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THE FREEZING POINTS OF AQUEOUS SOLUTIONS. III. AMMONIUM CHLORIDE, BROMIDE, IODIDE, NITRATE AND SULFATE

BY GEORGE SCATCHARD AND S. S. PRENTISS

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Another common and interesting ion whose dilute solutions can be studied only by freezing point determinations is the ammonium ion. Since accurate measurements are not available, we have determined the freezing points of ammonium chloride, bromide, iodide, nitrate and sulfate by the method previously described.¹

It might appear that the hydrolysis of ammonium salts should make the interpretation of the measurements complicated. A simple calculation will show, however, that the effect of hydrolysis is well within the experimental error of the freezing point measurements. Given the reaction $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$: at 0°, $K = (\text{NH}_3)(\text{H}^+)/(\text{NH}_4^+) = 10^{-10}$, we can consider that in the hydrolysis H^+ replaces NH_4^+ , so that the net effect is the addition of one ammonia molecule. Since there is no change in the ionic concentration, we may expect the law of mass action to hold well in terms of concentrations, and we can determine the effect on the freezing point accurately enough by assuming ideal solutions. The total number of ions present, neglecting hydrolysis, is twice the number of ammonium ions, so that the fractional increase in the freezing point depression, p , is

$$p = (\text{NH}_3)/2(\text{NH}_4^+) = 0.5 \sqrt{K/(\text{NH}_4^+)} = 0.5 \times 10^{-5}/\sqrt{M}$$

When $M = 0.001$, $p = 16 \times 10^{-5}$ or 0.016%, and it decreases for larger values of M , so it must always be negligible in the range of experimental measurements.

All salts were manufacturer's c. p. or reagent products. The chloride and bromide were recrystallized three times from doubly distilled water; the sulfate was crystallized only twice on account of its great solubility; for the same reason and because of their instability, the iodide and nitrate were not crystallized. The iodide solution was reduced with aluminum amalgam immediately before use. The concentrations of the halide stock solutions were determined gravimetrically as the silver halides; that of the sulfate, gravimetrically as barium sulfate; that of the nitrate was determined by distilling from potassium hydroxide into excess dilute hydrochloric acid and titrating with methyl orange as indicator.² The

¹ Scatchard, Jones and Prentiss, Paper I, THIS JOURNAL, 54, 2676 (1932).

² Dr. P. T. Jones very kindly carried out the determination of the ammonium nitrate concentration.

mean deviation from the average was less than 0.05% for the halides and 0.1% for the sulfate and nitrate. For the chloride and iodide two stock solutions were prepared and analyzed, with excellent agreement between the two series of conductance measurements.

The conductance results are given in Table I and the freezing point results in Table II. The significance of the various symbols is the same

TABLE I
CONDUCTANCE AT 10°

M	M/L	Diff.	M	M/L	Diff.
NH ₄ Cl					
1.3862	12.972	0.000	0.26465	11.471	+0.001
1.2248	12.819	- .004	.14995	11.085	.000
1.2149	12.819	+ .004	.087620	10.763	.000
1.0818	12.682	- .004	.044237	10.418	+ .001
0.83112	12.413	- .003	.044237	10.417	- .001
.79033	12.368	+ .001	.016149	10.031	.000
.65609	12.193	- .004	.007223	9.808	- .001
.51495	11.994	+ .005	.004805	9.731	.000
.47401	11.919	- .002	.001613	9.569	- .004
.33232	11.636	- .004	.000577	9.490	+ .004
NH ₄ Br					
1.18095	12.277	0.000	0.034615	10.125	0.000
0.85534	11.996	.000	.017078	9.877	+ .002
.55746	11.672	.000	.015518	9.841	- .004
.34386	11.343	.000	.009230	9.700	- .003
.20916	11.029	.000	.005761	9.597	+ .002
.16130	10.876	+ .002	.002230	9.404	- .002
.13354	10.766	.000	.001272	9.305	.000
.10199	10.613	- .007	.000608	9.147	.000
.064574	10.396	+ .002			
NH ₄ I					
1.8840	12.695	+0.002	0.057943	10.388	+0.012
1.8213	12.649	.000	.044088	10.258	.000
1.4685	12.389	- .002	.044088	10.256	- .002
1.2830	12.251	.000	.034590	10.171	+ .009
1.1171	12.122	- .001	.017559	9.928	.000
0.79561	11.853	.000	.016613	9.928	+ .016
.68876	11.754	+ .007	.013512	9.860	+ .008
.59485	11.646	.000	.007631	9.718	+ .009
.45559	11.478	.000	.005491	9.642	.000
.37657	11.363	.000	.004682	9.634	+ .021
.25613	11.131	.000	.003757	9.578	.000
.19048	10.966	+ .004	.001907	9.485	+ .002
.12038	10.718	.000	.001691	9.470	.000
.096743	10.607	- .003	.000940	9.414	.000
.096743	10.608	- .002	.000568	9.376	- .001
.081154	10.528	+ .001	.000511	9.371	+ .001

