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EFFECT OF PRESSURE ON THE MELTING OF CESIUM CHLORIDE*

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Abstract—Melting curve of cesium chloride has been determined to 50 kbar in a single-stage piston-cylinder apparatus. Our results agree with Clark's experimental data which extend up to 15 kbar. We have also found that the melting temperature of cesium chloride changes linearly with its specific volume up to 45 kbar in contrast to the behavior of other recently studied ionic compounds.

1. INTRODUCTION

THE EFFECT of pressure on the melting of ionic compounds has recently been discussed by Kennedy and Vaidya[1]. They note that when melting temperatures are plotted against the isothermal compression of Van der Waals solids, melting curves concave to the temperature axis results. They also note that when melting curves are plotted for metals, melting temperatures are linear with the volume of the melting solid and that when melting curves are plotted for ionic compounds, resulting curves appear to be concave toward the volume axis of the plot. This relationship has been explored to compressions of as much as 30 per cent in the case of the Van der Waals solids, helium and methane, and to compressions of as much as 40 per cent in the case of the metals, rubidium and potassium. Unfortunately, no highly compressible ionic compound has been examined. A casual search of the literature suggested that cesium chloride was one of the most compressible of ionic compounds and that its fusion curve had a very steep initial slope. Thus, we elected to examine the melting of cesium chloride to the highest pressures and temperatures readily attainable with precision.

The melting curves and phase diagrams of sodium, potassium, rubidium, silver, cuprous and thallous halides have recently been determined, by methods of differential thermal analysis, to pressures of circa 50 kbar[2–10]. Melting curves of the lithium and cesium halides have not been examined over this pressure range.

Cesium chloride, CsCl, undergoes a phase change to a new polymorph with NaCl structure at about 469°C[11] at 1 atmosphere. Its melting point at atmospheric pressure is approximately 645°C. The melting of CsCl, to pressures of approximately 15 kbar, has been investigated by Clark[2]. He finds a triple point between two polymorphs and liquid at approximately 1 kbar and 665°C. The initial slope of the melting curve of CsCl above the triple point is 42°C/kbar. This is the steepest melting curve of any substance which has come to our attention. Further, the cesium halides are the most compressible of the metal halides. Recent data on a density as a function of pressure are available[12].

2. EXPERIMENTAL METHOD

Cesium chloride of 99·5 per cent stated purity was supplied by Research Organic and Inorganic Chemical Co. This is the same stock we recently used in compressibility measurements[12]. The powdered material was dried for 48 hr at 200°C and then tightly packed in a niobium metal capsule with a reentrant thermocouple well. A boron nitride sleeve insulated the niobium capsule from the graphite fur-

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nace tube. Molten pyrex glass served as the pressure transmitting medium. Further experimental details are given by Akella *et al.*[4] and by Williams and Kennedy[13].

CsCl melts at temperatures in excess of 1800°C at 50 kbar. Consequently thermocouples stable to very high temperatures are required. We have found that Pt/Pt-10Rh thermocouples deteriorate rapidly at temperatures much above 1500°C and the W-3Re/W-25Re thermocouples are stable to at least 2000°C. The behavior of Englehart premium grade W-3Re/W-25Re thermocouple in high pressure differential thermal analysis assemblies has been extensively studied by Williams and Kennedy[13]. Because of the mechanical and chemical stability of these thermocouples, they were selected for use in this study.

Determinations of the melting temperature were made by differential thermal analysis on both compression and decompression cycles. In a particular experiment, lasting nearly 10 hr, a large number of DTA points could be determined over a 20–25 kbar range. Most of the experiments were terminated owing to capsule failure and consequent loss of sample. Capsules of tantalum and molybdenum were tried, but niobium capsules seemed to serve best at the highest temperatures and pressures.

