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Experimental Heat Contents of SrO, BaO, CaO, $BaCO_3$ and $SrCO_3$ at High Temperatures. Dissociation Pressures of $BaCO_3$ and $SrCO_3$

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The high temperature heat contents of SrO, BaO, CaO, $BaCO_3$ and $SrCO_3$ have been measured using the "drop" method. Values have been obtained for the heats of the transitions of the carbonates. The dissociation pressures of the carbonates have been measured to pressures below 0.1 mm. and values calculated for lower pressures from the observed heat contents and observed dissociation pressures at higher temperatures.

Estimates for some of the thermodynamic properties of alkaline earth oxides and carbonates have been made by Kelley and Anderson,[1,2] and they review early work in the field. In none of their work has account been taken of the first transition of $SrCO_3$ (ortho. to hex. at 924°) and the second transition of $BaCO_3$ (hex. to cubic at 968°). Moreover, following Finkelstein,[3] they assume the existence of a basic carbonate, $BaO \cdot BaCO_3$, in the solid phase. Finkelstein assumed the existence of this basic carbonate because he observed a eutectic in the $BaCO_3$–BaO system. He offered no further evidence for its existence. Hackspill and Wolf[4] assigned the composition $2BaCO_3 \cdot BaO$ to the eutectic and report that there is no evidence for the existence of a basic carbonate in the solid phase. This system has been reinvestigated with the results described in a note to the editor (this issue). No evidence was found for the existence of a basic carbonate below 968°.

Incidental to these studies X-ray diffraction patterns of BaO–SrO mixtures were obtained. The results agree with previously published work in which complete solubility for all compositions was observed.[5] The solid solutions follow Vegard's rule very closely in that the lattice constant is a linear function of composition.

1.0 Heat Contents of BaO, SrO, CaO, $BaCO_3$ and $SrCO_3$

1.1 **Method and Apparatus.**—The heat contents of BaO, SrO, CaO, $BaCO_3$ and $SrCO_3$ have been measured using the "drop" method in which the sample at a measured temperature in a capsule of known heat content is dropped from a furnace into a calibrated calorimeter, usually made of copper. The total change in heat content of the capsule and the sample is obtained from the rise in temperature of the calorimeter. A very detailed description of apparatus said to be accurate to 0.1% is given by B. F. Naylor.[6]

Some of the refinements described by Naylor were omitted in equipment used for the present work, and in particular the copper calorimeter was calibrated with platinum. Thus, the absolute accuracy of the measurements is limited by the accuracy with which the heat capacity of platinum is known. The values given by Jaeger and Rosenbohm[7] have been used for this calibration and for the platinum containers of the test materials.

1.2 **Materials.**—The $BaCO_3$ and $SrCO_3$ were from Mallinckrodt and were of exceptionally high purity. Before use they were heated to 1000° in a platinum crucible in pure dry CO_2. SrO was obtained by thermal decomposition of $SrCO_3$ in the capsule itself at 1000° in a vacuum. CaO was similarly obtained but a calcining temperature of 800° was used. Negative tests for CO_2 were obtained from both oxides.

In the case of BaO a serious difficulty is encountered. Heating above 1030° causes melting of eutectic. Below 1030° decomposition is slow and exhaustion of the final 2% CO_2 is exceedingly slow. This difficulty may be largely overcome by adding about 20 mole per cent. $SrCO_3$ to $BaCO_3$. An alternative is to decompose BaO_2. Both of these expedients were adopted. The results for a set of runs with added $SrCO_3$ are expected to be slightly low. The BaO_2 used contained about 1% silica and therefore these results are expected to be high. Actually the results were found to vary in the direction indicated and to differ on the average by about 1%.

