ However, we find it desirable to include measurements on other electrolytes, generally less accurate than our own, and shall therefore compare the osmotic coefficients ($1 - j$) in one molal solutions. We include in our discussion the results on other alkali halides summarized by Fajans⁵ largely from measurements in his laboratory, and those on the alkali hydroxides and on the acids corresponding to the salts included.⁶

(2) Earlier measurements have been reported only for potassium and sodium acetates. The references are given in "International Critical Tables," Vol. IV, pp. 258-259.

(3) THIS JOURNAL, **54**, 2696 (1932).

(4) Prentiss and Scatchard, *Chem. Reviews*, **13**, 139 (1933).

(5) Fajans and Karagunis, *Z. angew. Chem.*, **43**, 1046 (1930); Fajans, "Chemistry at the Centenary (1931) Meeting of the British Association for the Advancement of Science," W. Heffer and Sons, Cambridge, 1931, p. 49.

(6) From "International Critical Tables," Vol. IV, pp. 258-262.

TABLE I
CONDUCTANCE AT 10°

M	M/L	M	M/L	M	M/L
KOOCH		NaOOCH		LiOOCH	
1.2921	16.438	1.3037	24.767	1.2902	35.652
0.90128	15.538	1.1619	23.928	1.1834	34.254
.65873	14.926	1.0461	23.247	1.1434	33.733
.49158	14.468	0.89848	22.381	1.0071	31.987
.31413	13.887	.68334	21.122	0.81478	29.568
.28078	13.763	.56892	20.394	.61969	27.127
.17904	13.301	.41634	19.387	.47293	25.265
.071753	12.582	.24015	18.055	.34701	23.588
.044195	12.276	.17240	17.436	.24383	22.102
.023248	11.946	.10929	16.737	.11871	19.991
.007505	11.527	.066365	16.139	.071090	18.961
.003317	11.206	.042924	15.703	.024485	17.532
.000895	11.132	.014023	14.888	.017320	17.208
		.008526	14.637	.005615	16.461
		.003022	14.241	.001939	16.065
		.001233	14.043		
KOOCCl ₂		NaOOCCl ₂		LiOOCCl ₂	
1.4472	22.179	1.4240	35.276	1.2893	51.284
1.2531	21.192	1.1182	31.740	1.1382	47.608
0.95623	19.703	1.0414	30.890	1.0086	44.600
.82995	19.079	0.87194	29.041	0.82661	40.522
.58354	17.829	.71627	27.382	.74936	38.855
.45884	17.166	.56459	25.756	.66864	37.134
.32130	16.382	.39003	23.830	.54821	34.585
.22671	15.777	.27943	22.524	.45620	32.630
.19485	15.550	.23777	21.999	.38737	31.182
.18129	15.446	.17415	21.127	.27167	28.646
.081949	14.537	.10602	20.042	.14643	25.622
.053949	14.171	.069812	19.334	.10213	24.351
.022410	13.622	.024871	18.071	.063608	23.089
.009787	13.236	.013542	17.562	.032220	21.759
.003775	12.936	.004673	16.937	.012701	20.552
.001065	12.727	.001722	16.590	.004611	19.747
				.001897	19.318

