[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity and Entropy of Barium Fluoride, Cesium Perchlorate and Lead Phosphate

BY KENNETH S. PITZER,[1] WENDELL V. SMITH AND WENDELL M. LATIMER

While the calculation of ionic entropies was the immediate purpose for which these heat capacity measurements were made, the data so obtained should, nevertheless, have considerable value from other points of view. The present paper contains the heat capacity results together with calculations of the entropies of the three salts. The ionic entropy calculations will be presented in another publication.

Materials.—The precipitation of barium fluoride from aqueous solution gives a very fine powder which would seem questionable as a thermodynamic reference state. The sample employed in the following measurements was prepared by melting "c. p." barium nitrate and potassium fluoride together in a platinum crucible, and then extracting the potassium nitrate and excess barium nitrate from the cooled melt with hot water. The extraction was continued until the wash water gave no test for either potassium ion or nitrate ion. The product appeared to be definitely crystalline on examination with a microscope. Analysis by precipitation of barium sulfate from dilute nitric acid solution gave 99.7 ± 0.5% of the theoretical barium content. The authors wish to extend their thanks to Dr. Oliver L. I. Brown for the greater part of the work in preparing this sample.

The tertiary lead phosphate was prepared from lead acetate and Na_2HPO_4, both of "c. p." grade. Hot, dilute solutions of the two salts were slowly mixed with vigorous stirring, and the resulting precipitate was washed thoroughly and then dried by heating for several days at 300°. Electrolytic analysis showed the theoretical amount of lead within 0.2%.

The cesium perchlorate was prepared from samples of "c. p." cesium nitrate and iodochloride by the addition of perchloric acid in dilute solution. Chemical tests indicated the absence of appreciable amounts of nitrate or iodochloride, while the absence of other alkali metals was established by spectroscopic examination. The product was dried by prolonged heating at 140°. The lack of any rise near the ice point in the heat capacity curves shows that none of the salts contained an appreciable amount of water.

Heat Capacity Measurements.—The general method of Latimer and Greensfelder[2] was followed, including, however, certain improvements which also have been reported.[3] The calibrated thermocouple in the calorimeter was rechecked against the vapor pressure and triple point of hydrogen between the measurements on barium fluoride and those on lead phosphate and cesium perchlorate, while the heat capacity of the empty calorimeter was remeasured after their conclusion. The results are expressed in terms of a defined calorie (=4.1833 int. joules). The barium

TABLE I

HEAT CAPACITY OF BARIUM FLUORIDE

BaF_2, 175.37 g. = 1 mole

T, °K.	Molal C_p	T, °K.	Molal C_p
13.79	0.25	130.01	12.91
15.25	.29	134.94	13.22
17.72	.42	139.63	13.49
23.23	.90	144.10	13.65
26.20	1.20	149.75	14.01
27.70	1.37	155.28	14.21
29.35	1.56	160.66	14.41
30.00	1.65	166.14	14.62
32.43	1.96	173.17	14.92
34.73	2.27	177.59	15.02
38.08	2.72	178.32	15.13
41.45	3.18	183.31	15.27
44.96	3.62	188.17	15.39
49.20	4.20	193.05	15.54
54.24	4.90	198.09	15.65
59.34	5.61	203.93	15.85
64.36	6.34	210.14	15.96
64.64	6.38	216.91	16.14
68.65	6.94	223.27	16.22
74.76	7.79	229.73	16.32
79.83	8.36	237.32	16.49
84.72	8.94	244.95	16.62
89.48	9.49	252.69	16.68
94.41	9.99	259.32	16.76
99.52	10.44	266.35	16.81
104.78	10.98	272.87	16.89
110.11	11.47	273.94	16.91
115.03	11.84	279.44	16.90
119.76	12.19	293.08	16.90
124.79	12.56	300.69	16.98

(1) Shell Research Fellow, Academic Year 1936-1937.

(2) Latimer and Greensfelder, THIS JOURNAL, **50**, 2202 (1928).

(3) (a) Brown, Smith and Latimer, *ibid.*, **58**, 1758 (1936); (b) Ahlberg and Latimer, *ibid.*, **56**, 856 (1934).

