sliding one plot vertically with respect to the other, the points representing $^1/_8 \log K_m$ will superimpose upon one of the characteristic curves of Fig. 2 of Randall and Vietti. The value read from the superimposed curve at zero ionic strength is the value of the constant, or $^1/_8 \log K$.

The values of $^1/_8 \log K_m$ are plotted in Fig. 1 against the square root of the ionic strength. The solid curve, $^1/_2 \log \gamma$ for barium chloride, is plotted on the same scale.[2] The points superimpose on the curve of barium chloride better than that of any other salt. The value of $^1/_8 \log K$ which is the point of intersection of the superimposed curve of $^1/_2 \log \gamma$ for barium chloride at $\mu^{1/2} = 0$ is 0.566. We thus find

$$PbI_2(s) + 2SO_4^{=} + 2K^+ = PbSO_4 \cdot K_2SO_4(s) + 2I^-; \quad \log K_{298.2} = 4.528; \; \Delta F^\circ_{298.2} = -6266 \text{ cal.} \quad (9)$$

Combining Equations 4 and 9 we have

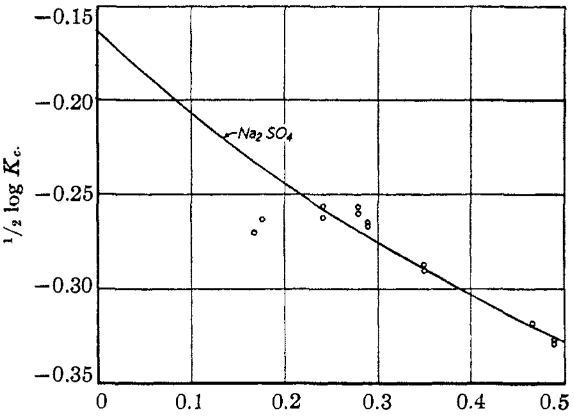
$$PbI_2(s) + SO_4^{=} = PbSO_4(s) + 2I^-; \quad \log K = -0.416; \; \Delta F^\circ_{298.2} = 476 \text{ cal.} \quad (10)$$

The values of $^1/_2 \log K_c$ (Equation 3) as determined by Findlay[1a] are plotted against the square root of the ionic strength in Fig. 2. The solid curve is $^1/_2 \log \gamma$ for sodium sulfate at 25°. The superposition is satisfactory, giving $^1/_2 \log K = -0.163$ and $\log K = -0.326$ (*cf.* Equation 10)

$$PbI_2(s) + SO_4^{=} = PbSO_4(s) + 2I^-; \quad \Delta F^\circ_{298.2} = 445 \text{ (Findlay)} \quad (11)$$

Findlay also measured cells from which the free energy of this reaction can be calculated disregarding liquid potentials. Using late unpublished values for the activity coefficients, we find

$$PbI_2(s) + SO_4^{=} = PbSO_4(s) + 2I^-; \quad \Delta F^\circ_{298.2} = 250 \text{ (Findlay)} \quad (12)$$



Square root of ionic strength, $\mu_c^{1/2}$.

Fig. 2.—$PbI_2(s) + 2SO_4^{--} = PbSO_4(s) + 2I^-$.

Summary

1. From new equilibrium measurements involving solid lead potassium sulfate, lead sulfate and lead iodide and potassium, sulfate and iodide ions, a new determination of the equilibrium between lead iodide, sulfate ion, lead sulfate and iodide ions has been calculated.

2. The mean activity coefficient of the ions in the equilibrium solutions is closely related to that of barium chloride and the equilibrium data as well as analysis of the solid show that one of the solid phases involved in the equilibria was $PbSO_4 \cdot K_2SO_4$.

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The Heat Capacities at Low Temperatures of the Oxides of Strontium and Barium[1]

BY C. TRAVIS ANDERSON[2]

In a previous report from the Pacific Experiment Station of the United States Bureau of Mines, low-temperature thermal data were presented for the carbonates of calcium, strontium and barium.[3] The present paper presents data on the oxides of strontium and barium. Low-temperature specific heat measurements on calcium oxide have been published previously.[4]

The method, apparatus, and accuracy have also been described previously.[5]

Materials

The samples of strontium and barium oxides were Kahlbaum best grade. An analysis of the

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[2] Assistant physical chemist, U. S. Bureau of Mines, Pacific Experiment Station, Berkeley, California.

