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Thermal Properties of Alkali Halide Crystals with the CsCl-type Structure. I.*[1] Construction of a Calorimeter for the Temperature Region 1—20°K and Heat Capacities of Caesium Bromide and Caesium Iodide between 1.5 and 300°K

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An adiabatic low-temperature calorimeter, capable of measuring the heat capacities of solid or liquid between 1.4 and 21.0°K, was constructed. A mechanical thermal switch is used for cooling the sample cell, the temperature of which is measured with a doped germanium thermometer. The resistance-temperature calibration data for the resistor was fitted to a function of the form $\log_{10}R=A/T+B+CT+DT^2$. By using this formula the thermodynamic temperature scale is represented to within ±0.02°K and by combining the correction curves the final deviations of the calibration data from the thermodynamic temperature scale were within ±0.003°K in the whole temperature range investigated. The heat capacity measurements of CsBr and CsI crystals were made with two kinds of adiabatic calorimeter assemblies, one for the temperature range 1.4 to 21°K and the other for the range 12 to 300°K. Values of the heat capacity $C_p°$, entropy $S°$, enthalpy function $(H°-H_0°)/T$, and Gibbs energy function $-(G°-H_0°)/T$, at 298.15°K are: 12.441, 26.785, 10.415, and 16.370 for CsBr and 12.571, 29.127, 10.788, and 18.339 for CsI, respectively, in cal·mol^{-1}·°K^{-1}.

It is of some interest to note the fact that the alkali halides crystallize at standard temperature and pressure in the NaCl-type structure, with the exception of CsCl, CsBr, and CsI which crystallize in the CsCl-type structure, although polymorphic transitions between the NaCl and CsCl structure have been observed to occur for some of these crystals with increasing temperature or pressure. Although a great deal of work has been done on the alkali halides with the NaCl structure, theoretical and experimental studies of the alkali halide crystals with the CsCl structure seem to have received little attention in the past. Some theoretical investigations have been made to interpret which structure will be more stable under a given set of conditions. Among them Mayer[1] showed that van der Waals potential contributes to the stability of the CsCl-type lattice for CsCl, CsBr, and CsI at absolute zero. Tosi and Fumi[2] succeeded in establishing which phase has the lower free energy and is thus thermodynamically more stable under a given set of conditions. From the standpoint of lattice dynamics Hardy and Karo[3] accounted for the instability of the NaCl-type lattice under the condition just below the pressure-induced phase transition. Some experimental results[4-7] have been also reported in which the difference in the crystal structures seems to be reflected.

The purpose of the present investigation is to obtain detailed thermal data on CsBr and CsI crystals in the temperature range from 1.5 to 300°K, and, in particular, to study how the difference in structure is reflected in their thermal properties. An adiabatic calorimeter for the heat capacity measurements below 20°K is also described.

Experimental

Calorimeter and Cryostat. The main parts of the adiabatic calorimeter consist of calorimeter cell, cryostat, thermometer and electrical circuit. Figure 1 shows diagrammatically the cryostat assembly and its essential features are depicted in Fig. 2. There are two refrigerant compartments; an outer one (for the liquid nitrogen) consisting of a stainless-steel Dewar vessel and an inner one (for the liquid helium or liquid

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*[1] The first half was read before the 18th Annual Meeting of the Chemical Society of Japan (1965), Osaka and the latter half before the 1st Japanese Calorimetry Conference (1965), Osaka.

[1] J. E. Mayer, *J. Chem. Phys.*, **1**, 270 (1933).

[2] M. P. Tosi and G. F. Fumi, *J. Phys. Chem. Solids*, **23**, 359 (1962).

[3] J. R. Hardy and A. M. Karo, "Lattice Dynamics," Pergamon Press, Oxford (1964), p. 195.

[4] E. E. Havinga and A. J. Bosman, *Phys. Rev.*, **140**, A292 (1965).

[5] S. P. Nikanorov and A. V. Stepanov, *Fizika Tverdogo Tela*, **6**, 1987 (1964) (English translation; *Soviet Phys.—Solid State*, **6**, 1569 (1965)).

[6] S. P. Nikanorov, A. A. Nran'yan and A. V. Stepanov, *Fizika Tverdogo Tela*, **6**, 1996 (1964) (English translation; *Soviet Phys.—Solid State*, **6**, 1576 (1965)).

[7] G. K. White, *Proc. Roy. Soc.*, **A286**, 204 (1965).

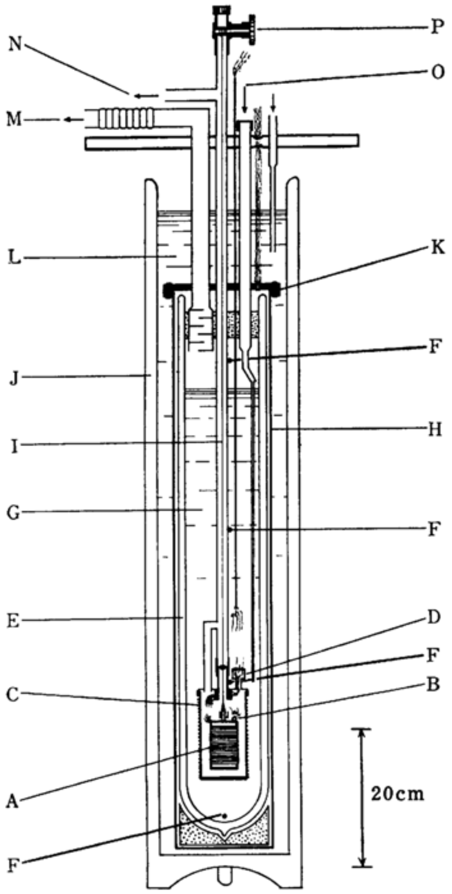

Fig. 1. Calorimeter and liquid helium cryostat assembly: (A) calorimeter cell; (B) germanium resistance thermometer; (C) vacuum jacket; (D) hermetic seals for lead outlets; (E) glass Dewar; (F) carbon resistors for level indicator; (G) liquid He or H_2; (H) brass jacket; (I) nylon thread; (J) metal Dewar vessel; (K) compression seal with a lead O-ring; (L) liquid N_2; (M) liquid He pumping line; (N) to high vacuum pump; (O) liquid He transfer tube; (P) winch.

