6. The partial molal heat capacity of cadmium sulfate is estimated to be approximately -200 cal./deg./mol. at 15°.

7. In the extended theory the equation for the activity coefficient converges more rapidly than the corresponding equation for the integral heat of dilution. Calculations of "a" based upon activity coefficients are consequently more reliable than those based upon equally accurate data of the heat of dilution.

NEW YORK CITY

RECEIVED MARCH 24, 1933
PUBLISHED NOVEMBER 7, 1933

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 312]

The Freezing Points of Aqueous Solutions. IV. Potassium, Sodium and Lithium Chlorides and Bromides

BY GEORGE SCATCHARD AND S. S. PRENTISS

The freezing points described in this paper were determined primarily as a part of a study of the freezing points of mixtures now being undertaken in this Laboratory.[1] They were made so early in order to give a comparison with the measurements on other salts, particularly the ammonium salts studied in our earlier paper; and to give a comparison of our temperature scale with that of other observers, most of whom have measured either potassium or sodium chloride. It is suggested that every freezing point apparatus be used to measure the freezing points of solutions of the easily purified potassium chloride; we believe in fact, that, for all but work of the very highest precision, the freezing point curve given in this paper would give a sufficient calibration in the range we have studied.

Recalibration of Apparatus.—In correlating the measurements previously reported[2] it was found that the precision of the measurements was about twice as good as anticipated for solutions more concentrated than 0.01 M, and that the greatest uncertainties lay in the purification of materials and the calibration of the apparatus. The apparatus was therefore carefully recalibrated. Although no change from our previous value was found greater than five hundredths of a per cent., the confirmation of our previous results warrants a brief description.

The resistance box used in the conductance measurements is frequently

---

(1) The references to earlier measurements on these salts are given in "International Critical Tables," Vol. IV, pp. 258–259 and in reference 3. After these measurements were completed one of us (G. S.) had the opportunity of seeing in the thesis of Damköhler (Munich, under Professor Fajans) the results of measurements with LiBr, NaBr and KBr. Those with potassium and sodium bromides are related to ours very much as are those of Karagunis, Damköhler and Hawkinson with KCl, which were used by Damköhler to calibrate his thermocouple. The measurements with LiBr show an additional difference approximately linear in the concentration and equal to $0.005/M$, our j values being more positive.

(2) Scatchard, Jones and Prentiss, THIS JOURNAL, **54**, 2690; Scatchard and Prentiss, *ibid.*, **54**, 2696 (1932).

checked, and the most recent calibration is used. During the five years of its use there has been no change greater than 0.05%. In the first calibration of the thermocouple and the temperatures computed from it, a correction to the potentiometer varying from zero to 0.04% was ignored because it could not then be determined accurately, but is considered in the recalibration.

The calibration of the thermocouple was carried out as before with additional measurements. The comparative measurements of the freezing points of salt solutions from −1 to −10° were made with two platinum resistance thermometers of the standard type used before, and with a third one with a very compact resistance oil. The correction factors for the exposed stem, determined as in the previous paper, are No. 103, 1.0020; No. 104, 1.0016; short coil, 1.0000. The determination of the temperature coefficient of electromotive force from these measurements alone requires extrapolation through the least certain of the measurements. To avoid this, the comparison was also made from +1 to +10° by filling one vessel with water alone and the other with an ice–water mixture, and regulating the temperature of the outer bath so that the temperature of the water vessel remained constant at the desired value. The correction factor for exposed stem was unity for all the thermometers.

