

tions. This method of fitting and of estimating uncertainty assumes that the experimental points are perfectly accurate. Larger corrections might be required if neighboring points are in error in the same direction.

Small changes in c can be largely offset by changing A in the opposite direction. Hence the product cA is better determined than either quantity taken separately. The initial slopes of the melting curves are inversely proportional to this product, and they are fixed by the experiments within a few percent. But because the best value of A depends on the value adopted for c , extrapolation of the experimental results by means of the Simon equation is hazardous.

Agreement between the data from the low-pressure apparatus and the curves of Figs. 1 and 2 is excellent except for KCl. In this case the slope of the melting curve at $P=0$ is about $0.002^\circ\text{C}/\text{bar}$ higher than that found experimentally. Taking this slope as $0.0245^\circ\text{C}/\text{bar}$ from the low-pressure experiments and insisting that the curve pass through the triple point at 18 950 bars and 1315°K yields $A=8350$ bars and $c=5.1$ (cf Table I). The new parameters lead to a standard deviation roughly 50% greater than that given in the table. A discrepancy of this magnitude is hardly surprising, and it is difficult to say which pair of values of A and c is to be preferred.

The exponent c is considerably higher for NaF than for the other sodium halides. The values for LiCl and NaCl are smaller than those for KCl and RbCl. Since the properties of potassium and its compounds commonly show greater similarity to those of rubidium than to those of sodium, this result is perhaps not surprising. The high-pressure polymorphs have lower values of c than do the low-pressure forms, judging mainly from the data for RbCl.

The values of A are comparatively small when c is large. A is small for NaF and declines with increasing molecular weight for the remaining sodium halides. It reflects the changes in c for the alkali chlorides. The product Ac depends somewhat more regularly on molecular weight than either parameter by itself; this may be the result of the difficulty in uniquely fitting a two-parameter equation to the experimental results.

Other qualitative features of the data are the convergence of the melting curves of the sodium halides, and the crossing of those of several of the alkali chlorides. At 30 000 bars the order in which the four heaviest chlorides melt is reversed, and the melting points of all these salts increase with molecular weight.

III. DISCUSSION

Thermodynamic Calculations

The initial slope of the melting curve, $(dT/dP)_{P=0}$, is T_0/Ac according to Eq. (1). It is also equal to $\Delta V_f/\Delta S_f$, where ΔV_f and ΔS_f are the changes of volume and entropy on melting. Observed values of the initial slopes are compared with those calculated from Clapeyron's equation in Table II. The two sets of data agree

TABLE II. Melting parameters.

Compound	ΔS_f cal/mol deg	ΔV_f cm ³ /mol	$\Delta V_f/\Delta S_f$ deg/bar	dT/dP observed deg/bar
A. At zero pressure				
LiCl	3.6 ^a 5.6 ^b	5.88 ^b	0.039 0.025	0.0242
NaF	5.5 ^b 6.2 ^a	4.64 ^b 4.15 ^c	0.020 0.016	0.0161
NaCl	6.3 ^a 6.7 ^b	7.55 ^b	0.029 0.027	0.0238
NaBr	5.9 ^a 6.0 ^b	8.07 ^b	0.033 0.032	0.0287
Na I	5.6 ^{a,b}	8.58 ^b	0.037	0.0327
KCl	5.8 ^a 6.2 ^b	8.35 ^c 7.23 ^b	0.034 0.028	0.0265 (0.0245)
RbCl	4.4 ^{a,b}	6.72 ^b	0.036	0.0249
CsCl	3.9 ^{a,b}	5.69 ^b 5.5 ^d	0.035 0.034	0.017
B. At the triple points				
KCl I	5.6 ^e	2.1 ^e		0.0089
KCl II	5.5 ^e	6.3 ^e		0.0272
RbCl I	5.1 ^e	2.8 ^e		0.0131
RbCl II	5.4 ^e	8.9 ^e		0.0391
CsCl I	4.2 $\pm$ 0.6 ^e	3.0 $\pm$ 0.4 ^e		0.017
CsCl II	5.0 $\pm$ 0.7 ^e	10.0 $\pm$ 1.4 ^e		0.0483

^a Rossini *et al.*⁶

^b H. Schinke and F. Sauerwald, Z. anorg. u. allgem. chem. **287**, 313 (1956).

^c G. J. Landon and A. R. Ubbelohde, Trans. Faraday Soc. **52**, 647 (1956).

^d Johnson, Agron, and Bredig, J. Am. Chem. Soc. **77**, 2734 (1955).

^e Estimated values. See text.

well for NaF. For most of the remaining salts the discrepancy is less than 20%, but RbCl and CsCl are inconsistent by factors of 1.5 and 2. Discrepancies of 20% are probably not surprising considering the present state of high-temperature thermochemistry, but it is disturbing to find that the observed slopes tend to be systematically lower than those calculated. ΔV_f has been consistently overestimated or ΔS_f consistently underestimated unless, improbably, unsuspected systematic errors affect the results obtained in both the high-pressure and low-pressure equipment by the same amount.

The source of the discrepancy for CsCl can be deduced from relations at the triple point. The I-II transition at atmospheric pressure takes place at 470°C ;⁴ if the phase boundary is linear between this point and the triple point (which is probably nearly true for a solid-solid transition over the short range of P and T involved), its slope is $0.20^\circ\text{C}/\text{bar}$. Wagner and Lippert⁵ give $6\text{ cm}^3/\text{mole}$ for the volume change (ΔV_{tr}), and a compilation of data yields a value of $8\text{ cm}^3/\text{mole}$.⁴ These

⁴ Johnson, Agron, and Bredig, J. Am. Chem. Soc. **77**, 2734 (1955).

⁵ G. Wagner and L. Lippert, Z. physik. chem. **B31**, 263 (1936).