1.3 **Heat Content** of SrO.—Representative experimental values obtained for the heat contents of SrO are given in the second column of Table I. A small correction has been added to bring the values to 25°. In the next column are values calculated using the equation

$$H_T - H_{298.16} = 12.34T + 0.56 \times 10^{-3}T^2 + 1.806 \times 10^5T^{-1} - 4.334 \quad (1)$$

which corresponds to

$$C_p = 12.34 + 1.120 \times 10^{-3}T - 1.806 \times 10^5T^{-2} \quad (2)$$

TABLE I

HEAT CONTENT OF SrO, CALORIES PER MOLE

T, °K.	$H_T - H_{298.16}$ (obsd.)	$H_T - H_{298.16}$ (calcd.)	Deviation, %
405.9	1,209	1,212	−0.3
363.3	725	722	+ .4
485.5	2,139	2,162	−1.1
665.1	4,345	4,405	−1.3
754.1	5,514	5,530	−0.3
865.5	7,036	6,976	+ .9
1029.7	9,148	9,145	...
1093.5	10,005	10,002	...
1181.3	11,138	11,178	− .4
1265.5	12,399	12,322	+ .6

1.4 **Heat Content** of BaO.—Representative values obtained from a sample containing 0.01771 mole of BaO and 0.00655 mole of SrO are given in Table II and values obtained from a sample of 0.03600 mole of BaO obtained by thermal decomposition of BaO_2 are given in Table III. The observed values are compared with values calculated from the formula

$$H_T - H_{298.16} = 12.74T + 0.520 \times 10^{-3}T^2 + 1.984 \times 10^5T^{-1} - 4510 \quad (3)$$

which corresponds to

$$C_p = 12.74 + 1.040 \times 10^{-3}\,T - 1.984 \times 10^5\,T^{-2} \quad (4)$$

The average deviation of the observed values was −0.4% and +0.6%. The average represented by equation 4 should be a good approximation to pure BaO.

1.5 **Heat Content** of CaO.—Representative values obtained from a sample of 0.02544 mole CaO are given in Table IV. The calculated values have been obtained from the equation

$$H_T - H_{298.16} = 11.68T + 0.54 \times 10^{-3}T^2 + 1.660 \times 10^5T^{-1} - 4139 \quad (5)$$

which may be reduced to

$$C_p = 11.86 + 1.080 \times 10^{-3}T - 1.660 \times 10^5T^{-2} \quad (6)$$

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[1] K. K. Kelley and C. T. Anderson, Bur. Mines Bull. No. 384 (1935).

[2] K. K. Kelley, Bur. Mines Bull. No. 371 (1934).

[3] A. Finkelstein, *Ber.*, **39**, 1585 (1906).

[4] L. Hackspill and G. Wolf, *Compt. rend.*, **204**, 1820 (1937).

[5] W. G. Burgers, *Z. Physik*, **80**, 352 (1933).

[6] K. K. Kelley, B. F. Naylor and C. H. Shomate, Bur. Mines Tech. Paper, 686 (1946).

[7] F. M. Jaeger and E. Rosenbohm, *Physica*, **6**, 123 (1939).

TABLE II

HEAT CONTENT OF BaO + 27% SrO, CALORIES PER MOLE

T, °K.	$H_T - H_{298.16}$ (obsd.)	$H_T - H_{298.16}$ (calcd.)	Deviation, %
391.1	1,069	1,060	+0.8
439.1	1,645	1,640	− .3
467.8	2,001	1,989	+ .4
541.5	2,877	2,909	−1.1
647.1	4,253	4,260	− .2
909.6	7,632	7,729	−1.4
1099.5	10,272	10,311	−0.4
1262.1	12,461	12,500	− .8

TABLE III

HEAT CONTENT OF BaO FROM BaO₂, CALORIES PER MOLE

T, °K.	$H_T - H_{298.16}$ (obsd.)	$H_T - H_{298.16}$ (calcd.)	Deviation, %
420.8	1,406	1,413	−0.5
462.1	1,918	1,919	...
570.1	3,296	3,273	+0.7
725.6	5,299	5,271	+1.1
760.5	5,778	5,741	+0.7
972.8	8,589	8,579	+0.1
1090.4	10,341	10,191	+1.5
1176.7	11,403	11,370	+0.4
1298.8	13,207	13,062	+1.1