[3] Anderson, THIS JOURNAL, **56**, 340 (1934).

[4] Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

[5] Anderson, THIS JOURNAL, **52**, 2296, 2712 (1930); **54**, 107 (1932); **55**, 3621 (1933).

samples showed a considerable amount of carbonate as the principal impurity. The samples were crushed to −14 +35 mesh size and placed in silica flasks, heated under a high vacuum at high temperatures to decompose the carbonates to the corresponding oxides. Pumping was continued until the products were practically free from carbonates and appeared very white. They were transferred to the calorimeter directly from the flask, out of contact with the air. Samples of 189.8 g. of the strontium oxide and 198.0 g. of barium oxide were used to fill the calorimeter.

The Specific Heats

The results obtained in this Laboratory on the heat capacities of strontium and barium oxides, expressed in gram calories (15°) per gram-formula weight, are shown graphically in Fig. 1. The experimental values for the heat capacities for these oxides are given in Tables I and II. The calculations were made on the basis of Sr = 87.63, Ba = 137.36, and O = 16.

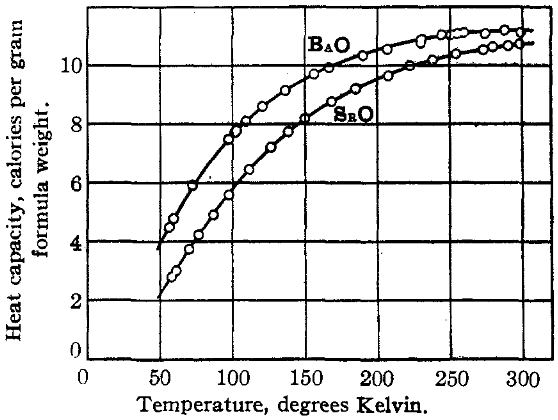

Fig. 1.—The heat capacities of strontium and barium oxides per gram formula weight.

TABLE I

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF STRONTIUM OXIDE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
57.9	2.777	111.2	6.445	222.6	9.980
61.2	3.002	126.1	7.200	238.3	10.18
64.3	3.278	138.4	7.726	254.4	10.38
70.0	3.719	149.9	8.176	273.3	10.52
76.8	4.219	168.6	8.758	279.9	10.63
86.8	4.896	185.3	9.195	290.4	10.67
97.1	5.573	207.7	9.645	298.4	10.77

Calculation of Entropies

The usual graphical method was followed in calculating the entropies of these oxides. The experimental heat capacity curves coincided at low temperatures with Debye functions having the parameters (Θ) for strontium oxide 261 and barium oxide 173. The following combinations of Debye and Einstein functions were found to fit the specific heat curves per formula weight of these oxides.

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT OF BARIUM OXIDE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
56.1	4.467	120.6	8.591	244.2	11.05
59.2	4.761	136.6	9.134	250.1	11.04
72.1	5.897	156.2	9.695	255.7	11.08
97.0	7.469	166.8	9.925	259.4	11.11
101.5	7.710	190.2	10.34	274.3	11.07
102.8	7.783	207.1	10.55	287.6	11.19
109.1	8.078	230.1	10.75	298.6	11.11
		230.5	10.90		

$$C_{\mathrm{SrO}} = D\left(\frac{261}{T}\right) + E\left(\frac{444}{T}\right)$$

$$C_{\mathrm{BaO}} = D\left(\frac{173}{T}\right) + E\left(\frac{332}{T}\right)$$

The results of the entropy calculations, from the experimental heat capacity data and the function sums, are given in Table III.

TABLE III

ENTROPY DATA

	SrO	BaO
Extrap. (0–56.2), °K.	1.17	2.56
Graph. (56.2–298.1), °K.	11.84	14.28
$S^\circ_{298.1}$ graphical	13.0 ± 0.2	16.8 ± 0.3
$S^\circ_{298.1}$ calcd. from functions	13.0	16.8

Related Thermal Data

Values for ΔH_{298} and ΔF_{298} for the dissociations of the carbonates of calcium, strontium and barium to form the corresponding oxide and carbon dioxide are obtainable from existing data. These values enable ΔS of the dissociation reaction to be calculated from the expression $\Delta F = \Delta H - T\Delta S$. Using the direct experimental entropies of the carbonates and oxides, values may be obtained for the entropy of carbon dioxide. Figures for these reactions are given in Table IV, taken from the best available dissociation data.