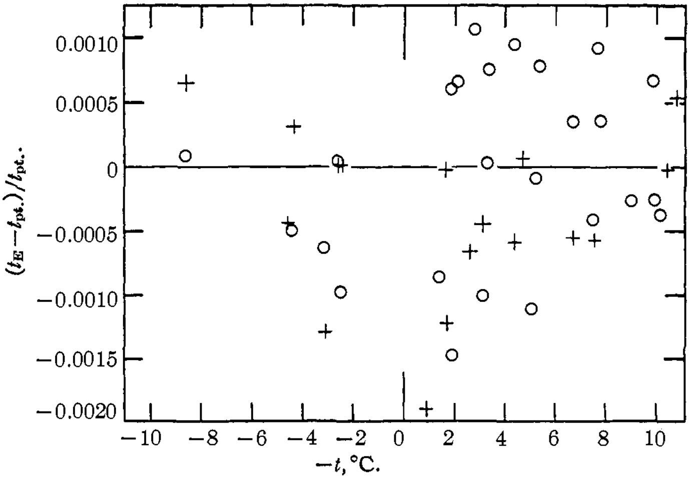

Fig. 1.—Calibration of thermocouple: ○, against large thermometers; +, against compact thermometer.

The relation between temperature and electromotive force was determined by the method of least squares. The measurements with a stem correction were considered half as precise as those without, and so given a weight of one quarter. In addition, the fact that the relative error decreases but the absolute error increases with increasing temperature was recognized by weighting each measurement as the reciprocal of the temperature difference. This is intermediate between giving the measurements equal weight as measurements of electromotive force and as measurements of its temperature coefficient. A two constant equation, explicit in either temperature or electromotive force, was found inadequate even over the range of twenty degrees. The equation used is $\Theta = 5.3857 \times 10^{-4}E + 3.38 \times 10^{-10}E^2 + 2.4 \times 10^{-15}E^3$. Θ is the temperature difference and E the electromotive force, both written positive for freezing points less than 0°. This equation gives temperature differences 0.03–0.04% larger than our former equation (with uncorrected electromotive forces), but does not warrant a revision of the results already published. Figure 1 shows the deviations of the measured values of Θ/E from this equation.

TABLE I

CONDUCTANCES AT 10°

M	M/L	M	M/L	M	M/L	M	M/L
KCl							
1.48296	12.781	0.38588	11.595	0.084451	10.651	0.004478	9.670
1.24054	12.575	.16411	11.038	.041269	10.308	.001439	9.501
0.97333	12.331	.11706	10.837	.040621	10.314	.000476	9.379
.83870	12.192	.098964	10.741	.012994	9.915	....	....
NaCl							
1.77709	18.429	0.62746	15.443	0.13891	13.509	0.003090	11.638
1.39591	17.461	.50148	15.057	.042195	12.601	.000965	11.438
1.11190	16.743	.35482	14.550	.026711	12.370	....	....
0.82681	16.000	.26452	14.178	.009428	11.934	....	....
LiCl							
1.87325	22.758	0.85314	18.819	0.14994	15.271	0.005727	13.066
1.36517	20.810	.67727	18.093	.078841	14.575	.001993	12.680
1.21237	20.223	.43647	17.004	.031174	13.859	.000774	12.626
1.02944	19.516	.26957	16.104	.015742	13.470	....	....
KBr							
1.29601	12.216	0.46754	11.073	0.046983	9.829	0.004512	9.402
1.07251	11.964	.28251	10.677	.020343	9.620	.001469	9.316
0.72135	11.497	.19939	10.452	.014042	9.551	....	....
.69490	11.457	.096075	10.085	.005370	9.420	....	....
NaBr							
1.41830	16.602	0.37751	14.076	0.10307	12.843	0.007195	11.537
1.13079	15.975	.34046	13.956	.053848	12.413	.003151	11.358
0.97107	15.604	.30817	13.840	.035359	12.180	.002179	11.292
.68019	14.918	.20002	13.403	.018742	11.881	.0010076	11.171
.53901	14.562	.160514	13.201	.007352	11.552	....	....
LiBr							
2.22009	22.023	0.73972	17.329	0.15765	14.778	0.008500	12.905
1.69499	20.369	.59056	16.801	.098129	14.308	.0024765	12.514
1.27569	19.064	.37793	15.955	.059407	14.146	.0008644	12.349
1.10305	18.523	.21755	15.156	.024885	13.338	....	....