TABLE IV

HEAT CONTENT OF CaO, CALORIES PER MOLE

T, °K.	$H_T - H_{298.16}$ (obsd.)	$H_T - H_{298.16}$ (calcd.)	Deviation, %
563.6	2,996	3,009	−0.4
687.3	4,523	4,506	+ .4
753.8	5,201	5,326	−2.4
788.5	5,762	5,757	+0.1
886.5	6,958	6,988	− .4
990.9	8,388	8,316	+ .9
1099.6	9,736	9,694	+ .4
1176.4	10,652	10,710	− .7

1.6 Discussion of the Observed Oxide Heat Contents.—The values of C_p for SrO at 298.1° obtained from equation 2 is 10.65 and it agrees with that obtained by Anderson to within about 1%. The value for BaO at 298.1° is 10.83, which is about 3% lower than Anderson's value.

The values of C_p for CaO in the high temperature region are about 1% higher than those of Von Gronow and Schwiete[8] and about 8% lower than those of Roth and Bertram.[9]

1.7 Heat Content of SrCO₃.—Representative values obtained for the heat content of $SrCO_3$ are given in Table V. To within about 40° of the orthorhombic to hexagonal transition at 924° these values are well fitted by the equation

$$H_T - H_{298.16} = 21.42T + 4.28 \times 10^{-3}T^2 + 3.396 \times 10^5T^{-1} - 7905 \quad (7)$$

which corresponds to

$$C_p = 21.42 + 8.56 \times 10^{-3}T - 3.396 \times 10^5T^{-2} \quad (8)$$

The heat of the transition cannot be obtained accurately by extrapolation of equation 7 because of the increasingly rapid rise in ΔH just before the transition. The value obtained from a plot of experimental points is 4,000 cal. per gram mole. For some purposes it will be more convenient to take the value 4,700 obtained by extrapolation of equation 7, and to use this equation for values up to the transition temperature. The average value obtained for C_p through 120° above the transition is 34.0.

TABLE V

HEAT CONTENT OF SrCO₃, CALORIES PER MOLE

T, °K.	$H_T - H_{298.16}$ (obsd.)	$H_T - H_{298.16}$ (calcd.)	Deviation, %
455.9	3,532	3,492	+1.1
672.3	8,997	8,979	+0.2
750.8	10,980	11,040	− .6
858.4	14,100	13,990	+ .2
983.7	17,550	17,590	− .2
1115.1	21,460	21,560	− .5
1144.9	22,520	22,500	+ .1
1156.6	22,870	22,860	...
1175.6	23,670	23,460	+ .9
1183.1	24,050	23,690	+1.5
1186.9	24,240	23,820	+1.8
(Transition from orthorhombic to hexagonal at 924°)			
1209.1	29,220		
1220.2	29,640		
1256.3	30,800		
1282.2	31,770		
1305.4	32,560		
1323.6	33,250		

1.8 Heat Content of BaCO₃.—Some of the observed values for the heat content of $BaCO_3$ are given in Table VI. An increasingly rapid rise is observed in the region just before the orthorhombic to hexagonal transition at 806°. The value of ΔH for the transition, obtained from a plot of the experimental points, is 3,880. The value obtained using equation 9, below, is 4,520.

The values in the low temperature range to within about 40° of the transition are well fitted by the equation

$$H_T - H_{298.16} = 20.77T + 5.85 \times 10^{-3}T^2 + 2.860 \times 10^5T^{-1} - 7670 \quad (9)$$

which yields

$$C_p = 20.77 + 11.70 \times 10^{-3}T - 2.860 \times 10^{-5}T^{-2} \quad (10)$$

At 968° the hexagonal form changes to cubic. The average value of C_p for the hexagonal form is taken as 37.0 cal. per degree. The heat of the hexagonal to cubic transition is about 700 and the average value of C_p for the cubic form is approximately 39. This value may be in error by as much as 10%.