TABLE II

HEAT CAPACITY OF LEAD PHOSPHATE

$Pb_3(PO_4)_2$, 811.7 g. = 1 mole

T, °K.	Molal C_p	T, °K.	Molal C_p
15.70	3.47	154.25	44.92
17.90	4.25	159.47	45.75
21.71	6.19	164.95	46.57
25.29	8.05	170.23	47.40
28.32	9.70	175.35	48.14
31.57	11.48	180.32	48.89
35.61	13.67	185.07	49.67
40.72	16.23	190.23	50.37
56.60	22.46	195.62	51.07
61.30	24.11	200.84	51.90
66.59	25.89	206.48	52.52
72.20	27.58	207.68	52.44
77.57	29.11	212.22	53.10
83.23	30.64	215.17	53.76
89.16	32.21	221.67	54.30
94.56	33.53	228.11	54.91
100.36	34.81	234.74	55.70
106.42	36.17	241.56	56.44
112.09	37.37	248.21	57.14
117.43	38.40	254.87	57.85
122.50	39.39	262.16	58.38
127.92	40.34	269.06	59.00
133.72	41.45	276.26	59.70
139.08	42.49	283.79	60.12
144.32	43.35	291.96	61.31
149.43	44.14		

TABLE III

HEAT CAPACITY OF CESIUM PERCHLORATE

$CsClO_4$, 232.27 g. = 1 mole

T, °K.	Molal C_p	T, °K.	Molal C_p
15.09	2.15	144.69	19.10
18.38	3.36	146.76	19.20
21.90	4.62	152.45	19.49
25.49	5.86	157.89	19.75
29.51	7.16	163.14	19.99
33.67	8.98	168.25	20.25
38.16	9.72	173.66	20.60
42.62	10.79	180.21	21.05
46.83	11.67	187.17	21.15
50.87	12.37	193.48	21.57
55.92	13.15	200.04	21.91
61.53	13.86	206.36	22.13
70.58	14.81	213.10	22.41
76.05	15.21	220.00	22.83
81.82	15.64	226.91	23.03
87.43	16.01	235.16	23.49
93.53	16.41	242.30	23.86
99.93	16.80	249.30	24.10
105.95	17.13	256.97	24.40
111.52	17.42	264.85	24.69
117.65	17.76	274.66	25.17
124.03	18.07	283.47	25.41
130.96	18.38	292.01	25.54
138.00	18.70		

fluoride sample weighed 242.88 g. (1.3849 moles); the lead phosphate sample, 196.59 g. (0.24220

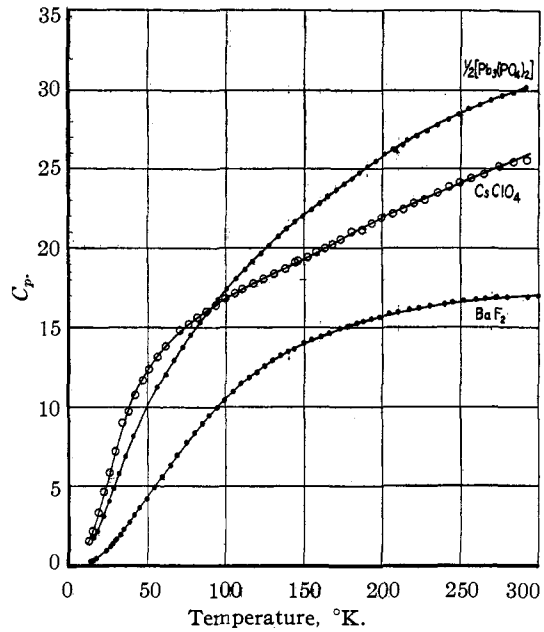

Fig. 1.—Heat capacity in cal. per degree for one mole of barium fluoride and cesium perchlorate and for one-half mole of lead phosphate.

TABLE IV

SMOOTHED VALUES OF THE HEAT CAPACITY AT EVEN TEMPERATURES

T, °K.	Molal C_p BaF_2	Molal C_p $CsClO_4$	Molal C_p $Pb_3(PO_4)_2$
15	0.28	2.12	3.25
20	.60	3.89	5.28
25	1.07	5.71	7.91
30	1.65	7.31	10.61
35	2.31	8.83	13.33
40	2.98	10.19	15.88
45	3.63	11.30	18.14
50	4.32	12.24	20.15
60	5.71	13.69	23.66
70	7.13	14.74	26.94
80	8.41	15.53	29.81
90	9.53	16.19	32.40
100	10.53	16.80	34.75
110	11.43	17.36	36.90
120	12.21	17.88	38.90
130	12.90	18.37	40.77
140	13.48	18.87	42.55
150	13.98	19.37	44.27
160	14.41	19.87	45.87
170	14.79	20.38	47.37
180	15.13	20.90	48.90
190	15.45	21.41	50.35
200	15.74	21.91	51.71
220	16.20	22.83	54.16
240	16.54	23.71	56.35
260	16.77	24.53	58.25
280	16.90	25.29	59.93
300	16.98	26.00	61.45

mole); while the cesium perchlorate weighed 139.12 g. (0.59896 mole). All weights are reduced to a vacuum basis. The results are presented in Tables I, II and III and shown as a function of the temperature in Fig. 1. Smooth values of the heat capacity for even temperatures are listed in Table IV.

