[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY CHEMISTRY DIVISION]

Molar Volume and Structure of Solid and Molten Cesium Halides[1]

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X-Ray diffraction patterns of solid cesium iodide and bromide taken at temperatures up to the melting points gave no evidence of any transition from a simple cubic to a face-centered cubic structure similar to the transition which occurs in cesium chloride at 469°. Discussion of the molar volumes of the solid and liquid salts at the melting points leads to the conclusion that the structural change from 8- to 6-fold coördination, which in the chloride takes place in solid phase at 469°, occurs in the bromide and iodide at their melting points as part of the fusion process. The per cent. volume expansions on melting for the bromide and iodide, 26.8 and 28.5, are essentially equal to the sum of the expansions in the chloride at its transition and melting points, 17.1 + 10.0 = 27.1%.

Introduction

In the course of investigations concerned with the miscibility of alkali metal halides with alkali metals,[2,3] a need for knowledge of the volume changes occurring in the melting process for these salts became apparent. A search of the literature revealed that information on this subject is scarce. Lorenz and Herz[4] compared the molar volume of the solid salt at room temperature with the volume of the liquid salt at the melting point and Stewart[5] calculated the ratio of the density of the solid at room temperature to that of the liquid at some temperature above the melting point. A compilation of densities, linear expansion coefficients, and lattice constants for the alkali metal halides in the solid and liquid state, as reported in the literature, was made as part of the present study. This information was used to calculate the volume changes for the transition solid–liquid at the melting point of each salt.

The alkali metal halides are naturally divided into two groups; first, those existing in the simple cubic structure at room temperature, under normal conditions, consisting of cesium chloride, bromide and iodide; and second, the much more numerous remaining members which exist in the face-centered cubic structure and which include cesium fluoride. This discussion will be confined to the first of these groups, while a subsequent paper deals with the second one.

A preliminary check of available data for the three cesium halides above indicated that the percentage volume expansion of the bromide and iodide on melting was approximately twice as large as that exhibited by the chloride. Since such a wide variation in the volume expansion of the halides of a given alkali metal was found to be unique, this was examined more thoroughly.

Wagner and Lippert[6] have measured lattice constants of these salts between room temperature and approximately fifty degrees below the melting point. It seemed desirable to extend these measurements to the melting point in an effort to confirm the large volume expansion of cesium bromide and iodide on melting.

Experimental

The cesium bromide and iodide in the form of clear fragments of optical grade salt were ground to a fine powder and mixed with nickel powder as an internal X-ray diffraction standard. The sample holder of the X-ray diffractometer was a flat plate and incorporated a cylindrical beryllium metal cover which prevented loss of the sample by vaporization while not obstructing X-ray passage. Heating to various temperatures was accomplished by a furnace the core of which was wound with nichrome V wire and had a semi-circular slit for the entrance of the primary beam and emergence of the scattered beams. The primary and scattered beams also passed through a beryllium strip 10 mil thick in the metal envelope surrounding the furnace, and the scattered beam was scanned with a Geiger–Müller counter tube connected to a Brown Electronik recorder. An atmosphere of helium was maintained inside the beryllium can of the sample holder and around the furnace core. Temperatures were measured with a chromel–alumel thermocouple whose junction was placed in the sample holder, and which was directly connected to a Rubicon potentiometer. Compensation for room temperature was made by subtracting the corresponding millivolts from the reading obtained on the potentiometer.

The validity of the temperature reading on the plate as a measure of the sample temperature was established by comparing the transition temperature of cesium chloride obtained in this fashion with that reported by Menary, Ubbelohde and Woodward[7] in their precise determination of the transition with X-ray diffraction. These authors reported the transtion in cesium chloride occurs at 469° and our measurements indicated a temperature of 470°. These temperatures are considerably higher than 451° Zemczuzny and Rambach,[8] and 443° Keitel[9] obtained from cooling curves, while it is lower than 479° Korrang[10] obtained from heating curves. Menary and co-workers[7] state that hysteresis accompanying the transition makes accurate determination of the transition temperatures by thermal methods very difficult. Wagner and Lippert[6] reported 445 ± 5° after determining the temperature from a calibration curve of temperature *vs.* wattage, without stating the melting points of the standards used.