TABLE I (Concluded)

<i>M</i>	<i>M/L</i>	Diff.	<i>M</i>	<i>M/L</i>	Diff.
NH_4NO_3					
1.4366	14.702	+0.003	0.22780	11.981	-0.001
1.2607	14.388	- .006	.16834	11.712	+ .003
1.0900	14.090	+ .004	.099830	11.295	.000
0.81836	13.603	+ .043	.057259	10.929	- .001
.71732	13.355	+ .001	.042952	10.770	.000
.59504	13.080	- .002	.013872	10.280	- .002
.52595	12.921	+ .006	.007556	10.106	+ .002
.36832	12.480	+ .034	.003233	9.921	- .005
.32255	12.334	- .001	.001572	9.822	+ .001
.31691	12.342	+ .027	.001207	9.792	.000
			.000579	9.726	.000
$(\text{NH}_4)_2\text{SO}_4$					
1.2275	10.944	0.000	0.072118	6.891	+0.001
0.96710	10.292	.000	.043974	6.497	- .003
.82328	9.931	.000	.043974	6.502	+ .002
.78876	9.841	- .001	.021918	6.031	.000
.69009	9.580	.000	.011150	5.665	+ .001
.51041	9.072	.000	.006346	5.425	- .001
.31321	8.395	.000	.003447	5.223	- .002
.22160	7.987	.000	.001103	4.970	- .001
.21002	7.926	.000	.000816	4.925	+ .002
.15318	7.593	+ .001	.000310	4.811	.000
.10412	7.216	.000			

TABLE II

FREEZING POINTS

<i>M</i>	Diff. ^a	<i>M</i>	<i>j</i>	Diff.	
NH_4Cl , Series A					
0.001051	0.0245	+0.0104	0.080360	0.0744	+0.0001
.002771	.0230	- .0011	.11392	.0812	- .0001
.007949	.0379	- .0003	.15844	.0877	- .0004
.019383	.0513	+ .0015	.19550	.0920	- .0002
.041279	.0610	- .0006			
Series B					
0.001966	0.0199	0.0000	0.069680	0.0718	+0.0003
.006021	.0350	+ .0005	.12968	.0841	+ .0001
.010358	.0411	- .0005	.19792	.0913	- .0012
.029738	.0560	.0000	.25536	.0973	.0000
.052182	.0656	- .0004			
Series C					
1.0927	0.1106	-0.0011	0.46011	0.1062	-0.0006
0.97093	.1109	- .0011	.36611	.1041	+ .0006
.86311	.1115	- .0002	.26877	.0985	+ .0003
.72116	.1106	- .0004	.19818	.0928	- .0003
.59368	.1096	+ .0001			

TABLE II (Continued)