TABLE II
FREEZING POINTS

<i>M</i>		<i>M</i>		<i>j</i>	<i>M</i>		<i>M</i>				
KOOCH											
A	0.000893	0.0145	B	0.046477	0.0492	E	0.28357	0.0713	E	0.60476	0.0693
B	.002286	.0088	A	.068190	.0561	F	.34072	.0723	F	.67506	.0677
A	.006046	.0247	B	.093846	.0608	B	.38232	.0730	E	.75393	.0659
B	.010704	.0273	A	.11777	.0639	E	.40356	.0718	F	.84394	.0635
A	.016438	.0331	B	.15410	.0672	F	.43592	.0719	E	.94757	.0605
B	.021241	.0432	F	.19065	.0698	E	.49297	.0712	F	1.0804	.0567
A	.029945	.0425	A	.22630	.0706	F	.53850	.0705	E	1.1935	.0525
NaOOCH											
A	0.001668	0.0094	A	0.077829	0.0600	E	0.36013	0.0796	E	0.75667	0.0826
B	.003006	.0198	B	.10800	.0643	B	.40796	.0802	F	.82372	.0809
A	.005921	.0201	A	.13371	.0674	F	.44735	.0805	E	.92520	.0792
B	.009982	.0297	B	.17117	.0711	E	.51583	.0812	F	.99886	.0782
A	.016956	.0343	F	.21066	.0729	F	.55167	.0813	E	1.1171	.0777
B	.026497	.0454	A	.25405	.0764	E	.62615	.0819	F	1.2181	.0753
A	.037698	.0470	F	.30328	.0781	F	.67822	.0824	E	1.3908	.0731
B	.059993	.0562									
LiOOCH											
A	0.001661	0.0555	B	0.054475	0.0566	E	0.31184	0.0799	E	0.69146	0.0754
B	.003859	.0188	A	.078905	.0626	F	.37923	.0799	F	.76218	.0736
A	.006142	.0234	B	.11198	.0683	B	.41849	.0800	E	.84182	.0718
B	.010577	.0315	A	.13446	.0704	E	.46309	.0799	F	.92016	.0689
A	.014980	.0348	B	.17683	.0745	F	.50752	.0791	E	1.0297	.0666
B	.025351	.0460	F	.22410	.0776	E	.56314	.0786	F	1.1275	.0626
A	.037415	.0508	A	.26664	.0788	F	.62556	.0766	E	1.2701	.0599
KOOCH ₃											
A	0.000577	-0.0024	A	0.028042	0.0410	B	0.22112	0.0483	F	0.56263	0.0181
C	.002061	+ .0153	B	.039445	.0415	F	.26739	.0448	E	.62838	.0109
B	.002072	.0233	C	.041614	.0424	A	.31223	.0420	F	.69829	.0039
A	.003866	.0102	A	.057889	.0463	F	.34622	.0388	E	.77783	-.0052
C	.005497	.0213	B	.080671	.0487	E	.36908	.0366	F	.85618	-.0131
B	.008413	.0302	A	.10750	.0510	B	.40614	.0338	E	.94916	-.0237
A	.015280	.0342	B	.14223	.0510	F	.45150	.0291	F	1.0509	-.0347
B	.021154	.0455	A	.18446	.0504	E	.51303	.0230	E	1.1606	-.0478
C	.021647	.0386									
NaOOCCH ₃											
A	0.000682	0.0091	A	0.049766	0.0472	F	0.23725	0.0517	E	0.65213	0.0251
B	.002214	.0252	B	.054054	.0467	E	.27632	.0504	F	.71788	.0201
A	.002879	.0167	A	.080874	.0509	B	.32031	.0486	E	.79685	.0134
B	.005805	.0256	B	.111456	.0522	E	.39975	.0425	F	.90198	.0033
A	.007657	.0251	A	.13560	.0534	F	.43636	.0406	E	.98634	-.0026
B	.015628	.0335	F	.15614	.0535	E	.50946	.0353	F	1.0602	-.0093
A	.023479	.0417	B	.18475	.0537	F	.56806	.0312	E	1.2347	-.0208
B	.037656	.0447	A	.21264	.0534						
LiOOCCH ₃											
A	0.001842	0.0267	B	0.055988	0.0525	E	0.23233	0.0627	E	0.70398	0.0352
B	.002253	.0206	A	.082635	.0565	F	.28437	.0606	F	.77000	.0294
A	.006059	.0259	B	.10681	.0598	B	.31092	.0611	E	.84652	.0238
B	.010555	.0308	A	.13449	.0615	E	.38568	.0565	F	.92291	.0176
A	.015196	.0319	B	.16783	.0644	F	.46963	.0515	E	1.0080	.0102
B	.023164	.0424	F	.18282	.0636	E	.56001	.0455	F	1.0588	.0067
B	.033449	.0467	A	.21374	.0633	F	.61701	.0411	E	1.1965	-.0077
A	.039677	.0493									