Data and Calculations

A comparison of our smoothed data for the lattice constants of cesium bromide and iodide (Tables I and II) with the experimental data of Wagner and Lippert[6] (Fig. 1) shows some discrepancy between the two sets of values, especially in the curvatures at the higher temperatures. Expressions

$$\text{for CsBr: } a_t = 4.293 + 1.600 \times 10^{-4}t + 1.549 \times 10^{-7}t^2 \quad (25\text{–}630°) \qquad (1)$$

and

$$\text{for CsI: } a_t = 4.549 + 1.767 \times 10^{-4}t + 1.528 \times 10^{-7}t^2 \quad (25\text{–}619°) \qquad (2)$$

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[1] This paper is based on work performed for the U. S. Atomic Energy Commission.

[2] M. A. Bredig, J. W. Johnson and Wm. T. Smith, Jr., THIS JOURNAL, **77**, 307 (1955).

[3] M. A. Bredig, H. R. Bronstein and Wm. T. Smith, Jr., *ibid.*, **77**, 1454 (1955).

[4] R. Lorenz and W. Herz, *Z. anorg. Chem.*, **145**, 88 (1925).

[5] G. W. Stewart, *Trans. Faraday Soc.*, **33**, 238 (1937).

[6] G. Wagner and L. Lippert, *Z. physk. Chem.*, **B31**, 263 (1936).

[7] J. W. Menary, A. R. Ubbelohde and I. Woodward, *Proc. Roy. Soc (London)*, **A208**, 158 (1951).

[8] S. Zemczuzny and F. Rambach, *Z. anorg. Chem.*, **65**, 403 (1910).

[9] H. Keitel, *Neues Jahrb. Mineral. Geol.*, **A378**, (1925).

[10] E. Korrang, *Z. anorg. Chem.*, **91**, 194 (1915).

relating the lattice constant a_t in ångström units with the temperature in degrees centigrade (eq. 1, 2) were derived from our data and used to construct the curves in Fig. 1. The agreement between the experimental values and those calculated by eq. 1 and 2 is shown in Tables I and II.

TABLE I

LATTICE CONSTANTS AND DIFFERENTIAL LINEAR EXPANSION COEFFICIENTS OF CESIUM BROMIDE AS A FUNCTION OF TEMPERATURE

Run no.	Temp. t, °C.	Lattice constant (Å.) Obsd.	Lattice constant (Å.) Calcd.	Linear exp. coeff. $\times 10^6$, °C.
	25	4.296[a]	4.297	39.0
3	179	4.328	4.327	49.8
4	208	4.346	4.333	51.8
3	270	4.352	4.347	56.0
3	297	4.361	4.355	57.9
1	320	4.361	4.360	59.4
1	386	4.374	4.378	63.9
3	395	4.380	4.380	64.5
4	443	4.400	4.394	67.6
3	475	4.407	4.404	69.8
1	520	4.410	4.418	72.7
2	532	4.417	4.422	73.4
3	546	4.426	4.426	74.4
4	580	4.436	4.438	76.5
1	599	4.432	4.445	77.8
2	625	4.445	4.453	79.4
1	626	4.451	4.454	79.4
4	630	4.466	4.455	79.7
	636 (m.p.)		4.458	80.1

[a] Average of eight measurements.