TABLE II

FREEZING POINTS[a]

M		M	j	M	j	M	j
				KCl			
A 0.001389	0.0044	B 0.056239	0.0593	E 0.28624	0.0972	F 0.68415	0.1144
B .002865	.0344	A .076739	.0675	F .35110	.1016	E .77852	.1170
A .006449	.0235	B .10646	.0742	E .40548	.1042	F .87671	.1193
B .011136	.0353	A .13558	.0795	B .48560	.1077	E .98203	.1216
A .016217	.0371	B .16926	.0851	E .51103	.1086	F 1.1624	.1245
B .027000	.0462	F .20277	.0889	F .56055	.1103	E 1.2455	.1254
A .038173	.0537	A .23141	.0923	E .62645	.1122		
				NaCl			
A 0.000819	−0.0092	B 0.054924	0.0553	F 0.27394	0.0831	E 0.64857	0.0908
B .001866	+ .0092	A .078838	.0628	E .35492	.0863	F .72518	.0907
A .005120	.0192	B .10371	.0668	B .41547	.0881	E .80120	.0907
B .008605	.0265	A .12579	.0710	E .43370	.0884	F .90133	.0894
A .013540	.0334	B .15765	.0743	F .48597	.0892	E .99853	.0884
B .022648	.0445	F .18703	.0775	E .53070	.0899	F 1.1540	.0862
A .033489	.0468	A .22318	.0803	F .59159	.0902	E 1.2774	.0845
				LiCl			
C 0.000815	0.0125	B 0.028830	0.0442	F 0.22480	0.0552	F 0.60053	0.0244
B .001000	.0369	A .041929	.0484	A .25602	.0543	E .66599	.0177
A .001388	.0246	B .062321	.0534	F .29320	.0516	F .75093	.0076
C .001889	.0215	A .083317	.0552	E .35012	.0473	E .82305	− .0011
B .003350	.0263	B .10807	.0573	B .39572	.0445	F .91361	− .0119
C .003706	.0233	A .13317	.0577	E .43607	.0398	E 1.0050	− .0232
A .005982	.0264	B .15304	.0583	F .49181	.0351	F 1.1196	− .0370
B .010810	.0334	F .19001	.0567	E .54212	.0296	E 1.2458	− .0541
A .017113	.0393						
				KBr			
A 0.000407	0.0016	A 0.039203	0.0530	F 0.19254	0.0851	F 0.57808	0.1086
B .001077	.0155	B .054501	.0590	E .22465	.0883	E .64269	.1101
A .001824	.0130	A .081145	.0660	F .26581	.0924	F .71866	.1122
B .003996	.0235	B .099459	.0710	B .33814	.0982	E .80717	.1135
A .006101	.0217	A .12646	.0756	E .40910	.1017	F .97516	.1170
B .011641	.0327	B .13729	.0778	F .46834	.1046	E 1.0203	.1177
A .016397	.0363	E .15791	.0804	E .50792	.1061	F 1.2086	.1200
B .026573	.0447	A .17833	.0835				
				NaBr			
C 0.000780	0.0268	B 0.023990	0.0352	A 0.18545	0.0675	E 0.62685	0.0720
A .001558	.0086	A .035356	.0419	F .23609	.0701	F .69944	.0707
C .002859	.0154	B .054396	.0484	E .27647	.0713	E .77676	.0684
B .003263	.0025	A .077400	.0548	B .33054	.0727	F .87964	.0663
A .005966	.0194	B .098178	.0580	E .39038	.0732	E .96594	.0634
B .010280	.0202	A .12220	.0616	F .43827	.0734	F 1.0883	.0610
C .010303	.0279	B .14571	.0642	E .50805	.0733	E 1.2071	.0573
A .015339	.0302	F .16169	.0662	F .56626	.0728		
				LiBr			
A 0.000624	0.0253	A 0.076987	0.0474	B 0.31767	0.0352	E 0.69589	−0.0135
B .003072	.0189	B .099525	.0483	E .36432	.0294	F .75678	− .0223
A .006586	.0242	A .12791	.0482	F .40353	.0253	E .82116	− .0311
B .010013	.0268	B .15753	.0482	E .45999	.0188	F .91251	− .0455
A .015918	.0335	F .18709	.0461	F .52094	.0106	E .98507	− .0561
B .026640	.0377	A .23072	.0431	E .57843	.0032	F 1.0694	− .0692
A .036837	.0424	F .27647	.0386	F .62698	− .0040	E 1.1715	− .0855
B .055585	.0445						

[a] The letters indicate the series. Series A–C were run with increasing concentration; series E–F with decreasing concentration.