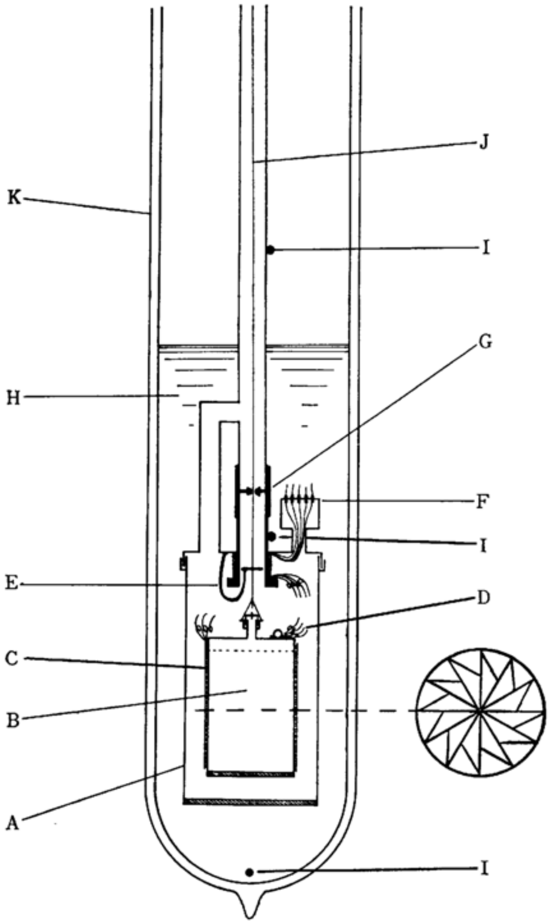

Fig. 2. Schematic diagram of low-temperature calorimeter (1.4−21.0°K): (A) vacuum jacket; (B) calorimeter cell; (C) heating element; (D) germanium resistance thermometer; (E) radiation shield; (F) hermetic seals for lead outlets; (G) radiation shield; (H) liquid He or H_2; (I) carbon resistors for level indicator; (J) nylon thread; (K) glass Dewar.

hydrogen) consisting of a large glass Dewar of approximately 7 *l* capacity. Carbon resistors (Allen-Bradley, 47 Ω nominal resistance) positioned conveniently on the stainless-steel tube serve as useful refrigerant-level indicators. The third innermost compartment, which houses the high vacuum for the calorimeter cell, consists of a brass can apart from its bottom made of thick copper plate. All conduits are made of stainless-steel. To prevent that large amount of energy is imparted to a sample from room temperature radiation, two radiation traps are placed at the bottom of the central tube (E and G in Fig. 2). Styro-form plate located at the entrant of the glass Dewar also serves as a radiation shield from liquid nitrogen temperature.

The body of the calorimeter cell consists of a cylinder of copper. Thin copper fins project radially from a small tube which is centrally located along the vertical axis of the calorimeter (see Fig. 2). These fins are soldered with the tube and the calorimeter wall. The filling tube of the calorimeter cell is fitted with a small brass cap to the center of which is brazed a short piece of tubulation that permits evacuation of the sample in the calorimeter and filling helium gas for heat exchange. The diameter of the calorimeter cell is about 4.5 cm, the overall length (including cap) being approximately 9 cm and the volume about 110 cm^3.

A Minneapolis-Honeywell germanium resistor (Honeywell Series II) was used as a working thermometer. It was firmly embedded in a small copper pipe brazed to the top of the calorimeter. To further insure the good thermal contact it was varnished (GE adhesive ♯ 7031). The current used for the measurements of resistance of the germanium resistor was selected as to render maximum accuracy; *i. e.* in the liquid helium region varied from 2.0 to 10.0 μA and in the liquid hydrogen region from 10 to 30 μA. The details of the calibrations of the thermometer will be described in the next section.

The heating element of the calorimeter is formed of about 1000 ohms of a strain-free constantan wire (Driver-Harris Co., ♯36). The wire was wound non-inductively around the calorimeter cell and varnished to insure good thermal contact. To minimize any exchange of energy between the calorimeter and the environment (refrigerant bath) the lead wires from the heating element and the thermometer were made thermal contact with the periphery of the calorimeter and coiled helically in the vacuum space. These wires entered the refrigerant compartments by means of hermetic seals (New Nippon Electric Co., Ltd., ♯A241). The electrical circuits for energy supply are the same as those for the calorimeter⁸⁾ previously described, which is operative in the temperature range 12 to 300°K. Determinations of the heat input and the resistances of the thermometer were all made on a Wenner-type potentiometer (Leeds & Northrup Co.). The heating time was read on a timer placed in the energy circuit.

The mechanical thermal switch consists of a "make and break" contact between the smoothly polished surface of the bottom of the calorimeter cell and the bottom of the vacuum jacket. The vertical movement of the cell is controlled by a winch mechanism located at the top of the cryostat. The connection between the winch and the calorimeter is accomplished by a fine nylon thread. The "making and breaking" of the contact is detected through a micro-ammeter by the "on and off" of the current controlled by the thermal switch. By means of this device the calorimeter cell may be cooled conveniently from room temperature down to about 1.4°K (lowest pumping temperature) in a vacuum better than 10^{-6} Torr without the use of any heat exchange gas.

