The enthalpy of the over-all discharge reaction of the cell is equal to the sum of the heat liberated and the energy delivered to the load during discharge. The electrochemical equivalent is 1.61×10^3 amp.-min. per gram-equivalent. Thus the enthalpies obtained from experiments 1, 2, and 3 are 32.2, 33.9, and 32.4 kcal. per gram-equivalent, respectively. The molar enthalpy for the discharge reaction is about 64 kcal. per gram-mole based on these results.

The above results are in excellent agreement with the enthalpies obtained by other methods. Salkind and Bruins (2) determined the voltage of nickel-cadmium cells as a function of temperature. From these data, they calculated the enthalpy of the cell reaction from the Gibbs-Helmholtz equation to be 64 kcal. per gram-mole. Salkind and Bruins also calculated the enthalpy of the cell reaction by means of the vapor reference plot originally developed by Othmer and Gilmont (1). The application of this method to the data resulted in a value of 62 kcal. per gram-mole for this reaction.

Salkind and Bruins (2) have proposed the following simplified reaction for the nickel-cadmium cell:

$$2\,NiOOH + Cd + 2H_2O = 2Ni(OH)_2 + Cd(OH)_2$$

They have shown that an enthalpy of 64 kcal. per gram-mole for this reaction is in agreement with the known thermochemical data for the individual components in this reaction.

The results of this calorimetric study have shown that the quantities of heat liberated during discharge of nickel-cadmium cells are directly proportional to the extent of discharge. The heat losses during discharge of a typical cell are about 15% of the total energy obtained from the cell. The enthalpy of the cell reaction calculated from the calorimetric data is in excellent agreement with those obtained by other methods.

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Heat Content and Entropy of Strontium Chloride from 298° to 1200° K.

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The heat content and entropy of $SrCl_2$ from 298° to 1200° K. have been measured by means of a copper block drop calorimeter. The following equations for the heat content (cal. mole^{-1}) were obtained: $H_T - H_{298.15} = -4875 + 15.28T + 4.045 \times 10^{-3}T^2$ (298° to 940° K.); $H_T - H_{298.15} = -12{,}430 + 28.53T$ (1040° to 1146° K.); $\Delta H_{(fusion)} = 3850$ (1146° K.); and $H_T - H_{298.15} = -7070 + 27.22T$ (1146° to 1205° K.). A second order transition was found between the temperatures of about 940° and 1040° K.

STRONTIUM CHLORIDE, which has the calcium fluoride type of structure, was recently found to have an unusually low entropy of fusion of 3.4 e.u. (3). This suggested the existence of a transition in $SrCl_2$ similar to that known for CaF_2 which also has an unusually low entropy of fusion (5). The heat content measurements reported here show such a second order transition occurring in $SrCl_2$ about 140° below its melting point.

EXPERIMENTAL

Materials. Strontium chloride hydrate (containing less than 0.01% nonvolatile anions), which was pretreated in a vacuum desiccator over P_2O_5 for several days, was further dehydrated by slowly heating under vacuum for a period of several days to 100° below its melting point. The salt was melted in a stream of dry HCl gas, purged with argon, and filtered in situ through sintered quartz. The anhydrous $SrCl_2$ was free of foreign metals as determined spectrographically and showed no alkalinity from pyrohydrolysis.

Heat Content. The copper block calorimeter used for the measurements and the experimental procedure were previously described in detail (2). Measurements were made with two samples of $SrCl_2$ designated as Series I and II in Table I. The "run number" indicates the order in which the measurements were made. The defined calorie is equal to 4.184 absolute joules, and the molecular weight of $SrCl_2$ is 158.54 grams.

RESULTS

The measured heat contents of $SrCl_2$ are given in Table I. The following equations were obtained by the method of least squares for $H_T - H_{298.15}$ (cal. mole^{-1}).