TABLE II

LATTICE CONSTANTS AND DIFFERENTIAL LINEAR EXPANSION COEFFICIENTS OF CESIUM IODIDE AS A FUNCTION OF TEMPERATURE

Run no.	Temp. t, °C.	Lattice constant (Å.) Obsd.	Lattice constant (Å.) Calcd.	Linear exp. coeff. $\times 10^6$, °C.$^{-1}$
	25	4.553[a]	4.553	40.4
4	83	4.563	4.565	44.3
4	234	4.596	4.598	54.0
3	251	4.615	4.603	55.0
2	276	4.617	4.610	56.6
1	278	4.606	4.610	56.7
4	320	4.619	4.621	59.4
3	331	4.628	4.624	60.1
3	343	4.630	4.628	60.8
2	354	4.630	4.631	61 5
2	388	4.637	4.640	63.6
3	393	4.651	4.642	63.9
3	398	4.636	4.635	64.4
3	446	4.660	4.658	67.2
2	462	4.659	4.664	68.2
3	485	4.672	4.671	69.6
4	498	4.670	4.674	70.4
3	512	4.681	4.679	71.2
1	525	4.680	4.684	72.0
4	539	4.680	4.688	72.8
3	572	4.696	4.700	74.8
1	594	4.710	4.708	76.1
4	602	4.708	4.710	76.6
3	607	4.716	4.712	76.9
4	619	4.713	4.716	77.6
	621 (m.p.)		4.718	77.7

[a] Average of eight measurements.

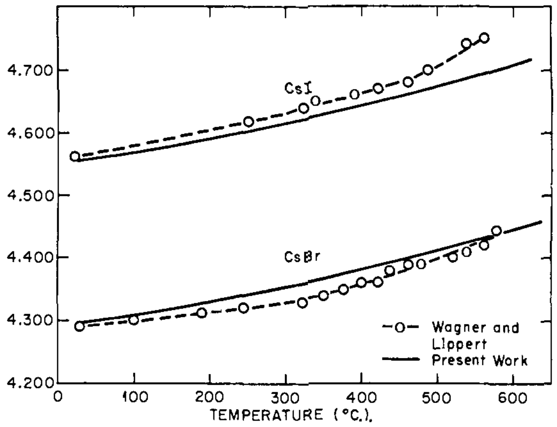

Fig. 1.—Lattice constants of cesium bromide and iodide as a function of temperature.

The reason for the discrepancy between the measurements of Wagner and Lippert[6] and the present results is not clear, but the methods of both temperature and lattice constant determination in their small camera are subject to some question.

Differential linear expansion coefficients, β, derived by differentiating the equations above and dividing by the lattice constant, a_t

$$\beta_t = \frac{1}{a_t} \times \frac{da}{dt} \qquad (3)$$

are also listed in Tables I and II. The value for CsI at 25°, 40.4 × 10^{-6} degrees C.$^{-1}$ is in fair agreement with the average linear expansion coefficient of cesium iodide, 48.6 × 10^{-6} degrees C.$^{-1}$ between 22 and 36°, reported by Rymer and Hambling[11] in their precision determination of the lattice constant of this salt.

Molar volumes of the solid salts were calculated directly from the lattice constants by multiplying the volume of the unit cell with Avogadro's number and dividing by the number of ion pairs per unit cell

Simple cubic $V = Na^3$
Face-centered cubic $V = Na^3/4$

where V is the molar volume in cc. and a is the lattice constant in cm. N was taken as 6.0235 × 10^{23} from the compilation of Dumond and Cohen.[12]

The molar volumes of crystalline cesium bromide and iodide (Table III) were calculated from smoothed values of the lattice constants and for cesium chloride from the smoothed values of Menary and co-workers.[7] The volume of the face-centered structure of cesium chloride was calculated from lattice constant measurements reported by Wagner and Lippert[6] up to 530° and a value reported by West[13] at 500°. The volumes of the metastable face-centered modifications at room temperature were calculated from lattice constants reported by Schulz.[14] The transition temperature in cesium chloride was taken as 469° as reported

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(11) T. B. Rymer and P. G. Hambling, *Acta Cryst.*, **4**, 565 (1951).

(12) J. W. M. Dumond and E. R. Cohen, *Revs. Mod. Phys.*, **21**, 651 (1949).

(13) C. D. West, *Z. Krist.*, (**A**)**88**, 94 (1934).