Temperature Scales. The germanium resistance thermometer was calibrated in the temperature range from 1.4 to 4.4°K against the vapor pressure temperature scale (the T_{58} scale) compiled by Brickwedde *et al.*⁹⁾ In the temperature range between 11.8 and 21.0°K, on the other hand, the thermometer was calibrated against a Leeds & Northrup platinum resistance thermometer certified by the National Bureau of Standards (the NBS scale). These calibrations were performed by separate experiments before the germanium thermometer being fixed to the calorimeter. To complete the calibration of a germanium thermometer, some adequate functional relationships between resistance, R, and temperature, T, should be needed. Such attempts to find an empirical formula were made by, for examples, Lindenfeld,¹⁰⁾ Ahlers,¹¹⁾ and Cataland and Plumb.¹²⁾ In the present case, however, a rather simple formula¹³⁾ of the form,

$$\log_{10} R = A/T + B + CT + DT^2, \qquad (1)$$

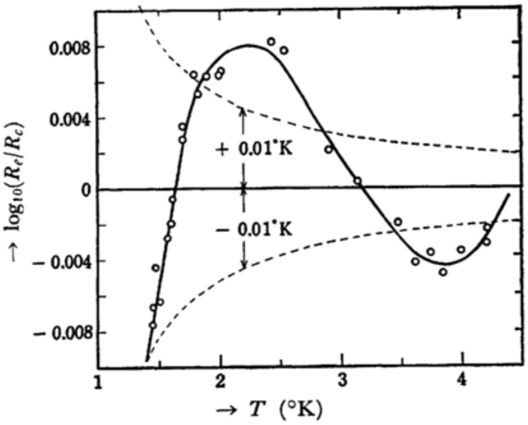

Fig. 3. Correction curve for the calibration of the germanium thermometer in the range 1.4 to 4.4°K.

was fitted to the experimental R_e and T_e calibration data of the germanium resistor by the method of least squares, where A, B, C, and D are numerical constants. A comparison between the R_e and the R_c (calculated value from formula (1)) is illustrated in Fig. 3 in the case of liquid helium temperature region. It is clear in the figure that formula (1) may reproduce the R_e and T_e relationship within ±0.02°K. The same held well in the liquid hydrogen temperature region where the last term of the right-hand side of formula (1) was

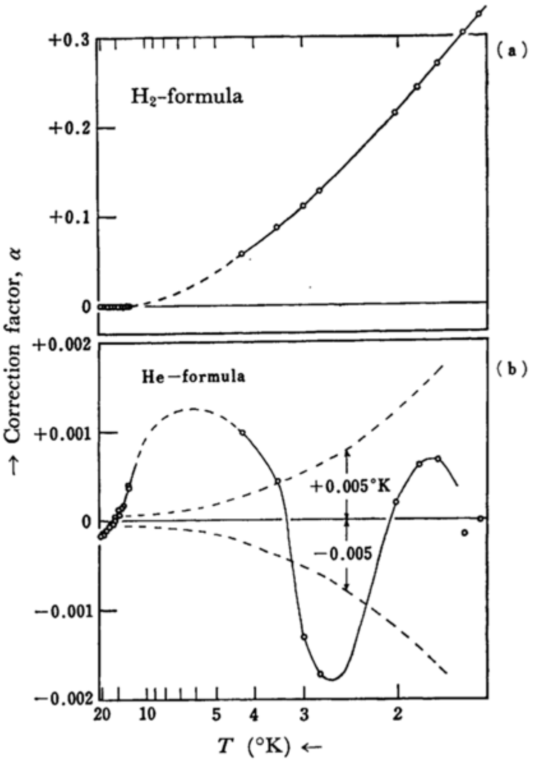

Fig. 4. Determination of the correction factor, α, for the carbon resistor in the range 4.4 to 11.8°K.

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8) H. Suga and S. Seki, This Bulletin, **38**, 1000 (1965).

9) F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement and J. K. Logan, *J. Res. Nat. Bur. Stand.*, **64A**, 1 (1960).

10) P. Lindenfeld, *Rev. sci. Instrum.*, **32**, 9 (1961).

11) G. Ahlers, *J. Chem. Phys.*, **41**, 86 (1964); *Phys. Rev.*, **135**, A10 (1964).

12) G. Cataland and H. H. Plumb, *J. Res. Nat. Bur. Stand.*, **70A**, 243 (1966).

13) M. Sorai, H. Suga and S. Seki, Preprints for the 18th Annual Meeting of the Chemical Society of Japan (April, 1965), 32311.

omitted. To improve the effectiveness of formula (1), it is necessary to define a correction term as

$$\Delta = \log_{10} R_e - \log_{10} R_c. \qquad (2)$$

Finally the smoothed values of resistance of the germanium resistor, R_s, were calculated by the following formula,

$$\log_{10} R_s = A/T + B + CT + DT^2 + \Delta, \qquad (3)$$

and the tables of R_s *versus* T were made every interval of 0.01°K in the region 1.40 to 4.40°K and of 0.1°K in the region 11.8 to 21.0°K by the NEAC 2203 computer. Deviations of the calibration points, T_e, from formula (3) are shown in Fig. 6. In order to check the stability of thermometer after temperature cycling the calibrations were repeated six times and no significant changes were observed. This fact is consistent with the results by Kunzler *et al.*,14) and Plumb *et al.*15) The final deviations of the calculated curve by using formula (3) from the T_{58} scale and the NBS scale, respectively, are within ±0.003°K.

