[CONTRIBUTION FROM THE FERTILIZER INVESTIGATIONS OF THE BUREAU OF CHEMISTRY AND SOILS, AND THE BUREAU OF STANDARDS]

Low Temperature Specific Heats. IV. The Heat Capacities of Potassium Chloride, Potassium Nitrate and Sodium Nitrate[1]

BY J. C. SOUTHARD AND R. A. NELSON

This paper represents part of a program to obtain data on materials involved in the manufacture of fertilizers. A knowledge of the thermal properties of both potassium chloride and nitrate is of importance in connection with the process recently considered by Whittaker, Lundstrom and Merz.[2]

Measurements of the heat capacity of potassium chloride over temperature intervals sufficiently small to make possible the determination of specific heat as a function of temperature were made by Nernst,[3] and by Lindemann and Schwers.[4] Koref[5] and others have also measured a few "mean" specific heats. No published data on the specific heats of potassium and sodium nitrate have been found at low temperatures.

TABLE I

THE MOLAL HEAT CAPACITY OF SODIUM NITRATE FROM 15 TO 285°K., 0°C. = 273.16°K.

T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.
16.23	0.454	64.40	8.197	136.79	14.99	220.08	18.91
19.78	.827	67.32	8.670	142.24	15.33	225.13	19.13
22.92	1.222	67.67	8.694	147.63	15.72	230.18	19.33
23.29	1.273	71.90	9.251	152.98	15.98	235.21	19.55
26.78	1.785	71.94	9.238	158.30	16.24	240.24	19.77
27.56	1.927	76.22	9.842	163.59	16.52	245.25	20.08
30.03	2.312	80.61	10.40	164.48	16.59	247.21	20.04
31.84	2.626	85.37	11.04	168.85	16.72	250.25	20.18
33.85	2.974	90.20	11.49	169.70	16.74	255.45	20.46
35.63	3.279	91.42	11.56	174.09	16.96	258.16	20.52
38.80	3.847	94.87	11.97	174.90	16.97	260.65	20.64
40.08	4.059	96.60	12.12	180.09	17.21	263.04	20.72
44.35	4.805	99.42	12.37	185.25	17.45	267.91	21.00
45.90	5.075	101.61	12.55	190.39	17.65	272.77	21.15
49.73	5.752	106.51	12.96	204.86	18.26	277.23	21.37
51.57	6.143	111.30	13.33	207.61	18.39	277.62	21.35
54.91	6.688	116.00	13.69	209.95	18.47	282.06	21.58
56.99	6.921	120.62	14.05	214.99	18.73	282.47	21.56
59.64	7.469	125.72	14.36	215.02	18.74	286.86	21.78
62.37	7.888	131.29	14.74	220.06	18.92		

(1) Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

(2) C. W. Whittaker, F. O. Lundstrom and A. R. Merz, *Ind. Eng. Chem.*, **23**, 1410 (1931).

(3) Nernst, *Ann. Physik*, [4] **36**, 419 (1911); also Nernst and Lindemann, *Z. Elektrochem.*, **17**, 817 (1911).

(4) Lindemann and Schwers, *Physik. Z.*, **14**, 67 (1913).

(5) Koref, *Ann. Physik*, [4] **36**, 59 (1911).

The material used for these measurements was of C. P. quality, further purified by Dr. C. W. Whittaker by three or four recrystallizations. The salts were dried in a high vacuum with a liquid air trap to collect the water pumped off. Potassium chloride required further treatment as described later.

TABLE II

THE MOLAL HEAT CAPACITY OF POTASSIUM NITRATE FROM 15 TO 295°K.

T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.
15.96	0.664	93.95	13.95	159.62	17.54	233.04	20.39
19.52	1.159	94.01	13.97	164.93	17.76	238.53	20.51
23.45	1.787	98.68	14.33	170.22	17.99	238.90	20.58
27.28	2.601	98.74	14.32	175.49	18.17	243.75	20.74
27.41	2.593	103.38	14.71	180.76	18.33	244.12	20.73
31.07	3.552	108.23	15.03	186.03	18.54	248.96	20.97
36.78	4.808	113.30	15.31	191.28	18.81	249.33	20.97
41.37	5.928	118.31	15.65	196.12	18.96	254.53	21.13
46.20	6.886	123.26	15.91	196.53	18.93	259.73	21.37
51.57	8.069	128.17	16.16	201.37	19.14	264.93	21.53
56.86	9.159	133.31	16.45	201.79	19.12	270.11	21.84
61.79	10.05	138.69	16.70	206.62	19.32	275.29	21.95
66.43	10.76	143.63	16.92	207.03	19.36	280.46	22.19
71.16	11.42	144.04	16.97	211.87	19.55	285.63	22.41
74.84	11.85	148.98	17.07	212.27	19.55	290.78	22.70
84.24	13.08	149.36	17.18	217.11	19.74	295.92	22.93
89.15	13.55	154.30	17.38	222.34	19.99		
89.20	13.58	154.68	17.33	227.56	20.14		

TABLE III

THE MOLAL HEAT CAPACITY OF POTASSIUM CHLORIDE (FUSED) FROM 15 TO 285°K.

