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.

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

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

---

(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.

4.45, 5.25, 4.00 and 3.90 cal. with an average of 4.4 ± 0.4 cal. The heat absorbed in the dilution of 10 ml. of 0.5 molal lead nitrate solution with 875 ml. of water was also measured, with the results: 8.40, 8.30, 9.45, and 9.00 cal., average 8.8 ± 0.4 cal. Combining this value with the data of Plake,[3] the heat absorbed in the dilution to zero concentration of the lead nitrate solution was found to be 9.3 cal. With the aid of the Debye–Hückel theory, the increase in heat content with dilution was estimated to be 0.8 cal. greater for the final solution than for the initial phosphate solution. Combining these quantities, one finds $\Delta H^0 = -2460 \pm 360$ cal. for the above equation.

Making use of the heats of ionization of phosphoric acid recently published by the writer,[1] one obtains also the following results

$$Pb_3(PO_4)_2 + 2H^+ = 3Pb^{++} + 2HPO_4^{--};\quad \Delta H^0 = 860 \pm 400 \text{ cal.}$$

$$Pb_3(PO_4)_2 = 3Pb^{++} + 2PO_4^{---};\quad \Delta H^0 = 7860 \pm 1000 \text{ cal.}$$

All values given are for 25°.

Summary

Values have been obtained for the heats of solution at infinite dilution and 25° of the following substances: $CsClO_4$, $\Delta H^0 = 13{,}260 \pm 100$ cal.; $RbClO_4$, $\Delta H^0 = 13{,}570 \pm 60$ cal.; $RbClO_3$, $\Delta H^0 = 11{,}410 \pm 60$ cal.; $Pb_3(PO_4)_2$, $\Delta H^0 = 7860 \pm 1000$ cal.

BERKELEY, CALIF. RECEIVED MARCH 30, 1938

---

[3] Plake, *Z. physik. Chem.*, **A162**, 257 (1932).

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

The Entropies of Aqueous Ions

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

In the course of the research program for the evaluation of the entropies of aqueous ions, in progress for some time in this Laboratory, a considerable body of data has accumulated which makes possible the calculation of the entropies of eleven additional ions. Because in most cases the entropy values depend on those for other ions, an extensive revision would be necessary in order to make these new values the best possible. Consequently it seemed best to make a complete revision of all ionic entropies and to include the new ions at the same time.

In order to avoid unnecessary length, specific references have been given only where the data are not included in some summary publication. Most of the new calculations are based upon data taken from recent publications in this research series[1] and from the references cited in the earlier summary paper.[2] In general entropies have been taken from the excellent summaries of Kelley,[3] heats of reaction from Bichowsky and Rossini,[4] and activity coefficients and other free energy data from the Landolt–Börnstein Tabellen.[5]

The calculations are summarized in Table I and the best values of the ionic entropies collected in Table II. Different methods of obtaining a given entropy are included only if they are independent in the least accurate step. An attempt has been made to include all sources of error in estimating the uncertainty in the final values. For this reason the uncertainty given for a final value is often much larger than the difference between the various values for that quantity would indicate.

The standard state for ionic entropies has been defined in several earlier papers, wherein the theoretical significance and practical importance of ionic entropies also have been discussed. As the body of data becomes larger, however, its consistency becomes more notable, and offers more and more evidence of the validity of the third law of thermodynamics when applied to crystalline inorganic salts. The possibility of difficulties in the case of hydrated crystals has arisen recently and has been discussed elsewhere.[1b] It is felt that errors from this source cannot have any serious effect on the values obtained in this paper.

---

[1] (a) Pitzer, Smith and Latimer, THIS JOURNAL, **60**, 1826 (1938); (b) Pitzer and Coulter, *ibid.*, **60**, 1310 (1938). (c) Pitzer, *ibid.*, **60**, 1828 (1938); **59**, 2365 (1937); (d) Smith, Pitzer and Latimer, *ibid.*, **59**, 2640, 2642 (1937); (e) Pitzer and Smith, *ibid.*, **59**, 2633 (1937); (f) Smith, Brown and Pitzer, *ibid.*, **59**, 1213 (1937); (g) Brown, Smith and Latimer, *ibid.*, **58**, 1728, 2144, 2228 (1936); **59**, 921 (1937).

[2] Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

[3] Kelley, *Bur. Mines Bull.*, 350, 1932 and 394, 1936.

[4] Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, N. Y., 1936.

[5] Landolt–Börnstein "Physikalisch-chemische Tabellen," including Supplements 1, 2 and 3, Verlag von Julius Springer, Berlin, 1923–1936.