In general a commercially available germanium resistance thermometer had disadvantages such as that the resistance-temperature relation is complicated and should be established by calibration at many temperatures. Thus, without the use of a gas thermometer there is no method for evolving a "working" temperature scale between the liquid helium and the liquid hydrogen temperature region, *i. e.* 4.4—11.8°K, as far as a germanium resistor is used. For these reasons there is always an uncertainty in evaluating the thermodynamic temperature scale in this region, so the high-precision calorimetric investigations in this temperature region are rather scarce. An attempt has been made by DeSorbo and Nichols16) to circumvent

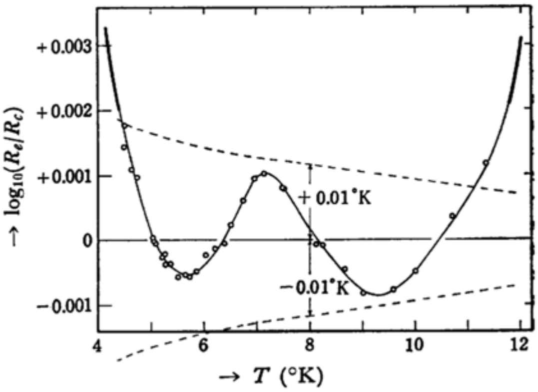

Fig. 5. Correction curve for the germanium thermometer in the temperature range 4.4 to 11.8°K.

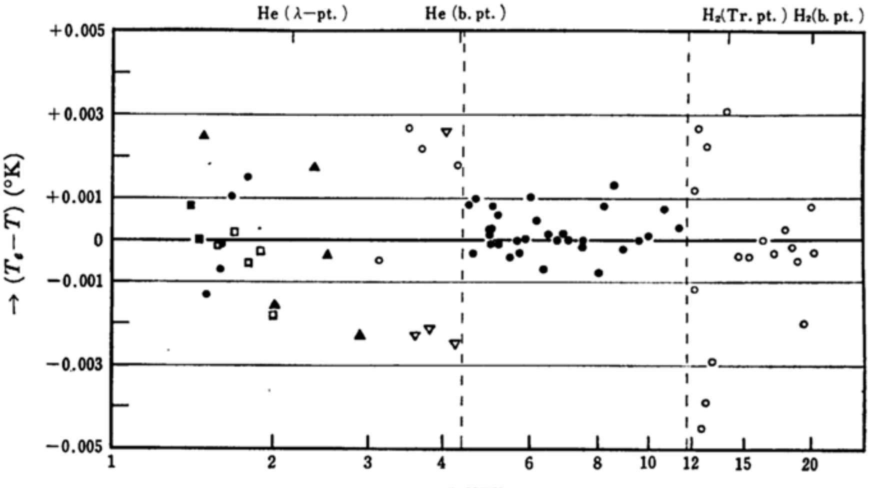

Fig. 6. Deviations of the calibration points for the germanium thermometer from the T_{58} scale (1.4—4.4°K), from "the Carbon scale" (4.4—11.8°K), and from the NBS scale (11.8—21.0°K). Various marks in the liquid helium region mean different runs of the calibration.

TABLE 1. SPECTROGRAPHIC ANALYSIS OF THE SALTS

Compound	Impurity, percent					
	K	Na	Rb	Ca	Mg	Al
CsBr	<0.01	<0.01	<0.01	0.06	<0.01	<0.01
CsI	<0.01	<0.01	<0.01	0.06	<0.01	<0.01

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14) J. E. Kunzler, T. M. Geballe and G. W. Hull, Jr., "Temperature. Its Measurement and Control in Science and Industry," Vol. 3, Part 1, Reinhold Pub. Corp., New York (1962), p. 391.

15) M. H. Edlow and H. H. Plumb, *ibid.*, Vol. 3, Part 1 (1962), p. 407.

16) W. DeSorbo and G. E. Nichols, *J. Phys. Chem. Solids*, **6**, 352 (1958).

this problem, at least approximately, with a careful analysis of the carbon resistor data obtained both in the liquid helium and liquid hydrogen temperature regions. The working temperature scale adopted here between 4.4 and 11.8°K is based on this convenient method, that is to say "the Carbon scale". The procedure adopted is to evaluate the correction factor, α, for the region 1.4—4.4°K and 11.8—21.0°K, first by using the constants A and B evaluated from the R-T data for the liquid hydrogen region (see Fig. 4(a)) and secondly by using constants A and B determined for the liquid helium region (Fig. 4(b)). Here A and B are constants appeared in the formula, $\sqrt{(\log R)/T}=A\log R+B$, for the R-T relation of carbon resistor proposed by Clement and Quinnell.17) By a method of successive approximation, the two interpolated segments of the curves shown in Figs. 4(a) and 4(b) by broken lines were determined to give a minimum discrepancy in $\Delta T(T(\mathrm{H_2}\text{-formula})-T(\text{He-formula}))$. Uncertain deviations of "the Carbon scale" from the thermodynamic temperature scale will probably be introduced in the process of drawing the interpolated segments. An ambiguity in this procedure, however, does not seem to exceed ± 0.02°K (see Figs. 4(a) and 4(b)). The working temperature scale for the germanium resistance thermometer was, thus, established by using both "the Carbon scale" and the formula (3).