T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.
16.69	0.427	96.10	9.204	179.76	11.36	229.29	11.85
21.21	.842	101.31	9.438	183.41	11.39	230.28	11.86
25.06	1.302	106.43	9.656	184.85	11.41	235.01	11.86
28.81	1.810	111.48	9.842	185.22	11.45	235.93	11.91
32.41	2.360	116.47	10.03	188.83	11.47	240.70	11.92
36.00	2.917	121.41	10.17	190.32	11.48	241.62	11.95
39.86	3.533	126.32	10.34	194.28	11.51	246.41	11.98
44.25	4.189	131.19	10.46	195.81	11.53	247.32	11.98
49.27	4.926	136.04	10.61	199.74	11.56	252.15	12.00
54.44	5.671	141.17	10.76	201.32	11.59	252.68	12.02
59.61	6.326	146.58	10.85	205.23	11.64	257.80	12.03
64.94	6.893	152.30	10.95	206.85	11.69	257.91	12.06
69.92	7.365	158.02	11.06	210.73	11.69	262.94	12.01
74.62	7.761	163.45	11.14	212.40	11.72	263.70	12.10
79.11	8.158	168.88	11.21	216.26	11.73	268.15	12.05
84.10	8.549	172.60	11.26	217.97	11.75	269.52	12.15
89.28	8.844	174.31	11.28	219.04	11.76	273.34	12.15
90.80	8.904	177.99	11.33	223.61	11.80	278.54	12.20
94.32	9.123	179.39	11.36	224.65	11.81	284.68	12.25

TABLE IV

THE MOLAL HEAT CAPACITY OF POTASSIUM CHLORIDE (HEATED TO 700°) FROM 90 TO 290°K.

T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.
92.26	9.024	146.29	10.85	187.01	11.48	239.20	11.93
96.84	9.248	151.13	10.93	192.72	11.53	245.11	12.02
101.70	9.459	152.99	10.99	198.44	11.63	251.05	12.06
106.86	9.675	155.97	11.04	204.18	11.63	257.02	12.10
111.94	9.851	158.65	11.05	209.95	11.69	263.03	12.14
116.96	10.05	164.31	11.19	215.74	11.71	269.06	12.17
121.93	10.19	169.88	11.24	221.59	11.76	275.12	12.23
126.86	10.36	175.64	11.36	227.42	11.83	281.20	12.31
136.58	10.62	181.29	11.40	233.30	11.85	287.30	12.34
141.44	10.73						

The measurements were made with the calorimeter described previously[6] and the data are shown in Tables I–IV and Fig. 1. The results are expressed in calories (one calorie = 4.1833 int. joules = 4.185 absolute joules). The errors were discussed in connection with the description of the apparatus. All weights are corrected to vacuum.

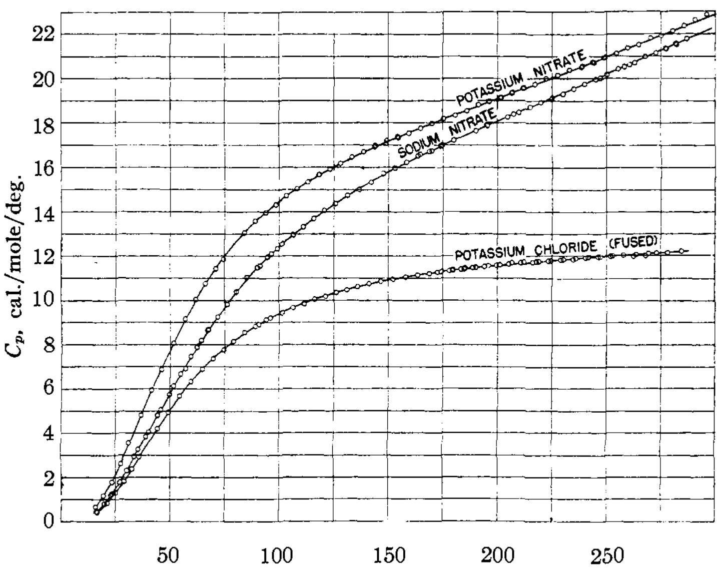

Fig. 1.—Heat capacities of potassium chloride, potassium nitrate and sodium nitrate as a function of temperature in the range 15 to 290°K.

The entropy from 15 to 298.16°K. was determined by plotting the experimentally found molal heat capacity against log T and integrating graphically. To find the entropy from 0 to 15°K., a characteristic temperature,

(6) Southard and Brickwedde, THIS JOURNAL, 55, 4378 (1933).

Θ_D, was calculated for each experimental point up to 40°K., assuming three degrees of freedom for each ion (a total of six for the molecule). The Θ_D found in this manner did not vary appreciably from 15 to 40°K. and was used, with the tables of Simon,[7] to find the entropy at 15°K.