$$H_T - H_{298.15} = -4{,}875 + 15.28T + 4.045 \times 10^{-3}T^2 \text{ (298-940° K.)} \quad (1)$$

$$H_T - H_{298.15} = -12{,}430 + 28.53T \text{ (1040-1146° K.)} \quad (2)$$

$$\Delta H\text{(fusion)} = 3{,}850 \text{ (1146° K.)} \quad (3)$$

$$H_T - H_{298.15} = -7{,}070 + 27.22T \text{ (1146-1205° K.)} \quad (4)$$

Table I. Measured Heat Contents of $SrCl_2$

Run No.	T, ° K.	$H_T - H_{298.15}$ Cal. Mole^{-1}
	Series I	
	Solid	
3	1033.7	16,960
4	1053.2	17,590
5	1072.8	18,180
6	1092.8	18,800
7	1109.8	19,230
10	1126.8	19,740
	Liquid	
8	1153.8	24,390
11	1156.7	24,490
2	1161.4	24,530
9	1165.5	24,710
1	1172.0	24,810
	Series II	
	Solid	
20	417.6	2,260
21	472.7	3,270
22	543.8	4,650
23	615.3	6,090
4	690.9	7,600
5	738.3	8,560
6	784.2	9,570
7	832.6	10,630
8	869.5	11,490
12	890.8	11,940
9	913.7	12,510
13	935.9	12,980
10	958.6	13,770
14	979.3	14,460
24	994.2	15,160
15	1007.9	15,810
11	1020.3	16,400
16	1043.2	17,260
3	1074.8	18,230
17	1104.5	19,110
18	1134.2	19,880
	Liquid	
2	1156.0	24,350
1	1178.9	25,000
19	1204.0	25,720

The fit of the above equation is $\pm 0.2\%$ while the estimated over-all accuracy is $\pm 0.5\%$.

Figure 1 shows that the transition occurs gradually between the temperatures of about 940° and 1040° K. with no discontinuity in the heat content curve. The smoothed heat content values in this temperature range which appear in Table II were obtained from the curve since no equation was calculated for the transition temperature range. The entropy values in Table II were calculated from the heat content data by the method suggested by Kelley (*4*).

The possibility that some disorder is quenched in, always exists if a drop calorimeter is used for measurements involving a slow transformation. Therefore, an additional measurement was made in which the sample was annealed for about 70 hours at 890° K. and then cooled over a period of 4 hours to 798° K. before the drop was made. The heat content of this run, 9870 cal. agrees very well with the results reported above. A number of low temperature points (runs number 20, 4, and 12) were obtained following drops from the higher temperatures. This information,

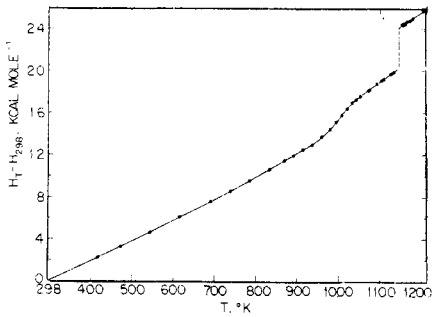

Figure. 1. Heat content of $SrCl_2$ as a function of temperature

Table II. Smoothed Values of Heat Content and Entropy for $SrCl_2$

T, ° K.	$H_T - H_{298.15}$ Cal. Mole^{-1}	$S_T - S_{298.15}$ Cal. Deg.$^{-1}$ Mole^{-1}	T, ° K.	$H_T - H_{298.15}$	$S_T - S_{298.15}$
400	1,885	5.45	990	14,950	24.78
500	3,780	9.62	1000	15,430	25.26
600	5,750	13.22	1020	16,420	26.23
700	7,805	16.39	1050	17,530	27.31
800	9,940	19.24	1100	18,950	28.64
900	12,160	21.84	1146(*c*)	20.270	29.82
930	12,860	22.60	1146(*l*)	24,120	33.18
950	13,380	23.17	1200	25,590	34.42
970	14,090	23.91			

together with the smoothness of the data, is a good indication that disorder was not quenched in. However, although the present results are certainly qualitatively indicative of the transformation, they cannot be regarded as definitive (especially in the temperature region 940° to 1040° K.) until corroboration by other calorimetric methods is obtained.

It is of interest to consider the possible nature of the second order transition observed here. The particular geometry of the fluorite type of lattice structure, which includes interstitial spaces at:

$$\frac{111}{222}, \frac{1}{2}00, 0\frac{1}{2}0, \text{ and } 00\frac{1}{2}$$

that are of the size and shape of the cations, suggests the possibility of disordering either in the cation or the anion semilattice. On the basis of x-ray diffraction measurements, the anion type of disorder has been reported by Croatto and Bruno (*1*) to occur in strontium chloride. Measurements are in progress at this laboratory to confirm that the transformation in CaF_2 is of similar nature.

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