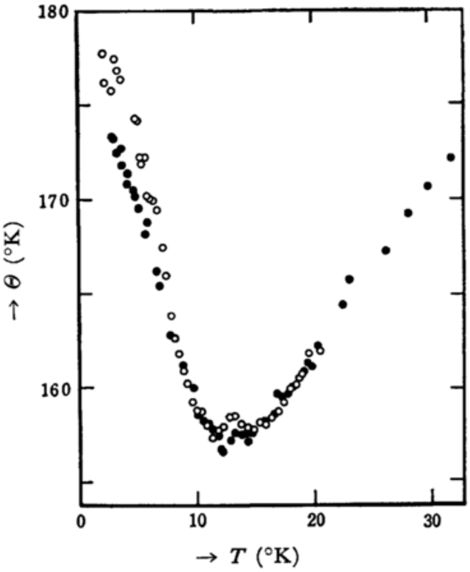

Fig. 7. Comparison of the heat capacity of KBr in terms of the Debye characteristic temperature below 21°K: ○, present work; ●, Berg and Morrison.18)

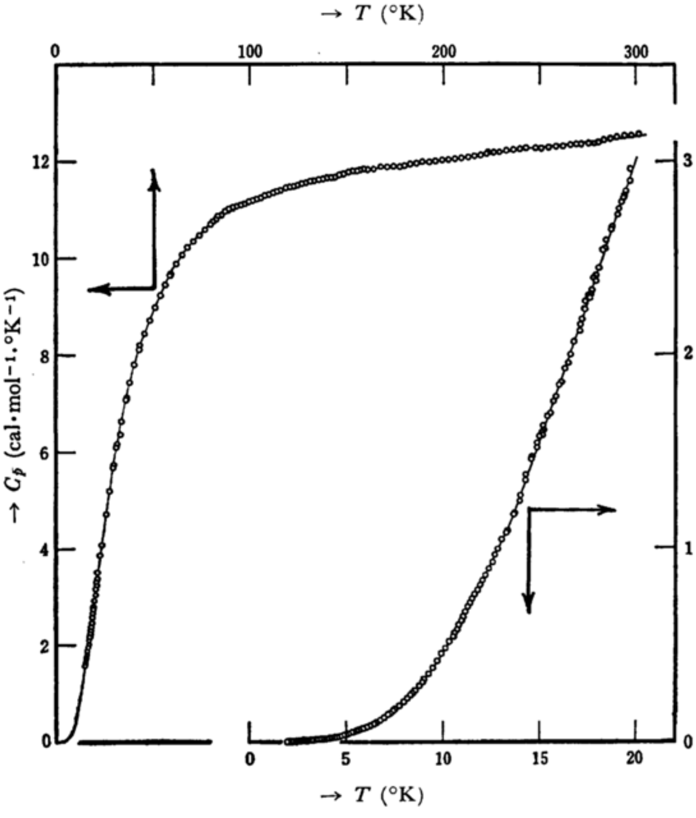

Fig. 8. Heat capacity of CsBr in the temperature region from 1.5 to 300°K.

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17) J. R. Clement and E. H. Quinnell, *Rev. sci. Instrum.*, **23**, 213 (1952).

18) W. T. Berg and J. A. Morrison, *Proc. Roy. Soc.*, **A242**, 467 (1957).

The correction curve in this region is illustrated in Fig. 5. Two thick solid lines in the vicinity of 4 and 12°K mean the T_{58} scale and the NBS scale, respectively. Final deviation plots of all the calibration points for the germanium resistor from "the Carbon scale" are shown in Fig. 6.

Materials. Powder crystals of CsBr and CsI of high purity optical grade were obtained from Mitsuwa's Pure Chemicals. The salts were recrystallized twice from distilled water and then dried at temperatures between 100 and 120°C in a vacuum for 15 hr. The results of spectrographic analysis of this purified samples are given in Table 1. Potassium bromide crystal of high purity optical grade was obtained from E. Merck AG. Procedure of purification was the same as mentioned above.

For the heat capacity measurements in the temperature range 1.5 to 21.0°K the calorimeter contained 104.743 g (0.49219 mol) of CsBr, 184.462 g (0.70999 mol) of CsI, and 150.582 g (1.2653 mol) of KBr, respectively, as well as a small amount of helium exchange gas. For the measurements at higher temperatures, on the other hand, the calorimeter contained 43.8972 g (0.20627 mol) of CsBr and 46.2041 g (0.17784 mol) of CsI, respectively, and helium gas as heat exchanger.

Heat Capacities of CsBr and CsI. The heat capacity measurements were made with the low-temperature adiabatic calorimeter (denoted as calorimeter-A hereafter) described above in the temperature region 1.5 to 21.0°K and with the automatic adiabatic calorimeter[8)] (calorimeter-B) described previously in the range 15 to 300°K. Approximately 230 heat capacity data were determined for CsBr and CsI with various small temperature rise (0.05—0.5°K below 20°K and 1—3°K above 15°K).

The Precision and Accuracy of the Measurements. The scatter of the results obtained with the calorimeter-A is at worst ±3% at the lowest temperatures and ±1% for $T>4$°K. The precision of the calorimeter-B appears to be ±2% for $T<20$°K, ±1% for $20°\text{K}<T<50°\text{K}$, and ±0.3% for $T>50$°K. The accuracy is more difficult to assess. It is likely that the most serious error arises from the uncertainty in temperature scales. The accuracy has therefore to be judged by comparison of results obtained from independent assemblies. A comparison of the two sets of results between 15 and 21°K provides a measure of accuracy in this range. For each of two salts the average deviation of one set from the other was within the experimental errors. The accuracy of the calorimeter-B had been checked previously[8)] by using it to measure the heat capacity of the Calorimetry Conference sample of benzoic acid in the temperature range 13 to 300°K. Another comparison may also be made with the measurements of other workers. In order to check the accuracy of the calorimeter-A heat capacity of potassium bromide was also measured between 1.5 to 21°K. The results are compared with the data by Berg and Morrison[18)] in Fig. 7 in terms of the Debye characteristic temperature. Agreement between them seems to be very satisfactory if the experimental errors are taken into account. For caesium iodide heat