<i>M</i>	<i>j</i>	Diff. ^a	<i>M</i>	<i>j</i>	Diff.
Series D					
1.1579	0.1117	+0.0001	0.37550	0.1039	0.0000
1.0305	.1122	+ .0003	.27770	.0993	+ .0004
0.80055	.1117	+ .0002	.22171	.0952	+ .0005
.55777	.1083	- .0007	.17424	.0914	+ .0015
Series E					
1.0891	0.1128	+0.0010	0.59181	0.1101	+0.0006
0.96328	.1132	+ .0012	.23783	.0973	+ .0013
NH ₄ Br, Series A					
0.001891	0.0195	-0.0044	0.50718	0.1038	+0.0001
1.1041	.1063	- .0010	.41374	.1018	+ .0003
0.92787	.1072	- .0002	.32062	.0978	- .0002
.76415	.1066	- .0001	.24996	.0941	- .0002
.61896	.1054	.0000			
Series B					
1.1538	0.1077	+0.0007	0.44897	0.1024	0.0000
1.0124	.1075	.0000	.34970	.0995	+ .0002
0.86818	.1075	+ .0003	.27229	.0956	.0000
.70411	.1066	+ .0003	.21457	.0917	.0000
.57637	.1047	- .0001			
Series C					
0.001006	0.0103	-0.0054	0.070111	0.0721	0.0000
.001888	.0251	+ .0013	.12805	.0828	.0000
.005694	.0373	+ .0008	.18896	.0902	+ .0006
.014531	.0477	.0000	.27362	.0961	+ .0005
.032780	.0591	- .0002			
Series D					
0.001416	0.0251	+0.0048	0.053369	0.0672	0.0000
.004199	.0336	+ .0005	.091455	.0767	.0000
.009026	.0415	- .0003	.16898	.0878	+ .0001
.024482	.0559	+ .0010	.22831	.0928	.0000
NH ₄ I, Series A					
0.001263	-0.0121		0.065404	0.0650	+0.0003
.002345	+ .0223	+0.0017	.11185	.0736	- .0002
.006267	.0347	+ .0038	.14664	.0780	- .0004
.018523	.0456	+ .0031	.20513	.0845	+ .0003
.044658	.0592	+ .0008			
Series B					
1.0820	0.1037	+0.0001	0.41264	0.0955	+0.0003
0.95324	.1033	+ .0003	.32475	.0923	+ .0005
.78434	.1011	- .0004	.23455	.0868	+ .0002
.63379	.0999	.0000	.18623	.0828	+ .0003
.52319	.0981	+ .0001			

<i>M</i>		TABLE II (Continued)			
		Diff. ^a	<i>M</i>	<i>j</i>	Diff.
Series C					
1.2945	0.1030	0.0000	0.42801	0.0952	-0.0005
1.0088	.1030	- .0002	.33385	.0916	- .0006
0.81930	.1015	- .0005	.26191	.0876	- .0008
.67123	.0998	- .0006	.20560	.0836	- .0007
.54718	.0975	- .0010			
Series D					
0.000941	0.0252	+0.0121	0.021759	0.0460	-0.0014
.002196	.0270	+ .0069	.055823	.0616	- .0005
.006556	.0309	- .0004	.10930	.0733	.0000
Series E					
0.001297	0.0248	+0.0091	0.094443	0.0708	0.0000
.003990	.0261	+ .0003	.14688	.0784	.0000
.012196	.0369	- .0024	.22405	.0867	+ .0009
.050610	.0614	+ .0009	.29927	.0913	+ .0008
NH ₄ NO ₃ , Series A					
0.000556	0.0126	+0.0013	0.083174	0.0840	-0.0011
.002942	.0231	- .0011	.14726	.1040	+ .0001
.011487	.0411	- .0009	.27633	.1293	- .0002
.042705	.0676	.0000			
Series B					
0.001743	0.0223	+0.0030	0.11225	0.0945	0.0000
.007521	.0400	+ .0044	.19919	.1140	- .0014
.024933	.0545	- .0013	.42305	.1507	- .0002
.061835	.0777	+ .0008			
Series C					
1.7415	0.2667	0.0000	0.75830	0.1880	-0.0002
1.4035	.2421	- .0007	.61929	.1739	- .0001
1.1402	.2221	- .0001	.48804	.1591	.0000
0.92408	.2034	- .0002	.32437	.1372	+ .0001
Series D					
1.2458	0.2310	+0.0002	0.54145	0.1657	+0.0002
1.0050	.2109	+ .0001	.37427	.1446	+ .0003
0.83275	.1954	+ .0001	.24326	.1239	+ .0001
.68833	.1811	.0000			
Series E					
0.001517	0.0172	-0.0010	0.007547	0.0369	+0.0012
.004245	.0294	+ .0012			
(NH ₄) ₂ SO ₄ , Series A					
0.000906	0.0412	-0.0028	0.052704	0.2031	+0.0006
.001764	.0633	- .0026	.10874	.2442	+ .0002
.004028	.0923	+ .0019	.16013	.2684	+ .0004
.009905	.1275	+ .0050	.21769	.2880	.0000
.023563	.1676	+ .0066			

