

Effect of Pressure on the Melting Points of Eight Alkali Halides*

SYDNEY P. CLARK, JR.

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D. C.

(Received June 15, 1959)

The melting curves of the alkali chlorides and the sodium halides have been determined at high pressures. The results can be represented within experimental error by Simon's equation. Comparison of the slope of the melting curve at low pressure with measurements of the changes of volume and entropy upon fusion suggests that the latter data are systematically in error.

I. INTRODUCTION

PREVIOUS investigations of the effect of pressure on melting points have largely been concerned with metals, organic compounds, and "solidified gases" (He, N₂, etc.). In the present work the list of substances studied is extended to include simple ionic compounds, thereby providing a further test of the validity of both Simon's equation of the melting curve and various interpretations of the parameters appearing in this equation.

The melting curves of the five alkali chlorides and of the remaining sodium halides have been followed to a maximum pressure close to 25 000 bars. Large changes in melting point were produced; in most cases the temperature of fusion was increased by 300 to 500°C. Experimental values of the initial slopes of the melting curves provide a measure of the internal consistency of the measurements of changes of volume and entropy upon fusion recorded in the literature. In addition, triple points at which two solid polymorphs and liquid coexist were located for KCl, RbCl, and CsCl.

II. EXPERIMENTAL METHOD AND RESULTS

Apparatus

Measurements at the higher pressures were made in the compound apparatus developed by Francis Birch at Harvard University. This equipment has been described previously.¹ Pressures were determined to within about 100 bars by the change in resistance of a coil of manganin wire. Temperatures were measured with Pt-Pt 10% Rh thermocouples. The charges were heated in a resistance furnace mounted inside the pressure vessel.

Temperatures of 1400°C have been reached in this apparatus by using small furnaces, but the present experiments required a furnace 0.25 in. in inside diameter. It was not possible to attain temperatures above about 1150°C without exceeding the capacity of the constant-voltage transformer which supplied the power.

Because of discrepancies between the results obtained in the high-pressure apparatus and thermochemical

data, the melting curves were redetermined up to 1300 bars in other equipment. This apparatus is a thick-walled tube, mounted in a horizontal position, containing a furnace that is somewhat larger than the vertically mounted one in the high-pressure equipment. Pressure was measured to within 10 bars with a Bourdon gauge, and temperature was measured with chromel-alumel thermocouples swaged in pressure-tight sheaths of inconel.

The power required to reach a given temperature roughly doubles as the pressure is raised from atmospheric to 1000 bars. The change over the remainder of the pressure range is less than this, even in the high-pressure apparatus. This is accompanied by changes in thermal gradients throughout the apparatus, and errors due to such causes should appear at the lower end of the pressure range. The low-pressure equipment was designed to make any such errors as different as possible from those in the high-pressure apparatus. Hence, the good agreement between the two sets of data can be taken as evidence that the results are free from instrumental bias.

Method

In the high-pressure apparatus, several Pt capsules containing the salt were packed around a thermocouple, and similar capsules, filled with Al₂O₃, surrounded another which was placed at the same level in the furnace. Melting and freezing were detected by changes in the rates of heating or cooling and by changes in the difference between the temperatures of the two thermocouples. Capsules with a reentrant tube in which the thermocouple was placed were used in the low-pressure apparatus. This improvement, and the greater sensitivity of the thermocouples, enabled the melting curve to be determined by arrests in heating and cooling without the use of a second thermocouple. In all cases the capsules were sealed by welding in order to prevent solution of the pressure media (nitrogen or argon) in the molten salt.

The accuracy with which the melting points could be located was limited by rounding of the arrests in the rates of heating and cooling. The melting curve was crossed several times at each pressure, and the rates of heating and cooling were varied. Because of the small thermal inertia of the system it was not possible to

* Published with the partial support of the Committee on Experimental Geology and Geophysics, and the Division of Geological Sciences at Harvard University.

¹ Birch, Robertson, and Clark, *Ind. Eng. Chem.* **49**, 1965 (1957).