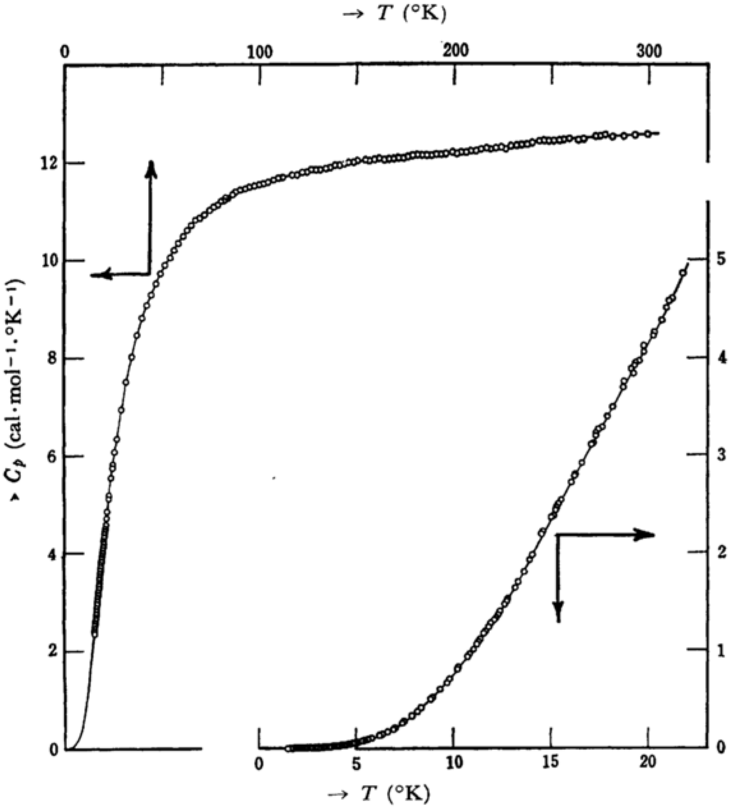

Fig. 9. Heat capacity of CsI in the temperature region from 1.5 to 300°K.

TABLE 2. HEAT CAPACITY OF CsBr
(Molecular weight 212.809)

T (°K)	C_p (cal/mol·°K)	T (°K)	C_p (cal/mol·°K)	T (°K)	C_p (cal/mol·°K)	T (°K)	C_p (cal/mol·°K)
	Calorimeter-A				Calorimeter-B		
2.810	0.00596	11.962	0.8083	15.100	1.579	122.935	11.507
3.242	0.00955	11.993	0.8252	17.233	2.183	125.088	11.523
3.358	0.01046	12.160	0.8568	19.260	2.794	127.231	11.556
3.493	0.01192	12.280	0.8804	19.373	2.814	129.365	11.563
3.757	0.01473	12.439	0.9164	21.701	3.509	131.490	11.597
3.877	0.01624	12.663	0.9739	22.830	3.884	133.651	11.607
4.282	0.02224	12.849	0.9967	23.538	4.097	135.848	11.631
4.688	0.02942	12.981	1.049	26.014	4.722	138.037	11.652
4.699	0.02998	13.607	1.186	27.777	5.206	140.219	11.673
4.913	0.03540	13.924	1.270	29.869	5.744	142.394	11.690
5.101	0.03972	14.200	1.329	31.726	6.161	144.564	11.688
5.258	0.04423	14.243	1.355	33.899	6.637	146.727	11.736
5.270	0.04458	14.510	1.415	36.103	7.082	148.884	11.758
5.476	0.05049	14.571	1.428	38.164	7.440	151.083	11.785
5.711	0.05784	14.822	1.484	40.392	7.795	153.324	11.807
5.920	0.06606	14.869	1.511	42.985	8.106	155.560	11.803
6.107	0.07366	15.108	1.563	45.659	8.441	158.599	11.843
6.323	0.08319	15.402	1.670	48.566	8.734	161.082	11.848
6.562	0.09477	15.561	1.687	51.336	8.981	164.449	11.837
6.774	0.1067	15.714	1.752	53.995	9.227	171.132	11.904
6.950	0.1180	15.864	1.781	56.563	9.443	174.506	11.899
6.968	0.1190	15.997	1.844	59.396	9.691	179.759	11.929
7.183	0.1348	16.171	1.854	62.062	9.880	183.056	11.945
7.254	0.1404	16.295	1.926	64.980	10.071	186.345	11.965
7.417	0.1529	16.481	1.960	68.140	10.223	189.527	11.986
7.519	0.1622	16.601	2.000	71.207	10.340	192.899	12.009
7.753	0.1824	16.798	2.071	74.250	10.462	196.214	12.015
7.966	0.2030	17.099	2.128	77.215	10.584	199.570	12.041
8.177	0.2240	17.110	2.161	80.127	10.696	202.918	12.049
8.388	0.2466	17.374	2.238	81.534	10.753	206.259	12.061
8.601	0.2694	17.644	2.302	82.992	10.798	209.612	12.076
8.815	0.2937	17.753	2.317	83.496	10.893	212.980	12.098
9.029	0.3218	17.913	2.382	85.516	10.901	216.340	12.127
9.265	0.3523	17.966	2.407	87.559	10.983	219.523	12.141
9.494	0.3835	18.119	2.451	89.586	11.025	222.865	12.173
9.705	0.4156	18.439	2.560	91.594	11.053	226.300	12.185
10.158	0.4842	18.760	2.661	93.647	11.081	229.626	12.203
10.404	0.5240	19.053	2.736	95.747	11.106	232.944	12.229
10.548	0.5464	19.091	2.764	97.832	11.143	236.252	12.253
10.610	0.5613	19.357	2.836	99.903	11.183	239.583	12.273
10.659	0.5685	19.426	2.852	101.963	11.210	247.602	12.252
10.786	0.5984	19.747	2.889	104.011	11.244	251.128	12.271
10.913	0.6134	20.318	3.055	106.047	11.274	254.645	12.275
11.031	0.6341	20.346	3.144	108.113	11.314	258.323	12.293
11.086	0.6492	20.645	3.226	110.207	11.339	262.142	12.309
11.170	0.6620	20.663	3.217	112.290	11.374	265.933	12.326
11.429	0.7190			114.363	11.403	269.715	12.339
				116.427	11.422	270.987	12.345
				118.771	11.475	278.834	12.363
				120.832	11.485	280.605	12.393