Experimental Results.—The freezing points were measured by the "equilibrium method" and the concentrations determined by conductance just as described in the previous papers[2], except that the nitrogen was always passed through an ice–water mixture to cool it and saturate it with water vapor before it was bubbled through the solution.

Table I contains the measurements of the conductance; M is the moles of salt per kilogram water and L the specific conductance. Table II contains the measured freezing points expressed as the Lewis and Randall

Table III

j Values of the Alkali Chlorides and Bromides

M	Lim. law	KCl	NaCl	LiCl	KBr	NaBr	LiBr
0.001	0.0118	0.0111	0.0108	0.0124	0.0111	0.0103	0.0107
.002	.0167	.0154	.0148	.0171	.0152	.0136	.0145
.005	.0264	.0233	.0222	.0254	.0230	.0195	.0212
.01	.0374	.0315	.0297	.0328	.0309	.0259	.0277
.02	.0529	.0417	.0388	.0404	.0407	.0341	.0347
.05	.0836	.0586	.0537	.0507	.0567	.0473	.0439
.1	.1182	.0734	.0663	.0568	.0707	.0585	.0482
.2	.1672	.0890	.0785	.0570	.0860	.0683	.0452
.3	.2047	.0978	.0843	.0515	.0950	.0720	.0366
.4	.2364	.1038	.0876	.0434	.1012	.0733	.0258
.5	.2643	.1082	.0895	.0341	.1056	.0733	.0135
.6	.2897	.1119	.0904	.0239	.1090	.0723	.0002
.7	.3127	.1149	.0907	.0129	.1117	.0704	− .0138
.8	.3343	.1175	.0902	.0015	.1138	.0682	− .0283
.9	.3546	.1199	.0896	− .0104	.1157	.0658	− .0434
1.0	.3738	.1218	.0884	− .0226	.1173	.0631	− .0586
1.1	.3920	.1236	.0871	− .0350	.1187	.0603	− .0741

Table IV

Values for $-\log \gamma'$ for the Alkali Chlorides and Bromides

M	Lim. law	KCl	NaCl	LiCl	KBr	NaBr	LiBr
0.001	0.0154	0.0148	0.0145	0.0159	0.0148	0.0143	0.0144
.002	.0218	.0206	.0201	.0223	.0205	.0191	.0199
.005	.0344	.0317	.0306	.0343	.0313	.0282	.0298
.01	.0487	.0434	.0416	.0463	.0428	.0377	.0400
.02	.0689	.0587	.0557	.0605	.0578	.0503	.0525
.05	.1089	.0857	.0804	.0830	.0839	.0721	.0720
.1	.1540	.1121	.1039	.1017	.1091	.0928	.0877
.2	.2178	.1430	.1309	.1192	.1392	.1161	.1008
.3	.2667	.1632	.1476	.1262	.1590	.1300	.1041
.4	.3080	.1782	.1596	.1285	.1737	.1394	.1032
.5	.3444	.1903	.1690	.1281	.1855	.1465	.0996
.6	.3775	.2006	.1764	.1259	.1955	.1516	.0943
.7	.4074	.2093	.1824	.1220	.2038	.1554	.0875
.8	.4356	.2171	.1872	.1175	.2111	.1583	.0798
.9	.4620	.2241	.1915	.1117	.2177	.1606	.0712
1.0	.4870	.2302	.1948	.1055	.2236	.1622	.0621
1.1	.5107	.2360	.1977	.0988	.2290	.1634	.0524

function $j = 1 - \theta/3.716\ M$ (θ is the freezing point depression). The smoothed values of M/L and of j were obtained by drawing smooth curves through the deviations of the experimental results from approximate analytical functions of the same types as those used in the earlier work. For M/L the average deviations of the experimental points from these curves are slightly more than one in the last place given. For j the average deviation for concentrations greater than 0.01 M is approximately three in the last place given. For more dilute solutions the average deviation corresponds to about 0.00003°. Table III contains the smoothed values of j at rounded concentrations, and Table IV the corresponding values of log γ'. γ' is the activity coefficient (moles per kilogram of water) uncorrected for heat of dilution, etc.