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 FORMATES AND ACETATES

<i>M</i>	Lim. law	KO-OCH	Na-OCH	Li-OCH	KO-OCCH ₃	NaO-OCCH ₃	LiO-OCCH ₃
0.001	0.0118	0.0108	0.0110	0.0111	0.0109	0.0110	0.0110
.002	.0167	.0146	.0150	.0150	.0148	.0149	.0151
.005	.0284	.0216	.0222	.0225	.0220	.0220	.0226
.01	.0374	.0286	.0295	.0304	.0289	.0288	.0301
.02	.0529	.0371	.0383	.0402	.0366	.0365	.0391
.05	.0836	.0505	.0519	.0552	.0463	.0468	.0517
.1	.1182	.0616	.0629	.0665	.0509	.0526	.0597
.2	.1672	.0697	.0732	.0761	.0492	.0531	.0631
.3	.2047	.0721	.0779	.0796	.0427	.0490	.0606
.4	.2364	.0721	.0802	.0802	.0340	.0431	.0559
.5	.2643	.0711	.0813	.0793	.0244	.0364	.0498
.6	.2897	.0694	.0816	.0776	.0142	.0290	.0428
.7	.3127	.0671	.0813	.0751	.0036	.0210	.0353
.8	.3343	.0646	.0807	.0727	—	.0131	.0274
.9	.3546	.0619	.0799	.0698	—	.0048	.0192
1.0	.3738	.0589	.0788	.0671	—	.0038	.0105
1.1	.3920	.0578	.0775	.0642	—	.0126	.0017

TABLE IV

VALUES FOR $-\log \gamma'$ FOR THE ALKALI FORMATES AND ACETATES

<i>M</i>	Lim. law	KOOCH	Na-OCH	Li-OCH	KO-OCCH ₃	NaO-OCCH ₃	LiO-OCCH ₃
0.001	0.0154	0.0145	0.0146	0.0147	0.0145	0.0146	0.0146
.002	.0218	.0199	.0203	.0204	.0201	.0203	.0204
.005	.0344	.0302	.0308	.0311	.0306	.0306	.0309
.01	.0487	.0406	.0416	.0424	.0411	.0412	.0421
.02	.0689	.0543	.0557	.0573	.0544	.0544	.0564
.05	.1089	.0774	.0794	.0826	.0750	.0754	.0799
.1	.1540	.0989	.1012	.1057	.0915	.0928	.1000
.2	.2178	.1221	.1262	.1312	.1061	.1089	.1201
.3	.2667	.1356	.1415	.1465	.1113	.1160	.1298
.4	.3080	.1445	.1522	.1565	.1122	.1192	.1349
.5	.3444	.1509	.1606	.1637	.1107	.1199	.1373
.6	.3775	.1556	.1669	.1692	.1076	.1191	.1379
.7	.4074	.1589	.1720	.1729	.1034	.1172	.1370
.8	.4356	.1616	.1763	.1761	.0985	.1156	.1353
.9	.4620	.1635	.1799	.1783	.0928	.1112	.1329
1.0	.4870	.1648	.1829	.1802	.0867	.1074	.1296
1.1	.5107	.1674	.1854	.1814	.0804	.1029	.1257

TABLE V

OSMOTIC COEFFICIENTS OF UNI-UNIVALENT ELECTROLYTES AT ONE MOLAL (APPARENT MOLAL VOLUMES IN PARENTHESES)

	Li (18.4)	Na (17.9)	K (28.4)	Rb (33.5)	OH ₃ (36.8)	NH ₄ (37.2)	Cs (40.7)
OH	(-3.1)	0.89	0.93	0.97			
F	(-0.6)	S	S	0.90	0.94	0.51	1.01
Cl	(17.9)	1.02	0.91	.88	.85	1.04	0.89
Br	(24.5)	1.06	.94	.88		1.06	.89
IO ₃	(26.4)	0.93	.92	.94		0.48	
NO ₃	(29.8)	1.00	.81	.69		.95	.79
I	(35.5)	>1.10	.99	.91		1.08	.90
ClO ₃	(37.2)	1.02	.84	S			S
Ac	(41.3)	0.90	1.00	1.03		0.47	
ClO ₄	(45.7)	1.08	0.87	S			

Fajans found that, even with the noble gas type ions, the osmotic coefficient is a complicated function of the sizes of the two ions. We may sum up qualitatively the findings of Fajans as follows: with increasing atomic number of the cation, the osmotic coefficient increases for the fluorides and decreases for the other halides, and the decrease is greater the larger the anion; with increasing atomic number of the anion, the coefficient

increases for the lithium and sodium salts and decreases for the cesium salts; the salts of potassium show a flat minimum at the chloride; the difference between rubidium chloride and fluoride is intermediate between those of the corresponding potassium and cesium salts; rubidium bromide and iodide have not been measured. These relations may be explained theoretically by including the three types of interaction: charge-charge, charge-molecule, molecule-molecule.⁷

These variations in behavior of the symmetrical ions show clearly that any consideration of the effect of dissymmetry must take into account the sizes of the ions. The radii of the alkali and halide ions may be determined from studies of crystal structure, but the method cannot be extended to the polyatomic ions. As a rough measure of the relative size of the cations we shall take the apparent molal volume of the chloride in one molal solution at 18°, and for the anions we shall take the apparent molal volume of the sodium salt under the same conditions.⁸ Any other choice of accompanying ion or of conditions would probably lead to slightly different relative values. Our choice was determined by the fact that measurements are thus available for all the ions.