TABLE II (Concluded)

<i>M</i>	<i>j</i>	Diff. ^a	<i>M</i>	<i>j</i>	Diff.
Series B					
0.001412	0.0572	0.0000	0.040621	0.1882	-0.0004
.002631	.0781	+ .0009	.088704	.2323	+ .0004
.008660	.1169	.0000	.16811	.2711	.0000
.014973	.1378	- .0019	.28660	.3069	+ .0003
Series C					
1.2141	0.4060	0.0000	0.49970	0.3458	0.0000
0.92493	.3877	- .0017	.38804	.3278	+ .0001
.75577	.3755	- .0001	.30218	.3099	- .0003
.61168	.3603	.0000	.23352	.2927	.0000
Series D					
1.0335	0.3964	0.0000	0.33982	0.3183	0.0000
0.83054	.3822	.0000	.26711	.3017	.0000
.68289	.3684	.0000	.19208	.2797	- .0001
.55992	.3535	- .0004	.13237	.2567	+ .0006
.43868	.3363	- .0001			
Series E					
0.002635	0.0795	+0.0021	0.043134	0.1926	+0.0009
.005001	.0974	.0000	.072053	.2193	- .0005
.012175	.1307	- .0001	.099183	.2383	- .0002
.025376	.1652	+ .0007			

^a For concentrations below 0.01 *M* the temperatures, in hundred thousandths of a degree, corresponding to the *j* differences are in order: NH₄Cl, A, 4, 1, 2; B, 0, 1; NH₄Br, A, 3; C, 2, 1, 2; D, 2, 1; NH₄I, A, 10, 1, 8; D, 4, 5, 1; E, 4, 0; NH₄NO₃, A, 0, 1; B, 2, 12; E, 1, 1, 3; (NH₄)₂SO₄, A, 1, 2, 4, 24; B, 0, 1, 0; E, 3, 0.

TABLE III

j VALUES OF THE AMMONIUM HALIDES AND NITRATE

<i>M</i>	Lim. law	NH ₄ Cl	NH ₄ Br	NH ₄ I	NH ₄ NO ₃
0.001	0.0118	0.0140	0.0161	0.0135	0.0150
.002	.0167	.0203	.0243	.0192	.0205
.005	.0264	.0321	.0349	.0282	.0302
.01	.0374	.0411	.0431	.0367	.0398
.02	.0529	.0503	.0520	.0461	.0517
.05	.0836	.0652	.0663	.0604	.0714
.1	.1182	.0787	.0784	.0718	.0908
.2	.1672	.0927	.0906	.0839	.1156
.3	.2047	.1003	.0971	.0905	.1334
.4	.2364	.1048	.1010	.0948	.1479
.5	.2643	.1078	.1035	.0975	.1606
.6	.2897	.1097	.1052	.0994	.1720
.7	.3127	.1108	.1063	.1006	.1824
.8	.3343	.1116	.1070	.1017	.1922
.9	.3546	.1118	.1073	.1025	.2015
1.0	.3738	.1119	.1074	.1032	.2104
1.1	.3920	.1116	.1072	.1036	.2189

as in the preceding paper.³ For the halides Table III gives the j values determined from the smooth curve at round concentrations, and Table IV gives the values of γ' determined from the same curves. Table V gives the same data for ammonium sulfate. The limiting laws are given in all cases.

TABLE IV

VALUES FOR $-\text{LOG } \gamma'$ FOR THE AMMONIUM HALIDES AND NITRATE

M	Lim. law	NH_4Cl	NH_4Br	NH_4I	NH_4NO_3
0.001	0.0154	0.0173	0.0159	0.0169	0.0181
.002	.0218	.0251	.0288	.0242	.0259
.005	.0344	.0405	.0451	.0375	.0401
.01	.0487	.0555	.0605	.0509	.0547
.02	.0689	.0732	.0786	.0674	.0736
.05	.1089	.1025	.1082	.0947	.1064
.1	.1540	.1298	.1351	.1193	.1390
.2	.2178	.1616	.1657	.1479	.1806
.3	.2667	.1818	.1849	.1659	.2101
.4	.3080	.1964	.1988	.1793	.2338
.5	.3444	.2081	.2097	.1897	.2542
.6	.3775	.2172	.2186	.1982	.2722
.7	.4074	.2249	.2260	.2052	.2884
.8	.4356	.2316	.2324	.2114	.3034
.9	.4620	.2373	.2379	.2168	.3174
1.0	.4870	.2423	.2427	.2218	.3306
1.1	.5107	.2466	.2469	.2261	.3431