TABLE VI

HEAT CONTENT OF BaCO₃, CALORIES PER MOLE

T, °K.	$H_T - H_{298.16}$ (obsd.)	$H_T - H_{298.16}$ (calcd.)	Deviation, %
431.5	3,045	3,043	...
531.6	5,605	5,558	+0.8
606.1	7,550	7,520	+ .4
727.1	10,810	10,890	− .8
846.8	14,450	14,450	...
992.3	19,030	18,970	+ .3
1049.3	20,990	20,828	+ .8
1061.8	21,590	21,220	+1.7
1054.3	21,150	21,000	+0.7
1067.0	21,730	21,380	+1.6
1071.9	22,040	21,580	+2.1
(Orthorhombic to hexagonal transition at 806°)			
1091.4	26,720		
1156.7	29,100		
1190.8	30,450		
1228.6	31,880		
(Hexagonal to cubic transition at 968°)			
1245.3	33,170		
1274.3	34,300		
1311.0	35,690		

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(8) H. E. Von Gronow and H. E. Schwiete, *Z. anorg. Chem.*, **216**, 185 (1933).

(9) W. A. Roth and W. W. Bertram, *Z. Elektrochem.*, **35**, 297 (1929).

1.9 **Discussion of the Carbonate Results.**—Kelley,[2] after consideration of data from three investigations, assigns to $BaCO_3$ the specific heat equation

$$C_p = 17.26 + 13.1 \times 10^{-3}T \qquad (11)$$

for the range from room temperature to the first transition. The heat of the first transition he takes as 4,600, and he takes no account of the second transition. The agreement between equation 10 and equation 11 is fair. The values given by equation 10 at 1000°K. are about 5% higher than those of equation 11.

High temperature data for the specific heat and heat of transition of $SrCO_3$ have not been reported heretofore. It should be noted that a second transition has not been observed in $SrCO_3$ in tests carried to 1300°.

The observed values of ΔH in the range of about 40° just before the first transitions indicate rapid increases of C_p to maximum values about double those expected, but the largest observed deviations of ΔH from the calculated values are only about four times the average deviation, and therefore little accuracy can be claimed. It is unlikely that these results are due to inhomogeneities with lower transition temperatures, to very poor thermal equilibrium, or to an unusual sequence of errors. A more plausible explanation may be advanced. The transitions in the alkaline earth carbonates have been described as produced by increased rotational disorder of the carbonate ion.[10] Anomalous specific heats are associated with such transitions and, therefore, the observed results are interpreted as additional evidence for rotational disorder. The effect in the specific heat curve may be described as a lambda point, associated with transitions of the second kind, interrupted by a transition of the first kind.

2.0 Dissociation Pressures of $BaCO_3$ and $SrCO_3$

The dissociation pressure of $BaCO_3$ has been measured by Finkelstein[3] and Dutoit.[11] Their results agree to within about 5%. The work of Finkelstein covers the wider range. He also reports pressures for temperatures above and below the melting point of the eutectic. The dissociation pressure of $BaCO_3$ at the first transition (806°) is too low (about 10^{-2} mm.) to measure accurately by ordinary methods. The heat of the second transition is only about 1% of the total heat of dissociation so that the change in slope at this point in a pressure–temperature plot must be small.

The dissociation pressure of $SrCO_3$ has been the subject of a number of studies. Wide temperature ranges have been covered by Dutoit,[11] Jones and Becker,[12] and Tamaru and Siomi.[13] Their results are in good agreement between 900° and 1000° but near 1250° the results of Dutoit are higher than those of Jones and Becker, which in turn are higher than those of Tamaru and Siomi. The last two investigations cover a temperature range of more than one hundred degrees below the transition (at 924°). This transition was not considered by them nor was a change in slope reported. Since the heat of transition is almost 10% of the heat of dissociation the change in slope should be observable.

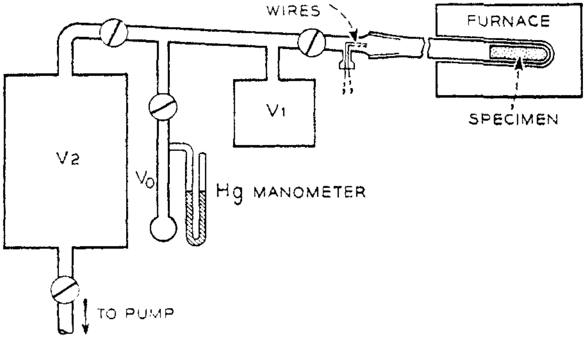

Fig. 1.—Apparatus for measuring the pressure of a condensable gas at low pressures.

