

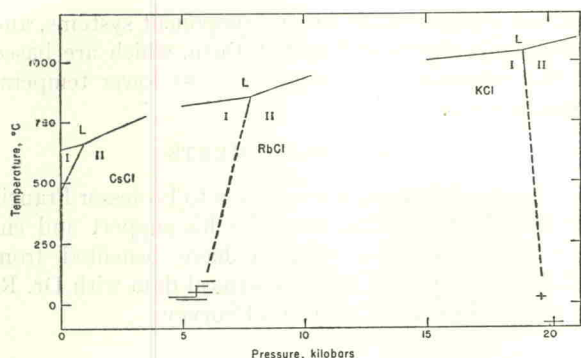


FIG. 3. Phase diagrams of KCl, RbCl, and CsCl near the triple points. The horizontal lines at low temperatures represent the ranges of pressure over which Bridgman observed the I—II transitions, and the vertical lines show his mean transition pressures.

data combined with the slopes of the melting curves at the triplet point serve to determine the remaining changes of volume and entropy (Table 2B). The uncertainties given in the table are only those arising from the uncertainty in ΔV_{tr} at atmospheric pressure; the slopes are assumed accurate.

Wagner and Lippert⁵ calculated the lattice energies of the two modifications of CsCl from the lattice constants. The difference between the two forms at the transition temperature, 1.8 kcal/mole, has crept into compilations of thermochemical data⁶ as the heat of transition. The value obtained from the mean slope of the transition line, 0.7 ± 0.1 kcal/mole, is to be preferred.

A similar analysis of the relations at the triple points of KCl and RbCl is subject to greater uncertainties because of the longer extrapolation required and because of the inferior purity of the RbCl used in this investigation. Assume, however, that the I—II transition can be represented by straight lines connecting the triple points with Bridgman's data at about room temperature (Fig. 3), and that $\Delta V_{tr} = 4.2$ cm³/mole for KCl⁷ and 6.1 cm³/mole for RbCl.⁸ The parameters of the melting curves are then those given in Table IIB.

The results suggest that the calorimetric value of ΔS_f is too low for RbCl, since this quantity decreases along the melting curves of other substances,⁹ and decreases initially for KCl. The large decrease in ΔV_f is to be expected in view of the high compressibility of molten salts.¹⁰ But these suggestions, depending as they do on assumptions about ΔV_{tr} and the slopes of the I—II transition curves, must be considered tentative.

⁶ Rossini *et al.*, Natl. Bur. Standards Circ. 500 (1952).

⁷ P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **74**, 21 (1940).

⁸ P. W. Bridgman, Z. Krist. **67**, 363 (1928).

⁹ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, England 1952), revised edition, p. 201.

¹⁰ J. O'M. Bockris and N. E. Richards, Proc. Roy. Soc. (London) **A241**, 44 (1957).

Parameters in the Simon Equation

Salter¹¹ has argued that $A = (\partial U / \partial V)_T$ for the solid. This result is the automatic consequence of the fact that both quantities equal the negative of the pressure required to cause melting at 0°K. But there is no *a priori* reason to single out the solid for emphasis, and by definition $A = (\partial U / \partial V)_T$ for the liquid as well. Besides, there is no guarantee that Eq. (1) is valid at temperatures near zero and at negative pressures.

The parameter A is compared with $(\partial U / \partial V)_T$ at atmospheric pressure and the melting point in Table III. It is smaller than the latter quantity for the solids, but agrees better with the values for the liquids and with the differences between solids and liquids. The interpretation of A as the difference between the "internal pressures" of solid and liquid at low external pressure has intuitive appeal; it apparently fails in the case of the alkali metals, however, since A has been found to be larger than $(\partial U / \partial V)_T$ of these solids.¹² There is a distinct possibility of experimental error here, since the chemical activity and mechanical softness of the alkali metals makes measurement of their properties near the melting point difficult.

Theoretical values of c given by Domb,¹³ de Boer,¹⁴ and Salter¹¹ are near unity for these salts. This is definitely too low. They fit experimental data for the rare gases better, but also fail for the alkali metals. Gilvarry's theory¹⁵ predicts values of A which are too high by a factor of 2 or 3 for NaCl and KCl. All these theories contain approximations which are not strictly valid for ionic crystals, and the disagreement is perhaps to be laid to their account.

The present work demonstrates that the Simon equation can represent the melting curves of ionic compounds at high temperatures. But this does not imply that this representation is unique or even the best at-

TABLE III. $(\partial U / \partial V)_T$ and A .

