TABLE I. Parameters of the Simon equation.

Compound	T_0		P_0 bars	A bars	c	Standard deviation °C
	°K	°C				
LiCl	878	605±0.5	0	14 500±1000	2.5±0.1	2.6
NaF	1265	992±0.5	0	14 300±3000	5.5±1	1.3
NaCl	1073.5	800.5	0	16 700±900	2.7±0.1	3.3
NaBr	1014	741±0.5	0	12 200±500	2.9±0.1	5.6
Na I	928	655±0.5	0	10 100±400	2.8±0.1	6.1
KCl I	1043	770	0	6 900±700	5.7±0.5	2.3
KCl II	1315	1042±5	18,950	12 100	4[a]	1.0
RbCl I	990.5	717.5±0.5	0	6 600±700	6±0.3	0.6
RbCl II	1127	854±5	7,800	7 200±1000	4±0.3	1.9
CsCl I	917	644±0.5	...	...	...	...
CsCl II	933	660±5	950	8 400±600	2.3±0.1	1.5

[a] Assumed value.

These values were established by the careful work of Roberts.[2]

Since the thermocouples in the high-pressure apparatus are exposed to pressure, it is necessary to correct for its effect on their thermal emf. The correction is given by $\Delta T = 0.7\times10^{-6}\,PT$, where P is the pressure in bars, T is the centigrade temperature, and ΔT is the correction to be added to the measured temperature. The correction was determined by linear extrapolation of Birch's measurements,[3] and its maximum value is 18°C in the present work. This is roughly ten times the maximum correction in Birch's range of pressure and temperature and the accuracy of the extrapolation cannot be high. The only alternative to the large extrapolation is to ignore this correction entirely, and this is felt to be the greater of the two evils.

Materials

Salts obtained from Mallinckrodt Chemical Works were used in the high-pressure experiments. All except RbCl and CsCl were of AR grade and all were used without further purification. The RbCl contained about 0.1% KCl and less that 0.1% NaCl. The CsCl contained less than 0.2% KCl and less than 0.1% NaCl and $CaCl_2$. Several different lots of salt were tried in the low-pressure apparatus. They included optical quality crystals of NaCl and KCl from Harshaw Chemical Company, CsCl from the Maywood Chemical Company, and several AR grade salts from the Fisher Chemical Company. The Maywood CsCl contained less than 0.1% KCl and the same amount of NaCl. All the analyses mentioned above were made with a flame photometer by Dr. P. M. Orville.

The influence of water on the melting curves was determined by partially dewatering the salts by heating them slowly to the melting point *in vacuo* and sealing the capsules in a dry box. Although this procedure does not remove all the water, it changes the water content, particularly for deliquescent salts such as NaBr or LiCl. This treatment affected the melting points at atmospheric pressure and the initial slopes of the melting curves by less than the experimental error (0.5°C and 0.001°C/bar, respectively). Results from the different lots of salts agreed to within the same limits. One experiment with KCl was made in a gold capsule; it agreed with the others.

Results

The data are shown in Figs. 1 and 2. The breaks in slope of the melting curves of KCl, RbCl, and CsCl mark triple points between solid I (NaCl structure), solid II (CsCl structure), and liquid. The curves in the figures were calculated from the Simon equation,

$$P - P_0 = A[(T/T_0)^c - 1], \tag{1}$$

where T_0 is the melting point at pressure P_0, and A and c are adjustable constants. P_0 differs from zero only for the high-pressure polymorphs of KCl, RbCl, and CsCl; in the latter cases P_0 and T_0 are the coordinates of the triple points.

Simon's equation is not readily adapted to rigorous treatment by least squares, and an approximate procedure was adopted. The right side of Eq. (1) was evaluated with trial values of c, and A was then calculated by linear regression. The value of c which minimized the sum of the squares of the residuals was found by graphical interpolation. The equation was fitted to the measurements made in the high-pressure apparatus only.

The parameters of the Simon equation are given in Table I. The differences between the chaotic values in the literature for the melting points of these salts at atmospheric pressure, and T_0 as given in the table may be due in part to differing purity of material, but many discrepancies must be attributed to erroneous pyrometry.

The uncertainties in c and A were estimated by examining the trend of the residuals. Changing these parameters by more than the limits given in the table definitely impairs the fit of the experimental observa-

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[2] H. S. Roberts, Phys. Rev. **23**, 386 (1924).

[3] F. Birch, Rev. Sci. Instr. **10**, 137 (1939).

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°C/bar higher than that found experimentally. Taking this slope as 0.0245°C/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 1). 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 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.

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	5.88^b	0.039	0.0242
	5.6^b		0.025	
NaF	5.5^b	4.64^b	0.020	0.0161
	6.2^a	4.15^c	0.016	
NaCl	6.3^a	7.55^b	0.029	0.0238
	6.7^b		0.027	
NaBr	5.9^a	8.07^b	0.033	0.0287
	6.0^b		0.032	
Na I	$5.6^{a,b}$	8.58^b	0.037	0.0327
KCl	5.8^a	8.35^c	0.034	0.0265
	6.2^b	7.23^b	0.028	(0.0245)
RbCl	$4.4^{a,b}$	6.72^b	0.036	0.0249
CsCl	$3.9^{a,b}$	5.69^b	0.035	0.017
		5.5^d	0.034	
		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 ± 0.6^e	3.0 ± 0.4^e		0.017
CsCl II	5.0 ± 0.7^e	10.0 ± 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.

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 in 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°C/bar. Wagner and Lippert[5] give 6 cm^3/mole for the volume change (ΔV_{tr}), and a compilation of data yields a value of 8 cm^3/mole.[4] These

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

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