2.1 **Apparatus and Materials.**—The diagram in Fig. 1 shows the apparatus used for the measurements. In principle, CO_2 at an equilibrium pressure in $V_0 + V_1$ or $V_0 + V_1 + V_2$ and at room temperature is condensed into V_0, brought to room temperature and the pressure measured with a mercury manometer. In practice the condensed gas was usually pumped at liquid air temperature to remove H_2, CO or CH_4, brought to room temperature and the pressure measured, then condensed and pumped at Dry Ice temperature after which a measurement of condensables in Dry Ice was made. The corrections obtained by this procedure were normally small but attained significance at pressures below 0.1 mm.

The volume V_0 depends on the pressure since it includes a portion of the manometer tube. The maximum correction at the highest pressures measured was about 2 cc., which was added to a constant volume of 8.66 cc. The volume V_1 was 376.7 cc. and the volume V_2 was 1395 cc. Thus the maximum obtainable amplification of pressure was about 205. Pressures above 10 mm. were observed directly on the manometer attached to the specimen chamber end of the system, which had a total volume of about 30 cc.

The specimen chamber was a 10″ × $^3/_8$″ i.d. porcelain tube of the type used for thermocouple wells. Sealed to a tube of 702P glass the chamber was found to be vacuum tight after baking and pumping. A platinum resistance furnace was constructed to cover 6″ of the end of the tube. The powdered specimen was placed in a 2″ × 0.35″ o.d. platinum capsule with walls equal to 0.012″. A calibrated Pt, Pt–10% Rh thermocouple was welded to the center of the capsule and brought out through glass seals above the glass-to-glass joint. The powder was packed into the capsule, then drilled to form a $^1/_{16}$″ passage running the length of the capsule. The weight of the charge was about 2 g.

The materials were of the ultra pure grade used in the specific heat measurements. After pumping thoroughly at about 500° the apparatus was filled with pure CO_2 at 200 mm. and heated to 1100° in the case of $SrCO_3$ and to 1200° in the case of $BaCO_3$. It was then cooled and again pumped thoroughly, after which measurements were made at temperatures up to the temperature at which the sample and chamber had been baked in CO_2. Equilibrium values as measured by the method of falling and rising temperatures were obtained in 15 minutes or less.

2.2 **Experimental Dissociation Pressures.**—The observed values for dissociation pressures of $SrCO_3$ are listed in Table VII. These data show a change in slope at the transition temperature. In the upper temperature range the results agree best with those obtained by Tamaru and Siomi.

TABLE VII

DISSOCIATION PRESSURES OF $SrCO_3$

T, °K.	p (mm.)	T, °K.	p (mm.)
1364	115.3	1158	4.21
1340	88.4	1137	2.84
1308	54.2	1117	2.08
1285	38.0	1113	1.71
1267	30.4	1077	0.706
1248	24.1	1052	0.378
1231	17.3	1023	.163
1209	11.9	999	.0804
1195	9.6	977	.0390
		969	.0335

Observed dissociation pressures for $BaCO_3$ are listed in Table VIII. It was not possible to obtain accurate values below the lower transition temperature with the apparatus used.

3.0 Calculated Dissociation Pressures

3.1 **Strontium Carbonate.**—A summation of equations 2, 8 and an equation for the specific heat

$$C_p = 9.69 + 3.47 \times 10^{-3}T - 1.64 \times 10^5T^{-2} \qquad (12)$$

of CO_2 calculated from the data of Kassel,[14] yields

$$\Delta C_p = 0.61 - 3.97 \times 10^{-3}T \qquad (13)$$

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[10] J. J. Lander, *J. Chem. Phys.*, **17**, 892 (1949).

[11] W. Dutoit, *J. chim. phys.*, **24**, 110 (1927).

[12] E. O. Jones and M. L. Becker, *J. Chem. Soc.*, 2669 (1927).

[13] S. Tamaru and K. Siomi, *Z. physik. Chem.*, **159**, 227 (1932).

[14] L. S. Kassel, This Journal, **56**, 1838 (1934).