TABLE V

 j AND $-\text{LOG } \gamma'$ VALUES FOR AMMONIUM SULFATE

M	Lim. law	j	$(\text{NH}_4)_2\text{SO}_4$	Lim. law	$-\log \gamma'$	$(\text{NH}_4)_2\text{SO}_4$
0.001	0.0409		0.0471	0.0533		0.0587
.002	.0579		.0689	.0754		.0856
.005	.0916		.0972	.1193		.1308
.01	.1295		.1228	.1687		.1749
.02	.1831		.1530	.2386		.2294
.05	.2895		.1996	.3772		.3194
.1	.4095		.2390	.5335		.4023
.2	.5791		.2824	.7545		.4994
.3	.7092		.3097	.9240		.5633
.4	.8190		.3298	1.0671		.6118
.5	.9156		.3458	1.1929		.6514
.6			.3590			.6851
.7			.3701			.7141
.8			.3796			.7399
.9			.3876			.7629
1.0			.3944			.7836
1.1			.4001			.8025

³ Scatchard, Prentiss and Jones, Paper II, THIS JOURNAL, 54, 2690 (1932).

With the ammonium salts there is no question of j approaching the limiting law asymptotically within the range of experimental measurements. The curves all cross the limiting law between 0.005 and 0.02 M . This is illustrated in Fig. 1 by the deviation curve for ammonium bromide, in which the theoretical limiting law is drawn in as a broken line. The existence of this "hump" makes the extrapolation to zero concentration difficult. Since we consider that there is enough evidence from other salts of the general accuracy of the Debye-Hückel limiting law, we have used it, and we have made use of the plot of j/\sqrt{M} to aid in the extrapolation.⁴

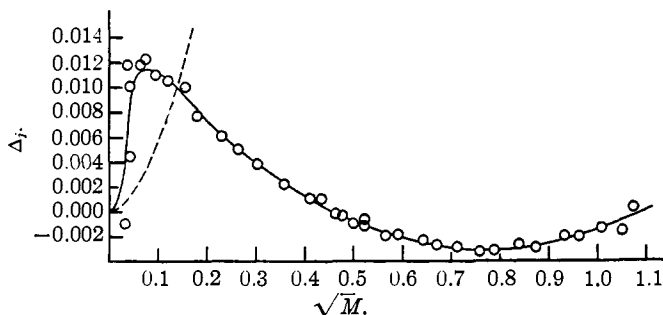


Fig. 1.— Δj Values for NH_4Br : $\Delta j = j - \frac{0.3738 \sqrt{M}}{1 + 1.6 \sqrt{M}} + 0.0349 M$.

Broken line represents the limiting law.

This uncertainty of extrapolation makes no difference of course in the j values in the region where the curve is fixed by the experimental measurements, and would make no difference in the values of γ' if the standard state were chosen in this same region. Since we have chosen zero concentration as the standard state, however, any change in the extrapolation will add the same quantity to each value of $\log \gamma'$, in the region where j is unchanged.

We know of no other uni-univalent salts which show evidence of j values larger than those of the Debye-Hückel limiting law and have therefore searched carefully for some other explanation of our measurements. We have already shown that the effect of hydrolysis would decrease j rather than increase it, and that it is much smaller than the measured increase. If the ammonia formed by hydrolysis were carried away by the stream of nitrogen, the net result would be the replacement of some ammonium salt by the equivalent amount of the corresponding acid. This would not change the freezing point measurement appreciably but would give a much higher conductance and apparent concentration, and so too large a value of j . Although calculations indicated that such an effect must be of a much smaller magnitude than the measured effect, we decided

⁴ Randall and White, *THIS JOURNAL*, **48**, 2514 (1926).

to test it experimentally. A stream of nitrogen was passed through ammonium bromide solution at 0° after passing through potassium bromide solution of about the same concentration. The rate was the same as the rapid flow during the freezing point measurements; the time was 160 minutes, or five times that in a regular run. The initial conductance corresponded to a concentration of $0.017979 M$, the final to $0.017976 M$. The change was -0.017% , again much too small and in the wrong direction to account for our results. An error of more than 1% in analyses that agree to better than 0.1% seems out of the question, and we can find no other reasons to doubt the accuracy of our measurements.