(14) L. G. Schulz, *J. Chem. Phys.*, **18**, 996 (1950).

by Menary, Ubbelohde and Woodward,[7] which is not sensibly different from our own value of 470°. The melting points used are those listed by the N.B.S. compilation.[15] The molar volumes of the liquids at the melting points were calculated from density values reported by Jaeger.[16]

TABLE III

MOLAR VOLUMES OF SOLID AND LIQUID CESIUM HALIDES

Temp., °C.	CsCl CN8	CsCl CN6	CsBr CN8	CsBr CN6	CsI CN8	CsI CN6
25	42.1	50.3[a]	47.8	56.9[a]	56.8	67.7[a]
100	42.6		48.2		57.4	
200	43.2		48.9		58.2	
300	44.0		49.8		59.2	
400	44.8		50.7		60.3	
469	45.4	53.4				
500		53.6	51.7		61.5	
600		54.4	52.9		62.9	
621 (s)					63.2	(73.6)[c]
621 (1)					81.2	
636 (s)			53.4	(62.0)[c]		
636 (1)			67.7			
645 (s)	(47.0)[b]	54.8				
645 (1)		60.3				

[a] Calculated from Schulz data for metastable forms. [b] Extrapolated from lower temperatures. [c] Extrapolated from per cent. volume change in CsCl transformation and Schulz data at room temperature.

TABLE IV

VOLUME CHANGES ON MELTING FOR CESIUM HALIDES

	CsCl CN8	CsCl CN6	CsBr CN8	CsBr CN6	CsI CN8	CsI CN6
Mol. vol. solid (m.p.)	(47.0)[a]	54.8	53.4	(62.0)	63.2	(73.6)
Mol. vol. liquid (m.p.)	60.3	60.3	67.7	67.7	81.2	81.2
% Expansion over solid	(28.3)	10.0	26.8	(9.2)	28.5	(10.3)

[a] Figures in brackets by extrapolation from lower temperatures.

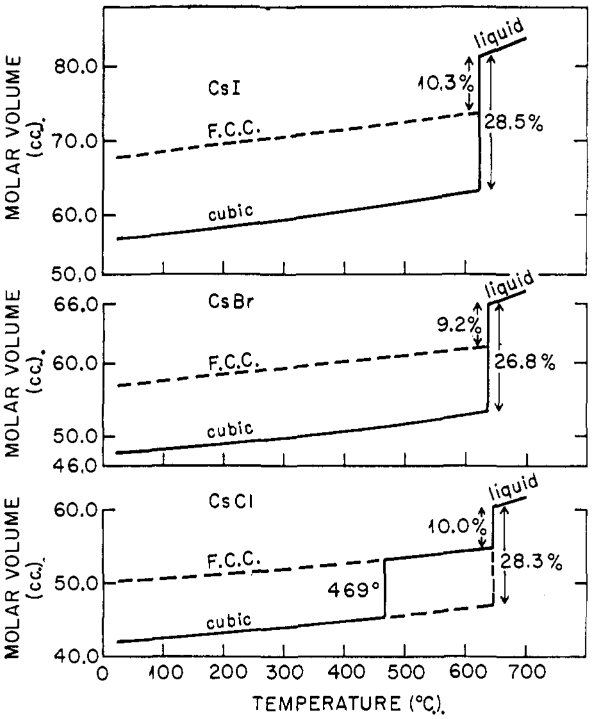

Fig. 2.—Molar volumes and volume expansions on melting for cesium halides.

Table III presents the volume of these salts in the two modifications and Table IV gives the volume expansion in the melting process in percentage. The data of Tables III and IV are summarized in Fig. 2.

Discussion

An examination of the data on the molar volumes of the solid and liquid salts shows the per cent. volume expansion on melting to be considerably lower for cesium chloride than for the bromide and iodide. An extrapolation of the molar volume of the low temperature or simple cubic modification of cesium chloride up to the melting point would result in a volume expansion on melting of 28.3%, in good agreement with that observed for the bromide and iodide, 26.8 and 28.5%, respectively. If the data of Wagner and Lippert[6] were used the volume changes would be 26.8 and 23%, respectively, the latter still being considerably larger than the 10% expansion exhibited by cesium chloride.