The results of the entropy calculations were as follows:

	KCl (fused) cal./mole/deg.	KNO₃ cal./mole/deg.	NaNO₃ cal./mole/deg.
$(S_{298.16°}-S_{15°})$ graph.	19.65 ± 0.04	31.58 ± 0.06	27.75 ± 0.06
$(S_{15°}-S_{0°})$ calcd.	0.10 ± .02 (Θ_D = 218)	0.19 ± .04 (Θ_D = 178)	0.12 ± .02 (Θ_D = 206)
$S_{298.16}-S_0$ total	19.75 ± .06	31.77 ± .10	27.87 ± .08

Two different samples of potassium chloride were dried as described above, one for two and one for five days. Both samples showed a region of about 10° in which the heat capacity was abnormally high, the maximum of the "hump" occurring at about −10°. Since the presence of occluded water was suspected, two further samples were prepared, one by heating to 700° and the other by fusion with subsequent grinding. All heating was done in platinum vessels. Measurements showed the heat capacities of these two latter samples to be free from abnormalities and coincident from the lowest temperatures up to about −13°. The results at low temperatures were in good agreement with the results on the unheated salt. Above this temperature the specific heat of the heated but unfused salt appeared to be about 0.5% higher than that of the fused. The entropy difference at 298.16°K. between unfused and fused chloride was less than 0.02 cal./mole/degree.

The free energy of formation of these salts may now be calculated by the third law of thermodynamics using the heats of formation given in the "I. C. T.," Vol. V, the entropies of sodium and potassium as given by Kelley,[8] and the entropies of oxygen, chlorine, and nitrogen as given by Giauque and co-workers.[9] The results are summarized below.

Reaction (T = 298.16°K.)	$\Delta H°$ cal./mole	$\Delta S°$ cal./mole/deg.	$\Delta F°$ cal./mole
$Na + 1/2N_2 + 3/2O_2 = NaNO_3$	−112,410	−80.77	−88,300
$K + 1/2N_2 + 3/2O_2 = KNO_3$	−118,780	−79.87	−95,000
$K + 1/2Cl_2 = KCl$	−104,300	−22.11	−97,700

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Summary

1. The molal heat capacities of potassium chloride, potassium nitrate and sodium nitrate have been determined in the range from 15 to 290°K.

(7) "Handbuch d. Physik," Vol. X, p. 370.

(8) Kelley, Bureau of Mines Bull. 350 (1932).

(9) Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929); Giauque and Overstreet, *ibid.*, **54**, 1731 (1932); Clayton and Giauque, *ibid.*, **54**, 2610 (1932).

2. The molal entropies of these compounds at 298.16°K. are found to be 19.75 ± 0.06, 31.77 ± 0.10 and 27.87 ± 0.08 cal./mole/deg., respectively.

3. The free energies of formation of these salts from the elements have been calculated.

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Magnetic Susceptibilities of Some Europium and Gadolinium Compounds

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The objects of this work were: (1) to provide an experimental check on the theoretical magnetic behavior of the trivalent europium ion at low temperatures,[1] (2) to determine to what extent the Sommerfeld–Kossel rule is followed by the ions Eu^{++} and Gd^{+++}, and if possible, to evaluate the spectral term of Eu^{++} from the temperature coefficient of magnetic susceptibility, and (3) by means of magnetic measurements on different gadolinium compounds to examine the influence of the Heisenberg exchange interaction with more precision than was possible in the writer's previous work[2] on neodymium, which, not being in an S state, is subject to the effect of the crystalline field on the orbital component of the magnetic moment.

Magnetic measurements on europium in the oxide and anhydrous sulfate from room temperature to 600° have been made by Cabrera and Duperier,[3] while the oxide has been examined from 183 to 673° by Sucksmith.[4] The values obtained are in fair agreement with the theoretical. However, as measurements on "magnetically dilute" substances are much to be preferred, data are given here on the octahydrated sulfate.

The only measurement made on the recently prepared compound europous sulfate is that of Hughes and Pearce,[5] who find a value some 15% lower than for gadolinium. Their work is open to the criticisms that the temperature is not stated explicitly, it is not stated what diamagnetic corrections, if any, have been made, and, finally, water, which they used for calibration, is very unsatisfactory for the measurement of a susceptibility 140 times as large.

The gadolinium compounds examined were the oxide, anhydrous chloride, and octahydrated sulfate. The first has been studied by Williams[6] over a large temperature range, and also by Cabrera and Duperier,[3] while

(1) Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford University Press, 1932.
(2) Selwood, THIS JOURNAL, **55**, 3161 (1933).
(3) Cabrera and Duperier, *Compt. rend.*, **188**, 1640 (1929).
(4) Sucksmith, *Phil. Mag.*, [VII] **14**, 1115 (1932).
(5) Hughes and Pearce, THIS JOURNAL, **55**, 3277 (1933).
(6) Williams, *Phys. Rev.*, **14**, 348 (1920).