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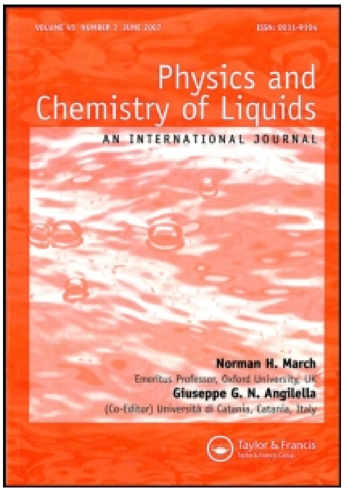

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Boiling of Alkali Halides: An Ionic to Molecular Phase Transition

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Letters

Boiling of Alkali Halides: An Ionic to Molecular Phase Transition

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When an alkali halide, say NaCl, boils, the hot ionic melt is in equilibrium with a vapour of NaCl molecules. These molecules are characterized by an equilibrium separation a_0 which naturally reflects their ionic nature. In contrast, in the hot melt, an appropriate ionic screening length must play a major role. The ratio of these two lengths, as we shall now demonstrate, by appeal to experimental data, is crucial in discussing boiling.

Thus the Table shows a_0, the boiling point T_b at atmospheric pressure[1] and the corresponding molar volume V_b for the alkali halide family. V_b has been calculated from the measured volume just above the freezing point, using the measured thermal expansion coefficient of the liquid.[1] The combination a_0^2/T_bV_b is then tabulated. It is seen to be remarkably constant for the Na,K and Rb halides, and to display a weak dependence on the ratio of the ionic radii as one moves to the Li, and to the Cs halides. This constancy can be represented by

$$\frac{a_0^2}{T_bV_b} = 0.7 \times 10^{-20}\ \text{mole/cm °K} \tag{1}$$

From the Table, it can be seen that V_b varies by a factor of ~2.5 through the series, which is approximately the same as the variation of a_0^2. That is V_b/a_0^2 is approximately constant through the family of alkali halides at atmospheric pressure. T_b varies much more weakly, but the inclusion of

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TABLE

Boiling properties of alkali halide systems[a]

Salt	a_0 (A°)	T_b (°K)	V_b (cm³/mole)	$(a_0^2/T_bV_b) \times 10^{20}$ (mole/cm°K)
LiBr	2.1704	1583(1562)	41.2(41.0)	0.722(0.736)
LiI	2.3919	1444(1449)	52.3(52.4)	0.758(0.754)
NaCl	2.3606	1738	46.1	0.695
NaBr	2.5020	1665	54.1	0.695
NaI	2.7115	1577	66.8	0.698
KCl	2.6666	1680(1710)	60.7(61.2)	0.697(0.679)
KBr	2.8207	1656(1671)	70.1(70.4)	0.685(0.676)
KI	3.0478	1597(1618)	84.9(85.5)	0.685(0.671)
RbCl	2.7868	1654	68.1	0.689
RbBr	2.9448	1625	77.4	0.689
RbI	3.1769	1577	92.8	0.690
CsF	2.3453	1524	49.9	0.723
CsCl	2.9062	1573(1597)	75.3(75.9)	0.713(0.700)
CsBr	3.0720	1573	85.6	0.701
CsI	3.3150	1573	102.6	0.681

[a] Values in parentheses for T_b have been taken from Ref. 2. As shown by the corresponding values in parentheses for the quantity reported in the last column of the Table, reasonable uncertainties in T_b do not significantly affect the correlation reported in Eq. (1). The measured equilibrium distances a_0 were obtained from Ref. 3.

T_b in Eq. (1) is nevertheless significant in exhibiting the regularities. Arguments which estimate the boiling temperature from the difference between the energy of the molecule, $\sim e^2/a_0$, and the Madelung energy proportional to $V_b^{-1/3}$ would lead to Eq. (1) only if V_b/a_0^3 were constant. Such a relation between V_b and a_0 is not consistent with the experimental data.

This correlation (1), with only weak dependence on the ratio of ionic radii, strongly supports the assumption that the hot ionic melt near the boiling point is behaving as a simple two-component plasma. It is therefore natural to expect that diminution of the screening of the ion-ion interactions with increasing temperature will play an important role in the transition from the ionic condensed state to the molecular vapour. A natural measure of the screening is afforded by the Debye-Hückel length κ^{-1}. This may be written

$$\kappa^{-1} = \left(\frac{k_bTV}{4\pi \mathrm{N}e^2}\right)^{1/2} \tag{2}$$

N being the number of ion pairs in volume V. In terms of κ^{-1}, the constancy of a_0^2/T_bV_b shown in the Table implies

$$\kappa(T_b)a_0 \doteqdot \text{constant} \tag{3}$$

This relation (3) establishes that the transition from ionic melt to molecular vapour occurs when the Debye–Hückel length κ^{-1} becomes a fixed fraction of the internuclear spacing in the molecule. Using the numerical value of a_0^2/T_bV_b from Eq. (1), the dimensionless constant in Eq. (3) is approximately 9. Thus, while the essential ingredients needed to determine the phase transition are established here as the equilibrium molecular separation a_0 and the Debye–Hückel screening length κ^{-1} the quantitative problem that remains is to show that the ratio on boiling is ~ 10 at atmospheric pressure.

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