If the volume expansion (17.6%) associated with the transition in cesium chloride from simple cubic to face-centered cubic structure[17] is applied to the bromide and iodide and corrected for the increased temperature a hypothetical per cent. expansion on melting of the (metastable) face-centered cubic modifications may be calculated. The calculation gives 9.2 and 10.3% expansion, *i.e.*, similar to the value of 10.0% for the chloride.

The X-ray diffraction patterns of solid cesium bromide (m.p. 636°) and cesium iodide (m.p. 621°) observed up to 2–3° below the melting points gave no indication of a transition in the solid. While the possibility that this occurs in these last few degrees before melting cannot be ruled out, it appears to be unlikely.

Thus the conclusion seems inevitable that there is something quite different in the melting process of the bromide and iodide from that in cesium chloride. In the chloride the melting consists essentially of the disappearance of the long range order of the crystal, while the short range order is maintained more or less the same as in the solid, *i.e.*, the coördination of six oppositely charged ions around a given ion is still present in the liquid.[18] The formation of a "hole" even in the first sphere of coördination of a certain fraction of the ions of the melt may or may not have to be assumed to explain the mobility of the liquid. It seems impossible, however, to explain the volume changes exhibited by cesium bromide and iodide on melting by anything but a structural change in the first sphere of coördination of all the ions. It is pro-

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[15] National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Washington, D. C., 1952, Series II, pp. 820.

[16] F. M. Jaeger, *Z. anorg. Chem.*, **101**, 1 (1917).

[17] L. Pauling, *Z. Krist.*, **69**, 35 (1928), pointed out that this expansion which is due to unfavorable packing economy in the face-centered form is reduced from 30% for a hypothetical structure change with constant Cs–Cl distance to one of 19% when the actual contraction of 3.3% in this distance is taken into account.

[18] K. Lark-Horovitz and E. P. Miller, *Phys. Rev.*, **49**, 418 (1936), observed an average coördination number of 5.8 for molten KCl.

posed that the structure of the liquid bromide and iodide is very similar to that of the chloride. On melting not only the long range order disappears but the coördination number of 8 in the crystals decreases to a coördination number in the liquid similar to that in cesium chloride, probably an average of 6.[19]

The above assumption should be checked by an examination of the entropy changes associated with the melting of cesium halides. An increase in the entropy of fusion of the bromide and iodide over that for the chloride would support this postulated coördination number decrease. The N.B.S. compilation[15] lists the heat of transition of cesium chloride as 1.8 kcal./mole. This corresponds to an entropy change of 2.4 e.u. at 469°. The entropy of fusion is given as 3.92 e.u at 645°. An estimate of 2 e.u. for this transition if it occurred at the melting point combined with the entropy of fusion of the face-centered cubic structure would result in an entropy of fusion of 5.9 e.u for simple cubic cesium chloride melting at 645°. Thus one might expect the entropy change associated with the melting of the bromide and iodide should be 5.8 to 6.0 e.u. since the melting points of all three salts are not greatly different. The N.B.S. compilation[15] gives a value of 1.9 e.u. for the entropy of fusion of cesium bromide and does not list a value for cesium iodide. Brewer[20] estimates 3 e.u. for both salts. The first of these two values appears to be inordinately low, and even the second one seems low in the light of this discussion. A direct experimental determination of the heat of fusion of these salts would, therefore, be of considerable interest. The most direct check, however, of the liquid salt structure proposed here will come from X-ray and neutron diffraction measurements of the radial distribution functions in the molten salts, which are in preparation at this Laboratory.

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(19) This prediction of a structure on the basis of comparing molar volumes recalls a similar prediction by K. Fajans and H. Grimm, *Z. Physik*, **2**, 304 (1920), of a structure for solid CsCl, CsBr, and CsI different from that of CsF, shortly thereafter verified by X-ray diffraction.

(20) Leo Brewer in "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," National Nuclear Energy Series, IV-19B, McGraw-Hill Book Co., New York, N. Y., 1950, p. 197.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

The Heat Capacity of Uranium Tetrafluoride from 5 to 300°K.