	$(\partial U / \partial V)_T$ solid	$(\partial U / \partial V)_T$ liquid	Difference	A
NaCl	26 000 ^a	13 250 ^d	12 750	16 700
NaBr	22 200 ^b	10 100 ^d	12 100	12 200
NaI	14 800 ^b	8 950 ^d	5 850	10 100
KCl	17 700 ^c	10 800 ^d	6 900	6 900 (8 350)

^a Thermal expansion from A. Eucken and W. Dannohl, Z. Elektrochem. **40**, 814 (1934); compressibility from L. Hunter and S. Siegel, Phys. Rev. **61**, 84 (1942).

^b Extrapolated from room-temperature data.

^c Thermal expansion from R. E. Glover, Z. Physik **138**, 222 (1954); compressibility from C. B. Cooper and F. D. Enck, Department of Physics, University of Maryland Technical Report No. 11 (1955).

^d Bockris and Richards.¹⁰

¹¹ L. Salter, Phil. Mag. **45**, 369 (1954).

¹² F. E. Simon, Nature, **172**, 746 (1953).

¹³ C. Domb, Phil. Mag. **42**, 1316 (1951).

¹⁴ J. H. de Boer, Proc. Roy. Soc. (London) **A215**, 5 (1952).

¹⁵ J. J. Gilvarry, Phys. Rev. **102**, 325 (1956).

tainable with two disposable constants. The significance of the parameters appearing in this equation cannot be determined because theory has failed thus far to predict the experimentally determined values.

Present experimental evidence is consistent with the conclusion that the melting curve rises indefinitely with increasing pressure, and the Simon equation contains this feature. It has been suggested that the melting curve passes through a maximum temperature, approaches an asymptotic temperature, or ends at a critical point. None of these alternatives has been

realized experimentally in one-component systems, and Bridgman's arguments⁹ against them, which are based on the behavior of melting curves at lower temperatures, are still valid.

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Fig. 3. Phase diagram of KCl, RbCl, and CsCl near the triple points. The horizontal lines at low temperatures represent the ranges of pressure over which Bridgman observed the I-II transition, and the vertical lines show the phase transition pressures.

data obtained with the slopes of the melting curves at the triple point serve to determine the remaining changes in volume and entropy (Table IV). The uncertainties given in the table are only those arising from the uncertainty in ΔV at atmospheric pressure; the slopes are assumed accurate.

Wagner and Lipfert¹⁰ calculated the lattice energies of the two modifications of CsCl from the lattice constants. The difference between the two forms at the transition temperature, 1×10^4 kcal/mole, has crept into computations of thermochemical data as the heat of transition. The value obtained from the true slope of the transition line, 0.1 ± 0.1 kcal/mole, is to be preferred.

A similar analysis of the relations of the triple points of KCl and RbCl is subject to greater uncertainties because of the longer extrapolation required and because of the lesser purity of the RbCl used in the investigation. Assume, however, that the I-II transition can be represented by straight lines connecting the triple points with Bridgman's data at about room temperature (Fig. 3), and that $\Delta V = 4.5$ cm³/mole for KCl and 0.1 cm³/mole for RbCl.¹¹ The parameters of the melting curves are then those given in Table I(b).

The results suggest that the thermodynamic value of ΔV is too low for KCl, since the quantity decreases along the melting curves of other substances, and decreases initially for RbCl. The large discrepancy is to be expected in view of the high compressibility of molten salts.¹² But these suggestions, depending as they do on assumptions about ΔV and the slopes in the I-II transition curves, must be considered tentative.

- ¹ R. A. Robie, *U.S. Geol. Surv. Bull.*, **105** (1952).
- ² F. W. Bridgman, *Proc. Am. Acad. Sci.*, **11** (1916).
- ³ F. W. Bridgman, *Z. Krist.*, **67**, 361 (1926).
- ⁴ F. W. Bridgman, *The Properties of Matter under Pressure*, 2nd ed., McGraw-Hill, New York, 1947, p. 201.
- ⁵ J. O. H. Beattie and J. E. Rundle, *Proc. Roy. Soc. (London)*, **A241**, 44 (1957).
- ⁶ R. A. Robie, *U.S. Geol. Surv. Bull.*, **105** (1952).
- ⁷ F. W. Bridgman, *Proc. Am. Acad. Sci.*, **11** (1916).
- ⁸ F. W. Bridgman, *Z. Krist.*, **67**, 361 (1926).
- ⁹ F. W. Bridgman, *The Properties of Matter under Pressure*, 2nd ed., McGraw-Hill, New York, 1947, p. 201.
- ¹⁰ J. O. H. Beattie and J. E. Rundle, *Proc. Roy. Soc. (London)*, **A241**, 44 (1957).
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