Table V shows the osmotic coefficients of these electrolytes. Below each cation is the apparent molal volume of its chloride, and after each anion is that of its sodium salt (in parentheses). The ions are arranged in increasing order of these volumes, except the sodium and lithium ions for which it contradicts the sizes from crystal structure. For the acids the values given in the literature are molal depressions of HX at 1.0 *M* HX or 1.018 *M* OH₃X. The values in the table are computed from the molal depressions of OH₃X at this concentration, and are not very different from the values at 1.0 *M* OH₃X. The alkali halides are printed in heavy type. For certain salts measurements are available only at concentrations smaller than 1.0 *M*, generally on account of the limited solubility. These all have small osmotic coefficients, smaller than those of their neighbors on any side. They are marked S in the table.

There is not enough variety in the polyatomic cations to show very much. The large, tetra-

(7) Scatchard, *Chem. Reviews*, **13**, 7 (1933); Scatchard and Allen, unpublished.

(8) From densities in the "International Critical Tables," Vol. III, pp. 51-95.

hedrally symmetrical ammonium ion behaves like a much smaller noble gas type ion, intermediate between sodium and potassium. There is in addition the hump (negative in the osmotic coefficient) in dilute solutions which appears characteristic of the ammonium salts.³ The strong acids behave very much as the lithium salts in spite of the large difference in size between the "oxonium" and lithium ions. In the weak acids the equilibrium $\text{OH}_3^+ + \text{X}^- \rightleftharpoons \text{HX} + \text{H}_2\text{O}$ is doubtless involved, so that we should not expect them to fall into our classification. It may be noted, however, that extrapolation to a volume corresponding to that of the proton would give an effect in the right direction.

The anions may be divided into three classes. The first of these is made up of the halides, and may be taken as the norm since the ions are all spherically symmetrical. In the second class the coefficient of the lithium salt is smaller than that of a halide ion of the same volume, and the decrease with increasing volume of the cation is faster. This class includes the nitrates, chlorates and perchlorates. The third class shows a less rapid decrease, or a more rapid increase, than a halide ion of the same volume. The acetate ion is the most marked as it shows rapid increase in spite of its large volume, and the formate ion is also distinctly in this class; the hydroxide ion appears to be on the border line between this class and that of the halide ions. The doubt arises largely from the lack of knowledge about the fluorides of small cations.

There is little question but that the third class is the one which shows the effect of concentration of the ionic charge far from the mechanical center of the ion. Such an ion might be expected to be roughly equivalent to a much smaller symmetrical ion, plus a neutral tail which should give an increase in the osmotic coefficient especially for small cations. The behavior of the acetates and formates may in fact be calculated approximately by summing that of an ion about the size of the

fluoride ion and that of the neutral tail. The dissymmetry of the hydroxide ion is so small that it might be expected to behave almost as the fluoride ion, and its behavior may be attributed mostly to its small size.

The behavior of the second class—nitrate, chlorate and perchlorate—is more difficult to explain. We have succeeded only in eliminating certain factors. The fact that the behavior is directly opposite to that of the acetates shows that it cannot be explained by a charge near the surface. The fact that the difference from the halide ions is no greater for the chlorate, which should have a dipole, than for the nitrate and perchlorate, which have no dipoles unless the structure in solution is very different from that in the crystal, eliminates the dipole moment as an important factor. It may be that the higher moments, produced by the first loss of spherical symmetry, are important factors; or it may be that the fact that the surface of these ions is largely made up of doubly bound oxygen atoms is of importance. It appears that a large amount of additional data will be necessary to give a closer insight into this problem.

Summary

The freezing point depressions of lithium, sodium and potassium formates and acetates have been measured up to concentrations a little greater than one molal.

The measurements obtained in this Laboratory on twenty-five uni-univalent electrolytes and many other data are correlated. The polyatomic anions are divided into two classes which deviate in opposite ways from the noble gas type ions. The deviations of the formates and acetates are explained by the concentrations of the ionic charge near the surface. For the nitrates, chlorates and perchlorates we cannot do more at present than eliminate this effect and the presence of a dipole as important factors.