

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
NaI	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*	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

* 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 $\Delta T = 0.7 \times 10^{-6} PT$, 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 than 0.1% NaCl. The CsCl contained less than 0.2% KCl and less than 0.1% NaCl and CaCl₂. 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,

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

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-

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

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