For the chlorides the water used was distilled from a new Kraus type still, and the ice used in some of the runs was prepared from this water. No effect of these changes could be noted.

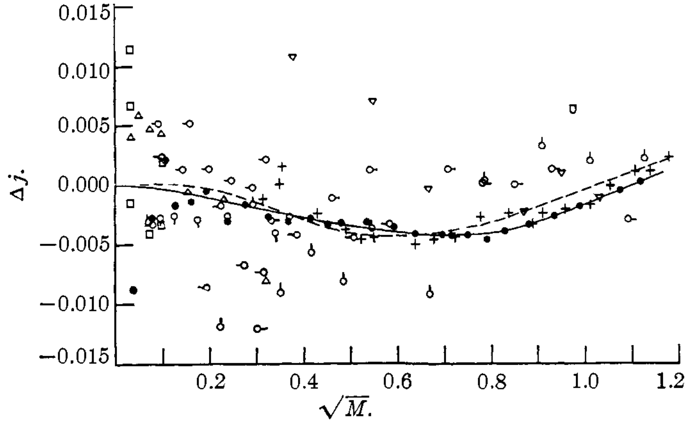

Fig. 2.—Δj Values for KCl; $\Delta j = j - [(0.3738\sqrt{M})/(1 + 1.7\sqrt{M})] + 0.0149\ M$; solid line, Scatchard and Prentiss; broken line, Spencer; ●, Scatchard and Prentiss; +, Jones and Bury; ♀, Adams; ό, Menzel; -o, Jahn; o-, Karagunis, Hawkinson and Damköhler; △, Flügel; ▽, Rivett; Ū, Rodebush; □, Hovorka and Rodebush.

Potassium Chloride.—A C. P. product was twice crystallized from conductivity water and dried for ten hours at 250°. The stock solution was made up by weighing this salt. The filled circles in Fig. 2 show the results plotted as deviations Δ_j in the empirical equation

$$j = \frac{0.3738\sqrt{M}}{1 + 1.7\sqrt{M}} - 0.0149\ M + \Delta_j$$

The smooth curve which we draw through these results is shown by the full line. Some of the earlier measurements are included in the figure. Those of Jones and Bury, which are probably the best in the more concentrated range, agree excellently with our curve. The broken line represents the smooth curve determined by Spencer[3] from these earlier

---

(3) Spencer, This Journal, **54**, 4490 (1932).

measurements. We believe that the full curve, determined from our own measurements alone, fits the earlier measurements as well as the curve determined from them; but we consider it much more important that Spencer's curve fits our experimental measurements better than it does those from which it was determined, and that the difference between his curve and ours is always less than one part per thousand. There is a greater discrepancy in the values of γ', apparently due to some inaccuracy in his integration.

Sodium Chloride (C. P.) was dissolved in water, precipitated with hydrogen chloride gas, washed, dried at 200° and fused. The stock solution was made by weighing this salt.

Lithium Chloride (C. P.) was dissolved in water and added to a solution of ammonium carbonate saturated with ammonia. The precipitate was washed and dissolved in reagent hydrochloric acid. Lithium carbonate was again precipitated with ammonium carbonate as before, the precipitate washed, dried at 270° and then fused. After dissolving in hydrochloric acid the solution was titrated to a P_H of 6.6 with brom thymol blue with boiling to expel carbon dioxide. The concentration of the stock solution was determined by evaporation and conversion to lithium sulfate.