The measurements with ammonium iodide are less accurate because of the instability of this salt. The data definitely indicate a smaller "hump" than for the bromide, and we believe that our extrapolation with a much smaller "hump" best represents the measurements.

Fajans and Karagunis⁵ have noted that the freezing point curves for the alkali halides all belong to a consistent family in the sense that no curve appears to cross any other. On the other hand, the curves for ammonium chloride and bromide cross each other and each appears to cross the curve of the corresponding potassium salt, and presumably those of the rubidium and cesium salts. It must be admitted, however, that only for potassium chloride have we accurate enough measurements to be sure that there is not a "hump" of the same order of magnitude as for the ammonium salts. For the nitrate the evidence is much better because we have for comparison our measurements on the alkali nitrate made in the same apparatus. We have already noted that we obtained in no case a j value larger than the limiting law. Our measurements should be accurate enough to ensure that our curves do not cross the limiting law above $0.005 M$. For ammonium nitrate, on the other hand, the curve crosses the limiting law between 0.01 and $0.02 M$ and shows a hump about the same size as that of ammonium chloride. The ammonium and potassium nitrate curves also cross each other at about $0.04 M$.

There seems little doubt that there is some factor operative with the ammonium salts which is negligible with other uni-univalent salts. Its effect is similar to that of association, which proves only that it is operative only when the ions are close together, except that it is swamped out surprisingly soon by the factors which tend to increase the activity coefficient. We do not believe that it should be attributed to a small value of the "collision diameter," a ,⁶ because the value demanded would be improbably small, and smaller for the bromide than for the chloride. For the uni-

⁵ Fajans and Karagunis, *Z. Elektrochem.*, **43**, 1046 (1930).

⁶ 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).

bivalent sulfate a small collision diameter might explain part of the effect, but there is no reason to suppose that the factor which affects the halides is not also operative here. We are unable to say what this factor is.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE SPECIFIC HEATS OF FIVE ORGANIC LIQUIDS FROM THEIR ADIABATIC TEMPERATURE-PRESSURE COEFFICIENTS

BY WILLIAM T. RICHARDS AND JOHN H. WALLACE, JR.

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Introduction

Although the specific heats of liquids have been measured for nearly two centuries, there remains a distressing lack of agreement in the immense collection of numbers which have been reported to represent them. Because of the complexity of the correction factors which must be applied to the results of calorimetric determinations, it is not uncommon to find a divergence of ten per cent. between two investigations, although the estimated error of each is far below this value. While it is not at present possible to interpret the specific heats of most liquids even to this approximation, accurate knowledge of so fundamental a property must be ultimately both necessary and valuable. Any method other than the calorimetric should, therefore, be considered if it appears to offer a practical alternative.

From the first and second laws of thermodynamics, without further assumption, it follows that the adiabatic temperature-pressure coefficient of a system of heat capacity at constant pressure C_p is given by the expression

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{T}{C_p} \left(\frac{\partial v}{\partial T}\right)_p$$

where T , p , s and v represent temperature, pressure, entropy and volume, respectively. Oersted¹ appears to have been the first to sense this relationship qualitatively, for he subjected water to a sudden pressure and attempted to measure a rise in its temperature. The formal derivation was carried out by Joule,² who experimentally proved the second law of thermodynamics by measuring the heat capacity, coefficient of thermal expansion and temperature-pressure coefficient of water and of fish oil. Several other investigations have subsequently dealt with the last of these quantities for solids, liquids and gases, although the majority do not lend themselves even to approximate calculation of specific heats, owing to the magnitude of the pressures employed. Creelman and Crocket,³

¹ Oersted, *Ann. chim. phys.*, **2**, 22, 192 (1823).

² Joule, *Phil. Mag.*, **17**, 364 (1859).

³ Creelman and Crocket, *Proc. Roy. Soc. Edinburgh*, **13**, 311 (1885).