All of these values for the entropy of carbon dioxide are lower than about 51.1 obtained by specific heat measurements or calculated from spectroscopic data.

The method of calculating the entropy of carbon dioxide, illustrated in Table IV, is obviously not satisfactory, due to uncertainty in ΔH, and to not knowing the heat capacities of the materials at higher temperatures. Since the entro-

TABLE IV

SUMMARY OF HEATS OF FORMATION, FREE ENERGIES AND ENTROPIES

Reaction	$CaCO_3 \rightarrow CaO + CO_2$	$SrCO_3 \rightarrow SrO + CO_2$	$BaCO_3 \rightarrow BaO + CO_2$
ΔH_{298} cal.	42,600[a]	53,620[b]	63,400[c]
ΔF_{298} cal.	31,258[a]	42,400[b]	51,400[d]
ΔS	38.1	37.6	40.4
S_{298} R O	9.5	13.0	16.8
S_{298} R CO_3	22.2	23.2	26.8
S_{298} CO_2 calcd.	50.8	47.8	50.4

[a] Bäckström, THIS JOURNAL, **47**, 2443 (1925). [b] John Chipman, communication to this Laboratory, preliminary calculation. [c] De Forcrand, *Compt. rend.*, **146**, 512 (1908). [d] Johnston, THIS JOURNAL, **30**, 1357 (1908).

pies are known to be the more accurate, it is better to use an entropy value for carbon dioxide, such as that determined by use of spectroscopic data, and free energies which may be obtained by several methods, such as dissociation data, and adjust the heat of formation to a value giving a system consistent with the best estimates of specific heat. An extensive series of such calculations is included in a paper entitled "Contributions to the Data on Theoretical Metallurgy. IV. Metal Carbonates. Correlations and Applications of Thermodynamic Properties," which will shortly be published as a Bureau of Mines Bulletin.

Summary

The heat capacities of strontium and barium oxides from about 55 to 300°K. have been determined and their corresponding entropies calculated as 13.0 and 16.8, respectively.

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[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, THE UNIVERSITY OF CHICAGO AND THE JOHNS HOPKINS UNIVERSITY]

Specific Heat and Electronic Activation in Crystals

BY J. ELSTON AHLBERG AND SIMON FREED

The rare earths offer exceptional opportunities for studying activations of a now fairly well understood kind, namely, electronic activations in crystals. In a preliminary note[1] we have pointed out how it is possible in the rare earths, at least, to determine the energy and other characteristics of these activations by means of specific heat measurements. We wish to consider the problem again here in greater detail, and also we shall report more accurate experimental data than those which formed the basis of the previous note. The energies required for such activations probably account for the "anomalies" in the specific heats of many other kinds of substances, as well, especially at higher temperatures, but these activations are usually accompanied with complications, which we shall touch upon later. Suggestive of electronic activations of the "pure type" are the deviations of the measurements from the theoretical specific heats of Debye which Simon[2] has evaluated in a number of alkali metals and other elements. The nature of these is still obscure, perhaps for lack of a detailed theory of electronic levels in metals. Moreover, the theory of Debye lacks rigor,[3] and on this account as well, these interesting deviations must await further study for their interpretation.

The electronic energy levels in the crystals we are considering may be thought of most simply as arising from single degenerate levels of the "isolated" ion when it is subject to the electrical fields of the lattice—in the first approximation, to the electrical fields of the ions and dipoles immediately surrounding the ion under consideration. In a salt such as $SmCl_3 \cdot 6H_2O$, for example, the "isolated" ion would be Sm^{+++} while the electrical fields may be thought of as originating in the H_2O dipoles and in the chloride ions surrounding the Sm^{+++}. The number and separation of the levels resulting from the degenerate level of the "isolated" ion will furnish such information as the symmetry of the electrical fields, their magnitudes, the orientations of the ions, etc. Indeed, Bethe[4] has already derived important theoretical relations of this nature. In particular ions, energy levels near the basic level may arise within the "isolated" ion itself,

(1) J. E. Ahlberg and S. Freed, *Phys. Rev.*, **39**, 540 (1932).

(2) F. Simon, *Ber. Berl. Akad.*, **33**, 477 (1926).

(3) E. Schrödinger, "Handbuch der Physik," Vol. IX, Berlin.

(4) H. Bethe, *Ann. Physik*, [5] **3**, 133 (1929).