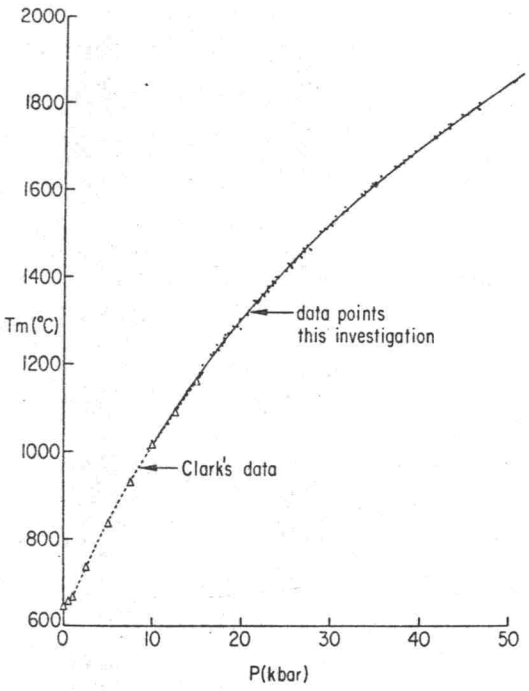


Fig. 1. CsCl melting data. Curve from least squares fit.

3. RESULTS

Our measurements of the melting temperature of CsCl along with Clark's results[2] are shown in Fig. 1. A smooth curve through the 116 data points was drawn by use of a polynomial regression fit

$$T_m = T_m^0 + b_1P + b_2P^2.$$

Davis and England[14] and Williams and Kennedy[13] have intercompared W-3Re/W-25 Re and *P*t/Pt-10Rh thermocouples at high temperatures and pressures. Differences in the apparent temperatures indicated by these thermocouple pairs at high temperatures and high pressures is attributed to the difference in the effect of pressure on the ther-

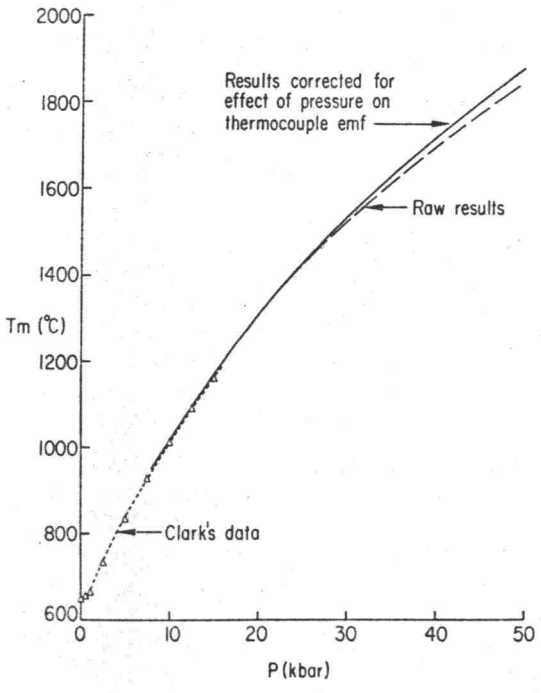


Fig. 2. CsCl melting curves.