TABLE V

MOLAL ENTROPIES OF BARIUM FLUORIDE, LEAD PHOSPHATE, AND CESIUM PERCHLORATE IN CAL. PER DEGREE

Substance	BaF_2	$Pb_3(PO_4)_2$	$CsClO_4$
Debye extrapolation, 0–15°K.	0.09	1.07	0.82
Graphical from data, 15–298.1°K.	22.94	83.38	41.07
Entropy at 298.1°K.	23.03 ± 0.1	84.45 ± 0.4	41.89 ± 0.2

Entropies.—The entropies were calculated by graphical integration, using large scale plots of C_p against log T, combined with extrapolations to the absolute zero, using the Debye specific heat equation. The calculations are summarized in Table V.

Summary

The heat capacities of barium fluoride, tertiary lead phosphate, and cesium perchlorate have been measured from 15 to 300°K. Their entropies have been calculated to be 23.03 ± 0.1, 84.45 ± 0.4, and 41.89 ± 0.2 cal. per degree, respectively, at 298.1°K.

BERKELEY, CALIF. RECEIVED MARCH 30, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heats of Solution of Cesium Perchlorate, Rubidium Perchlorate, Rubidium Chlorate, and Lead Phosphate

BY KENNETH S. PITZER

Using the calorimeter described in an earlier publication,[1] the integral heat of solution has been measured for the four salts listed in the title. These data were of particular interest in connection with the calculation of the entropies of the ions involved. The calculations will be presented in a later publication.

Material.—The cesium perchlorate and rubidium chlorate were taken from samples used in low temperature heat capacity investigations.[2] The rubidium perchlorate was prepared by precipitation from a dilute solution of the pure rubidium chlorate sample with perchloric acid. The lead nitrate and sodium phosphate solutions which were used in the precipitation of lead phosphate were prepared from "C. P." salts.

Heat of Solution Measurements.—The results of the heat of solution measurements are presented in Table I. The heat capacity of the calorimeter was determined frequently by electrical heating experiments. The volume of water was 885 ml. in each experiment.

Heat of Precipitation of Lead Phosphate.—It was found to be impractical to measure the heat of solution of tertiary lead phosphate, due to the slow rate of solution even in solvents which would eventually dissolve a very considerable amount. Consequently a heat of precipitation was measured. The reaction chosen was the following

$$3Pb^{++} + 4HPO_4^{--} = Pb_3(PO_4)_2 + 2H_2PO_4^-$$

Four measurements were made on the heat absorbed when 10 ml. of 0.5 molal lead nitrate solution was mixed with 875 ml. of 0.01 molal Na_2HPO_4 solution. The results obtained were

TABLE I

THE HEATS OF SOLUTION OF CESIUM PERCHLORATE, RUBIDIUM PERCHLORATE, AND RUBIDIUM CHLORATE IN WATER AT 25°

Wt., g.	Molal concn. of final soln.	Heat absorbed, cal. per mole	Estimated ΔH of diln.	ΔH^0, cal. per mole
		$CsClO_4$		
1.7438	0.00848	13,160	−10	13,150
1.4462	.00704	13,400	−10	13,390
1.6530	.00804	13,190	−10	13,180
0.4932	.00240	13,320	−10	13,310
				13,260 ± 100
		$RbClO_4$		
1.2159	.00743	13,610	−10	13,600
2.2001	.01344	13,540	0	13,540
				13,570 ± 60
		$RbClO_3$		
1.5743	.01053	11,470	−20	11,450
1.7452	.01167	11,400	−20	11,380
				11,410 ± 60

(1) Pitzer, THIS JOURNAL, **59**, 2365 (1937).

(2) (a) Pitzer, Smith and Latimer, *ibid.*, **60**, 1826 (1938); (b) J. E. Ahlberg, Ph.D. Dissertation, University of California, 1930.