

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

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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

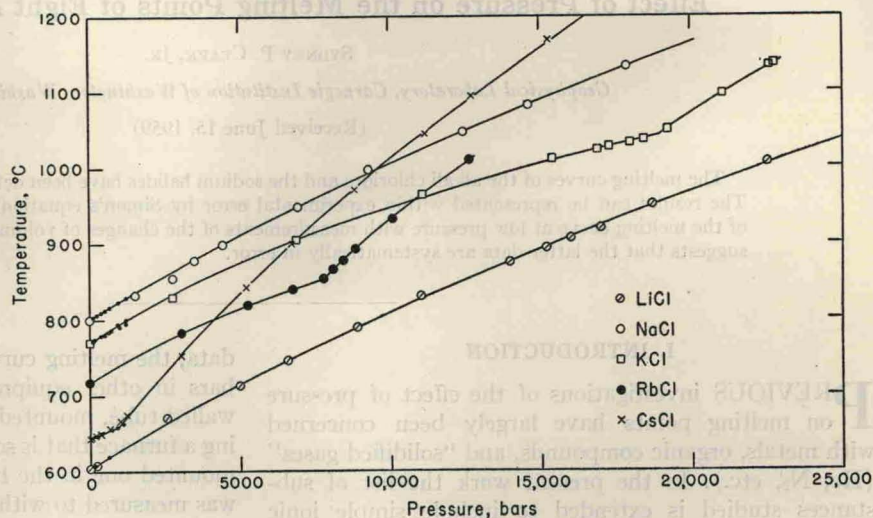
In the high-pressure apparatus, several Pt capsules containing the salt were packed around a thermocouple, and similar capsules, filled with Al₂O₃, surrounded another which was placed at the same level in the furnace. Melting and freezing were detected by changes in the rates of heating or cooling and 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

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

Fig. 1. Melting curves of the alkali chlorides. The small dots represent points obtained with the low-pressure apparatus.



change the temperature at a rate much less than 20°C per minute, but faster rates did not change the results. In the high-pressure apparatus melting points obtained from heating curves could be repeated to within 2°C. Cooling curves gave results that were irregularly lower because of supercooling. Arrests on heating rarely lasted more than a few seconds; they were accompanied by a pronounced maximum in the difference in temperature between the two thermocouples, which was taken as an equally good indication of the melting point. On the basis of the reproducibility of the data, a generous estimate of the uncertainty is $\pm 5^\circ\text{C}$ for most salts. For some unknown reason the melting curves of NaBr and NaI proved to be more difficult to locate in this apparatus, and the determinations of the melting points of these salts are uncertain by $\pm 10^\circ\text{C}$.

More accurate results were obtained in the low-pressure apparatus because of its greater sensitivity. Arrests on cooling were particularly sharp; the tempera-

ture remained constant to within 0.2°C for as long as 30 seconds in many instances. Results on heating and cooling rarely differed by as much as 1°C, and the data are almost certainly accurate to within $\pm 2^\circ\text{C}$. Results for NaBr were as sharp as those for the other salts in this apparatus.

The quantity that was actually measured was the change in melting point with pressure. Melting points of the salts at atmospheric pressure were measured in the pressure apparatus; the results served to calibrate the thermocouples *in situ*. The calibration always fell within a few degrees of the standard tables and did not change with time. Deviations from the tables varied smoothly with temperature for any particular thermocouple.

The melting points of the lots of salts used in the experiments were determined by conventional means with Pt-Pt 10% Rh thermocouples calibrated against the melting points of NaCl (800.5°C) and KCl (770°C).

Fig. 2. Melting curves of the sodium halides. The small dots represent points obtained with the low-pressure apparatus.