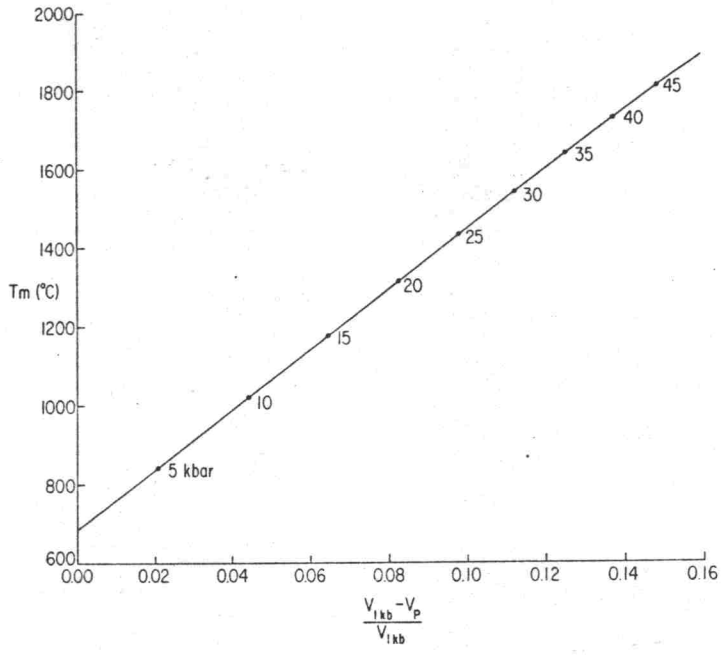


Fig. 3. Melting temperature of CsCl vs. volume compressions of the solid at ambient temperature.

mal emf of the two sets of material. Intercomparison experiments can only be made through the useful range of the Pt/Pt-10Rh thermocouples. Further, Getting and Kennedy's experiments[15] on the effect of pressure on Pt/Pt-10Rh wires extend only to 35 kbar and 1000°C. Thus large extrapolations are necessary in order to estimate the correction for the effect of pressure on W-3Re/W-25Re wires at the highest pressures and temperatures of the present experiment. The accuracy of our measurements is thus substantially less than the precision of the measurements, owing to uncertainties in extrapolation of the corrections and also owing to uncertainties involved in the calibration of individual pairs of wires[16]. The precision of our measurements at the highest temperatures and pressures is approximately ±5°C; however, the accuracy is certainly no better than ±10°C. Figure 2 shows the curve through the raw data points and the curve after applying extrapolated corrections for the effect of pressure on thermo-e.m.f. We also show the results from Clark's studies to 15 kbar. At 50 kbar the corrections to our raw data amounts to approximately 34°C. The results are also tabulated at regular pressure intervals. (Table 1).

Figure 3 is a plot of the temperature of melting vs. the room temperature compression of the solid. In this plot the recent compressibility data on the simple cubic phase above 1 kbar[12] is used. To our surprise the plot is exactly linear to within the precision of the measurements. In this respect CsCl behaves like a metal and does not show the slight curvature toward the volume axis as is shown by other studied ionic compounds[1]. Vaidya and Gopal[17] have suggested that substances melt in accordance with an equation

$$T_m = T_m^{0\prime} \cdot \left[1+2(\gamma-\tfrac{1}{3}) \cdot \left|\frac{V_0'-V}{V_0'}\right|\right]$$

where $T_m^{0\prime}$ and V_0' are the melting temperatures and specific volumes at the reference pressure.

Table 1. Melting data for Cesium Chloride. Melting temperatures, T_m, computed from the relation $T_m = 642{\cdot}55 + 42{\cdot}436P - 0{\cdot}53741p^2 + 0{\cdot}00341P^3$, where P is pressure in kbar. Standard deviation, 5°C

P (kbar)	Clark[1] T_m, °C Corrected for the effect of pressure on Pt/Pt–10Rh thermocouples	This Work T_m, °C Uncorrected for the effect of pressure on thermocouples	T_m, °C Corrected for the effect of pressure on W-3Re/W-25Re thermocouples
0	645		
5	841	842	843
10	1015	1017	1018
15	1160	1170	1173
20		1304	1308
25		1421	1428
30		1524	1535
35		1616	1631
40		1698	1719
45		1774	1802
50		1847	1881

The Gruneisen parameter, γ, estimated from the slope of the line in Fig. 3 is 4·29. The γ thus obtained is much too great. Vaidya and Gopal[17] have suggested these large values of γ result because the melting temperature is plotted against the room temperature specific volume of the solid and not against the specific volume of the solid along the melting curve. If corrections of the kind outlined by Vaidya and Gopal are made[4, 6, 17], γ reduces to 2·78. This is in fair agreement with the thermal value of γ for CsCl which is 2·02.

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