TABLE VIII

DISSOCIATION PRESSURES OF $BaCO_3$

T, °K.	p (mm.)	T, °K.	p (mm.)
1073	0.0240	1271	1.77
1079	.0256	1317	4.10
1109	.0561	1329	5.42
1121	.0788	1362	8.90
1132	.0940	1395	14.6
1143	.118	1421	22.8
1161	.187	1435	26.3
1173	.249	1436	26.7
1179	.279	1477	52.0
1220	.681		

for the reaction $SrCO_3 = SrO + CO_2$. This may be used to calculate an equation for the dissociation pressure of $SrCO_3$ below 1197° K., using data from Table VII and the Σ method of Lewis and Randall. The calculated value of integration constant I_1 is -39.03 ± 0.03 units for $\Delta H_0 = 59{,}250$. Thus

$$\Sigma = -R \ln p\,(\text{atm.}) + 0.61 \ln T - 1.985 \times 10^{-3}T = \frac{59250}{T} - 39.03 \quad (14)$$

and

$$\log p\,(\text{atm.}) = \frac{12950}{T} + 0.3068 \log T - 0.4340 \times 10^{-3}T + 8.530 \quad (15)$$

In the same way, from data for the high temperature range and with ΔC_p equal to -6.4, I_2 is found to be -83.00 ± 0.06 units for $\Delta H_0 = 55{,}300$. Thus above 1197° K.

$$\log p\,(\text{atm.}) = -\frac{12080}{T} = 3.222 \log T + 18.140 \quad (16)$$

From (14) ΔH_{1197} is calculated to be 59,400 and from (16) 54,800 is the calculated value. The difference, 4,600, is in good agreement with the experimentally observed value 4,700 reported in Section 1.7.

3.2 Barium Carbonate.—Since the dissociation pressure data for $BaCO_3$ below the first transition are few and not very accurate they should be given no weight in a calculated dissociation pressure equation. Moreover precision cannot be claimed for the reported $\Delta C_p = -10.0$ for the intermediate phase. Therefore, it seems better to obtain a calculated equation from the low temperature thermodynamic data and a weighed value for the pressure at the transition. This should yield an equation more accurate over a wide range than that obtainable by other alternatives.

Summing equations 4, 10 and 12 obtain for the reaction $BaCO_3 = BaO + CO_2$.

$$\Delta C_p = 1.66 - 7.19 \times 10^{-3}T - 0.76 \times 10^{5}T^{-2} \quad (17)$$

$$\Delta H = \Delta H_{298.1} + [1.66T - 3.595 \times 10^{-3}T^2 + 0.76 \times 10^{-5}T^{-1}]\,\frac{T}{298.1} \quad (18)$$

$$\Delta S = \Delta S_{298.1} + [3.82 \log T - 7.19 \times 10^{-3}\,T + 0.38 \times 10^{-5}T^{-2}]\,\frac{T}{298.1} \quad (19)$$

The calculated value of K. K. Kelley and C. T. Anderson[1] for $\Delta S_{298.1}$ is 41.1, a value we believe to be high (we find it practically impossible to remove a residual 2% CO_2 from $BaCO_3$ under the conditions used by Anderson) and which we therefore have reduced to 40.6. The result is

$$\Delta F = \Delta H_{298.1} - 430 - 31.2T + 3.595 \times 10^{-3}T^2 + 0.38 \times 10^{5}T^{-1} - 3.82T \log T \quad (20)$$

Using the value 3.55×10^{-5} (atm.) for the dissociation pressure at 1079° K., obtained from data for the intermediate phase, 64,330 is calculated for $\Delta H_{298.1}$, and the calculated dissociation pressure equation is

$$\log p = \frac{13{,}970}{T} + 0.786 \times 10^{-3}T + 0.083 \times 10^{5}T^{-2} - 0.835 \log T - 6.82 \quad (21)$$

For the temperature range above 1079° K. the data of Table VIII may be represented by

$$\log p = \frac{13{,}075}{T} + 7.668 \quad (22)$$

The short form implies that the data for $BaCO_3$ are considered somewhat less accurate than those for $SrCO_3$.

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