TABLE 3. HEAT CAPACITY OF CsI
(Molecular weight 259.809)

T (°K)	C_p (cal/mol·°K)	T (°K)	C_p (cal/mol·°K)	T (°K)	C_p (cal/mol·°K)	T (°K)	C_p (cal/mol·°K)
Calorimeter-A				29.433	6.959	148.358	12.008
1.501	0.00149	6.910	0.2016	32.083	7.534	150.704	12.043
1.760	0.00254	6.956	0.2062	34.817	8.035	154.228	12.071
1.931	0.00335	7.366	0.2574	37.465	8.479	156.730	12.043
2.091	0.00424	7.480	0.2714	39.974	8.816	159.219	12.063
2.175	0.00460	7.857	0.3279	42.342	9.086	161.703	12.081
2.249	0.00518	8.150	0.3764	44.615	9.309	164.183	12.050
2.309	0.00547	8.358	0.4117	46.999	9.527	166.652	12.069
2.440	0.00655	8.835	0.5016	49.465	9.730	169.120	12.059
2.557	0.00761	8.901	0.5137	51.847	9.899	171.584	12.097
2.568	0.00764	9.330	0.6019	54.154	10.062	174.041	12.083
2.694	0.00885	9.643	0.6735	56.399	10.197	176.492	12.118
2.709	0.00930	9.806	0.7119	58.589	10.351	178.939	12.152
2.817	0.01026	10.255	0.8231	60.731	10.496	181.382	12.152
2.860	0.01082	10.725	0.9427	62.892	10.617	183.823	12.142
2.947	0.01174	10.793	0.9667	65.077	10.721	186.086	12.153
3.016	0.01287	11.025	1.032	67.166	10.820	188.516	12.137
3.090	0.01352	11.182	1.074	69.502	10.860	190.938	12.174
3.186	0.01503	11.281	1.110	71.803	10.923	193.357	12.147
3.239	0.01561	11.307	1.124	74.159	11.031	195.772	12.168
3.244	0.01579	11.580	1.204	76.573	11.104	199.057	12.233
3.361	0.01784	11.646	1.216	78.953	11.127	201.488	12.183
3.408	0.01858	11.807	1.270	80.265	11.234	203.920	12.196
3.546	0.02112	11.933	1.288	81.396	11.201	206.355	12.199
3.604	0.02225	12.136	1.352	83.903	11.271	208.783	12.227
3.737	0.02515	12.322	1.394	86.380	11.349	211.250	12.231
3.805	0.02658	12.752	1.527	90.226	11.444	213.755	12.273
3.931	0.02922	13.266	1.702	92.733	11.469	218.758	12.259
3.983	0.03092	13.862	1.915	95.220	11.495	221.420	12.289
4.136	0.03369	14.473	2.140	97.670	11.536	224.082	12.302
4.364	0.04020	15.361	2.477	100.119	11.561	232.026	12.339
4.546	0.04677	15.514	2.527	102.574	11.566	234.666	12.355
4.594	0.04794	16.203	2.790	104.999	11.608	237.311	12.347
4.830	0.05744	16.572	2.924	107.396	11.651	239.951	12.392
5.074	0.06793	17.057	3.112	109.776	11.676	245.927	12.418
5.373	0.08350	17.108	3.124	112.143	11.696	248.553	12.430
5.430	0.08670	17.901	3.409	116.913	11.764	251.183	12.400
5.816	0.1105	18.708	3.705	119.414	11.759	253.813	12.396
6.207	0.1377	19.492	3.964	121.895	11.800	256.438	12.450
6.321	0.1472	20.272	4.247	124.363	11.809	264.190	12.450
6.578	0.1681	20.703	4.431	126.815	11.855	266.805	12.478
				129.252	11.847	272.474	12.547
Calorimeter-B				131.677	11.852	275.074	12.551
15.269	2.254	21.271	4.581	134.089	11.874	277.674	12.561
17.282	3.208	22.816	5.158	136.490	11.915	281.569	12.513
19.286	3.940	24.755	5.757	138.883	11.960	287.186	12.524
19.335	3.948	24.954	5.821	141.267	11.942	293.218	12.547
20.954	4.538	25.903	6.088	143.639	11.968	299.212	12.569
21.098	4.576	27.027	6.357	146.003	11.995		

capacity data have been reported by Taylor *et al.*[19] in the range 13 to 300°K. They agree with the present results to within ±1% above 60°K, but the systematic deviation appears with decreasing temperature to amount to +5% below 20°K. Heat capacities of CsBr and CsI above room temperature have been reported by Brönsted.[20] His value is 0.6% higher at 300°K for CsBr and 1.4% higher for CsI.