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The heat capacity of a pure sample of uranium tetrafluoride was determined from 5 to 300°K. and found to be at variance with measurements by Brickwedde, Hoge and Scott. The new data make possible a better evaluation of the magnetic entropy above 5°K. and suggest the probability of a thermal anomaly below 5°K. The values of C_p, $H° - H°_5$, and $S° - S°_5$ are 27.73 ± 0.03 cal. deg.$^{-1}$ mole^{-1}, 5389 ± 6 cal. mole^{-1}, and 36.13 ± 0.04 cal. deg.$^{-1}$ mole^{-1}, respectively, at 298.16°K.

Tentative values of the magnetic entropy of uranium tetrafluoride have been calculated[1] from previous heat capacity measurements on this substance in the temperature range 20 to 350°K.[2] The heat capacity of thorium tetrafluoride was taken to represent the lattice contribution to the heat capacity of uranium tetrafluoride. By comparing these values of the magnetic entropy of uranium tetrafluoride with those of neptunium dioxide and uranium dioxide it was concluded that an anomaly might well exist in the heat capacity of uranium tetrafluoride below 20°K. and thus invalidate the extrapolation made by Brickwedde, Hoge and Scott from 20 to 0°K. It was considered desirable, therefore, to extend the heat capacity measurements to lower temperatures in order to obtain more reliable thermodynamic functions for chemical thermodynamic purposes and in order to explore further the question of the magnetic behavior of this substance.

Uranium Tetrafluoride Samples.—Preliminary measurements were made from 5 to 300°K. on a sample of uranium tetrafluoride prepared by the Mallinckrodt Chemical Works. These heat capacity measurements were significantly higher than the values extrapolated by Brickwedde, Hoge and Scott[2] below 20°K. but were unaccountably lower near 300°K. Because of these discrepancies and because of the presence of 2% of uranyl fluoride in both the Mallinckrodt sample and the sample used by Brickwedde, Hoge and Scott, we prepared a purer sample for further measurements by twice subliming the Mallinckrodt sample in high vacuum. The platinum crucible containing the material to be sublimed was heated by a tantalum wire heater which fit into a re-entrant well in the center of the crucible. The crucible was surrounded by a cylindrical platinum radiation shield and rested on a base plate of Alsimag 222 ceramic, which in turn was supported by two tungsten rods serving also as electrical leads through a tungsten-glass seal. The heater was wound on a projection from the base plate. The sublimate crystallized on the inner surface of a bell-jar shaped platinum collector suspended directly above the crucible. Each sublimation required several hours at about 1100° and gave essentially 100% yield. After the first sublimation a small amount of oxygen was detected in the sample, perhaps because of adsorption of atmospheric water in the handling of the sublimate. After resublimation to remove the residual oxygen the sublimate was handled in an atmosphere of anhydrous nitrogen while it was being removed from the collector, broken up in a mortar, and loaded into the calorimeter. The mass of the sample used in the calorimeter was 123.417 g. (*in vacuo*).

Analyses of the purified sample indicated 75.83 ± 0.07% uranium by ignition to U_3O_8 (theoretical, 75.80%), 24.18 ± 0.06% fluorine by pyrohydrolysis and titration of the HF formed (theoretical, 24.20%), and 0.006 ± 0.003% oxygen by bromine trifluoride dissolution.[3] The oxygen content corresponds to 0.05% UO_2F_2. Spectrochemical analyses showed less than 0.002% each of Ag, Al, As, Be, Bi, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sn, Ta and Zr; less than 0.005% Ti, and less than 0.01%

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(1) H. R. Lohr, D. W. Osborne and E. F. Westrum, Jr., THIS JOURNAL, **76**, 3837 (1954).

(2) F. G. Brickwedde, H. J. Hoge and R. B. Scott, *J. Chem. Phys.*, **16**, 429 (1948).

(3) H. R. Hoekstra and J. J. Katz, *Anal. Chem.*, **25**, 1608 (1953).