Potassium, Sodium and Lithium Bromides (C. P. or reagent) were each crystallized once from conductivity water. The concentrations of the stock solutions were determined gravimetrically as silver bromide. These solutions were analyzed for chloride by the method of Berg.[4] In each case 40 cc. of 0.1 *M* solution was oxidized with 0.05 *M* potassium bromate in the presence of acetone, silver nitrate was added and the precipitate compared in Nessler tubes with known samples of silver chloride. The amounts of chloride found were: KBr, 0.25%; NaBr, 0.3%; LiBr 0.25%. Flame tests of the potassium bromide showed, as for potassium and lithium chlorides, the absence of sodium. The lithium bromide appeared by the same test to contain about 0.2% NaBr. By our method of analysis 0.25% chloride gives a total concentration 0.06% too small and sodium in place of lithium makes no difference except in the magnitude of the deviations. Since the method of testing for chloride is almost certain to give high results, we do not believe that our results are in error due to impurities by more than one part per thousand.

Discussion.—These measurements require very little discussion. Just as in the earlier less precise measurements, the bromides all show greater deviations from the limiting law than the corresponding chlorides, and the deviations for salts of the same anion increase in the order potassium, sodium, lithium with the exception of very dilute solutions of lithium chloride. Our most probable curve for this salt appears to cross the curves of sodium and potassium chlorides and the limiting law. The intersections all occur in very dilute solutions where the curves lie close together and where the percentage accuracy is not very great, so that we cannot be sure that the effect is greater than the experimental error. Such an effect should be expected for small ions from the Bjerrum–Gronwall, La Mer and Sandved correction, but the size required to give it if only the charge-charge effect be considered is smaller than the dimensions of the ions in the crystal lattice and the large deviations in the more concentrated solutions indicate that a much smaller size would be necessary to show such an effect.

We have now studied potassium, sodium and lithium nitrates, chlorides and bromides, corresponding to the three ammonium salts which gave

---

(4) Berg, *Z. anal. Chem.*, **69**, 342 (1926).

large "humps" in the j curves with well marked positive deviations from the theoretical limiting law. Eight of the alkali salts show no positive deviation at all, and that of lithium chloride is less than one-tenth of that of the ammonium salts. The behavior of the ammonium salts is still unexplained, but the present work shows conclusively that it is not due to a systematic error in our measurements. To make doubly sure on this score, since ammonium bromide showed the largest "hump," the alkali bromides were purified and their concentrations were determined by the same method as had been used for the ammonium salt.

CAMBRIDGE, MASS. RECEIVED MAY 25, 1933
PUBLISHED NOVEMBER 7, 1933

[CONTRIBUTION FROM THE PENNSYLVANIA SALT MANUFACTURING COMPANY CHEMICAL RESEARCH DEPARTMENT]

Addition of 8-Hydroxyquinoline by Thorium and Uranium 8-Hydroxyquinolates

BY FRANCIS J. FRERE

Introduction

F. Hecht and W. Reich-Rohrwig[1] have outlined an analytical procedure for the determination of thorium and uranium by means of 8-hydroxyquinoline. It was stated that uranium formed a compound of the formula $UO_2(C_9H_6NO)_2 \cdot C_9H_6NO$, which was stable up to about 200°.

As regards thorium, Hecht and Reich-Rohrwig[1] stated that this element formed a compound containing water of crystallization which did not start to dehydrate until at about 155°, and at 160 to 170° lost its water of crystallization rapidly and could be dried to constant weight at this temperature. The dried precipitate was dissolved and brominated and was found to contain four moles of 8-hydroxyquinoline, from which it was concluded that thorium formed a compound of the formula $Th(C_9H_6ON)_4$.

Hecht and Reich-Rohrwig later observed that when brominating the thorium precipitate, without drying, somewhat high results were obtained. This was claimed to have been overcome by washing the precipitate with 25% alcohol.

An investigation of this work found some of the above statements in error and has led to a rather interesting phenomenon.

Experimental

Materials Used.—C. P. reagent grade thorium nitrate and uranyl acetate were used in these experiments. The thorium nitrate solution was standardized by precipitating as oxalate, igniting and weighing as the oxide. The uranyl acetate solution was standardized by reducing in a Jones reductor and titrating with potassium permanganate. Pipets and burets certified by the U. S. Bureau of Standards were used throughout this work.

---

[1] Hecht and Reich-Rohrwig, *Monatsh*, **53–54**, 596 (1929).