TABLE 4. THERMODYNAMIC PROPERTIES OF CsBr CRYSTAL (in cal/mol·°K)

T (°K)	$C_p°$	$S°$	$\frac{H°-H_0°}{T}$	$-\frac{(G°-H_0°)}{T}$
2	0.00216	0.00108	0.00067	0.00041
4	0.01798	0.00662	0.00471	0.00191
6	0.06923	0.02239	0.01657	0.00582
8	0.2059	0.05905	0.04496	0.01409
10	0.4588	0.1308	0.1011	0.0297
15	1.549	0.5043	0.3863	0.1180
20	3.008	1.147	0.8567	0.2902
25	4.467	1.977	1.434	0.5423
30	5.766	2.910	2.052	0.8582
35	6.859	3.884	2.663	1.221
40	7.704	4.857	3.242	1.615
45	8.377	5.804	3.777	2.027
50	8.923	6.716	4.265	2.451
60	9.728	8.418	5.112	3.306
70	10.315	9.965	5.816	4.149
80	10.700	11.369	6.404	4.965
90	10.993	12.647	6.898	5.749
100	11.184	13.815	7.318	6.497
110	11.339	14.889	7.677	7.212
120	11.473	15.881	7.987	7.894
130	11.583	16.804	8.260	8.544
140	11.675	17.666	8.501	9.165
150	11.767	18.475	8.715	9.760
160	11.835	19.237	8.909	10.328
170	11.885	19.956	9.082	10.874
180	11.932	20.636	9.239	11.397
190	11.990	21.283	9.382	11.901
200	12.040	21.899	9.514	12.385
210	12.085	22.488	9.635	12.853
220	12.128	23.051	9.748	13.303
230	12.175	23.591	9.852	13.739
240	12.220	24.110	9.950	14.160
250	12.262	24.610	10.042	14.568
260	12.305	25.092	10.128	14.964
270	12.345	25.557	10.209	15.348
280	12.381	26.006	10.286	15.720
290	12.416	26.441	10.359	16.082
300	12.447	26.863	10.428	16.435
273.15	12.356	25.700	10.234	15.466
298.15	12.441	26.785	10.415	16.370

TABLE 5. THERMODYNAMIC PROPERTIES OF CsI CRYSTAL (in cal/mol·°K)

T (°K)	$C_p°$	$S°$	$\frac{H°-H_0°}{T}$	$-\frac{(G°-H_0°)}{T}$
2	0.00358	0.00178	0.00111	0.00067
4	0.03089	0.01115	0.00796	0.00319
6	0.1226	0.03867	0.02877	0.00990
8	0.3511	0.1019	0.0777	0.0242
10	0.7563	0.2217	0.1707	0.0510
15	2.363	0.8147	0.6190	0.1957
20	4.168	1.743	1.281	0.4615
25	5.791	2.852	2.026	0.8268
30	7.084	4.027	2.765	1.262
35	8.080	5.198	3.457	1.741
40	8.815	6.327	4.083	2.244
45	9.352	7.398	4.640	2.758
50	9.793	8.406	5.133	3.273
60	10.422	10.252	5.967	4.285
70	10.896	11.898	6.641	5.257
80	11.192	13.374	7.192	6.182
90	11.422	14.706	7.650	7.056
100	11.570	15.917	8.035	7.882
110	11.681	17.025	8.362	8.663
120	11.778	18.046	8.642	9.404
130	11.864	18.992	8.887	10.105
140	11.938	19.874	9.102	10.772
150	12.008	20.700	9.294	11.406
160	12.059	21.477	9.465	12.012
170	12.090	22.209	9.619	12.590
180	12.121	22.901	9.757	13.144
190	12.156	23.557	9.882	13.675
200	12.194	24.182	9.997	14.185
210	12.237	24.778	10.102	14.676
220	12.279	25.348	10.200	15.148
230	12.327	25.895	10.292	15.603
240	12.374	26.420	10.378	16.042
250	12.414	26.926	10.458	16.468
260	12.452	27.414	10.534	16.880
270	12.487	27.884	10.606	17.278
280	12.521	28.339	10.674	17.665
290	12.549	28.779	10.738	18.041
300	12.576	29.205	10.799	18.406
273.15	12.497	28.029	10.628	17.401
298.15	12.571	29.127	10.788	18.339

Experimental Results

The results of the heat capacity of CsBr and CsI in the region 1.5 to 300°K are plotted in Figs. 8 and 9, respectively. Tables 2 and 3 list their numerical values. The calorie defined as equal to 4.1840 absolute joules was used. The ice-point was taken as 273.15°K. The molecular weights are based on the 1966 IUPAC report on atomic weights.

Smoothed values of the heat capacity, entropy,

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[19] A. R. Taylor, Jr., T. E. Gardner and D. F. Smith, *U. S. Bur. Mines Rept. Invest.*, No. 6157 (1963).

[20] J. N. Brönsted, *Z. Elektrochem.*, **20**, 554 (1914).

enthalpy function, and Gibbs energy function, and also of the standard thermodynamic values at 298.15°K, are listed in Tables 4 and 5, for CsBr and CsI, respectively. The differential heat capacity, $C_p°$, listed in the tables, which is obtained from the observed values of $\Delta H/\Delta T$, was not corrected for curvature because of the small rise in temperature, ΔT.

Other thermal properties of these crystals and significant differences between the alkali halide crystals with the NaCl-type structure and the CsCl-type one are fully described in part II.[21]

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21) M. Sorai, *J. Phys. Soc. Japan*, **24** (1968) (in press).