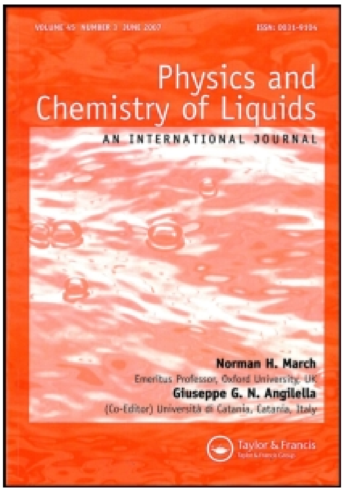

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Melting and Boiling from Ionic to Molecular Phases

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Ionic liquids, on boiling, are expected to be in equilibrium with molecular vapours. It is to be anticipated that the temperature range of the ionic liquid phase is extensive and comparable with the stability range of the solid. This is confirmed by available data. Boiling at low pressure is found from the data to occur when the Debye–Hückel screening length in the ionic melt is a fixed fraction, for the whole family of alkali halides, of the molecular equilibrium spacing. Starting from this regularity, a corresponding states argument is used to make predictions about the critical point.

Melting of a solid ionic phase into a molecular phase is a more system specific phenomenon. Characteristics favourable for such phase transitions are:

(i) Large valence difference between cation and anion.

(ii) Highly polarizable valence shells on the ions, such as arise with rather weakly bound d-electrons on the cation. To exemplify these points, the cases of the aluminium halides and the mercury halides are considered in some detail.

INTRODUCTION

In this paper we examine the consequences asociated with phase transitons from an ionic condensed system to a molecular assembly which may be either condensed or gaseous. Table I shows the melting and boiling points for selected representative halides at atmospheric pressure.[1] It can be seen that the alkali halides have an extensive temperature range of stability in the liquid phase, the boiling point being roughly twice the melting temperature.

Turning to the alkaline earth halides, it is noteworthy that their melting points are close to those of the alkali halides, in spite of a difference in

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cohesive energy per molecule of a factor of between two and three. When one examines the boiling points, the alkaline earth fluorides and chlorides have a stability range in the liquid comparable with that in the solid. But marked differences occur in the bromides and iodides, the stability range of the liquid being much narrower.

More striking, however, is the behaviour of the mercury halides. Here the melting temperatures are low and the range of stability of the liquid phase is remarkably narrow. This behaviour persists in the aluminium halides, with the notable exception of the high melting temperature of the fluoride, though again there is practically no temperature range of stability in the liquid phase. For a fuller discussion of these facts, the reader may refer to the book by Ubbelohde.[2]

That the molten alkali halides are good ionic liquids is clear both from the high ionic conductivities observed and from neutron diffraction studies of the liquid structure, using isotopes. These structural studies confirm that the number of near neighbours of each ion is close to that in the crystal and that there is a clear alternation of the charge distribution in space around each type of ion, in NaCl[3] and in RbCl[4]. In addition to these alkali halides, molten $BaCl_2$ has been investigated[5] by the same diffraction techniques, with similar conclusions as to the ionic nature of the melt.

The ionic nature of $BaCl_2$, and that of $CaCl_2$ which we infer from the large temperature range of stability shown in Table I, is to be contrasted with the behaviour of molten mercury halides referred to above. As summarized by Ubbelohde,[2] the ionic conductivity of molten $HgCl_2$ is $\sim 2 \times 10^{-4}$ $(\text{ohm cm})^{-1}$ which is three to four orders of magnitude lower than that of a good ionic liquid at a comparable temperature. For $AlCl_3$, the

TABLE I

Melting and boiling points for selected representative halides (°K)

Salt	Melting point	Boiling point	Salt	Melting point	Boiling point
LiF	1118	1954	NaCl	1081	1738
NaF	1268	1977	$CaCl_2$	1055	~1870
KF	1129	1775	$HgCl_2$	550	577
CaF_2	1696	~2800	$AlCl_3$	~460	~460
AlF_3	~1540	~1540	$FeCl_3$	573	592
NaBr	1020	1665	NaI	935	1577
KBr	1007	1656	KI	958	1597
$CaBr_2$	1015	~1082	CaI_2	1052	~1370
$HgBr_2$	514	592	HgI_2	530	627
$AlBr_3$	370	536	AlI_3	464	659

ionic conductivity is a further three orders of magnitude lower[2] than for $HgCl_2$.

Having summarized some of the relevant facts of the phase transitions we shall consider here, we turn first to discuss the boiling, and the critical behaviour of the alkali halides.

2 BOILING AND CRITICAL BEHAVIOUR OF ALKALI HALIDES

In another note,[6] we have pointed out a strong correlation between the boiling point T_b at atmospheric pressure, recorded in Table I, the molar volume V_b of the ionic liquid at T_b, and the equilibrium separation in the appropriate alkali halide molecule. This is expressed by[6]

$$\frac{a_o^2}{T_b V_b} = 0.7 \times 10^{-20} \text{ mole/cm °K} \tag{2.1}$$

This relation is obeyed to high accuracy by the Na, K and Rb halides. Some weak dependence on the ratio of the ionic diameters is apparent as one moves to Li and to Cs halides. We shall neglect this dependence for the purposes of the ensuing discussion.

Equation (2.1) relates the family of alkali halides at atmospheric pressure, which is essentially $p = 0$. To generalize Eq. (2.1), to enable the critical region to be embraced by the discussion, we shall appeal to corresponding state arguments. Denoting critical thermodynamic variables by p_c, V_c, T_c the relation (2.1) is assumed to take the more general form

$$\frac{a_0^2}{T_b(p)V_b(p)} = F\left(\frac{p}{p_c}\right) \tag{2.2}$$

Evidently the value $F(0)$ is fixed by Eq. (2.1). Following our other work,[6] it is helpful to rewrite Eqs. (2.1) and (2.2) in terms of the Debye–Hückel screening length κ^{-1}, defined by

$$\kappa^{-1} = \left(\frac{k_B T V}{4\pi N e^2}\right)^{1/2}, \tag{2.3}$$

where N is the number of ion pairs in volume V. Then Eq. (2.1) takes the form

$$\kappa(T_b)a_0 \simeq 10, \tag{2.4}$$

at atmospheric pressure whereas at pressure p on the boiling curve we may write

$$\kappa, a_0 = f\left(\frac{p}{p_c}\right). \tag{2.5}$$

From the left-hand side of Eq. (2.2), it is clear that the product $T_b V_b$ increases with pressure, from the general shape of coexistence curves. Therefore, since the vapour molecule equilibrium spacing a_0 is expected to be insensitive to pressure, it follows that $f(p/p_c)$ decreases from $f(0) \simeq 10$ as the critical point is approached. If $f(1)$ is ~ 1, Eq. (2.5) at $p = p_c$ acquires a physical meaning as a semiquantitative criterion for the critical point. This meaning is associated with the increased screening length from Eq. (2.3) as the critical point is approached and the criterion for ions, say Na^+ and Cl^-, to pair to form molecules is roughly that $\kappa^{-1} \sim a_0$.

Though the function $F(p/p_c)$ in Eq. (2.2) is not known from theory, but only in the general terms discussed above, it is an interesting qualitative prediction for the boiling curve of the alkali halides that (p/p_c) simply depends on the product TV.

Furthermore, at the critical point the assumption (2.2), with F the same function for the alkali halide family, evidently predicts.

$$T_c V_c = \text{constant } a_0^2 \tag{2.6}$$

where the constant is the same for the whole series. Of course, the measurement of the critical parameters for the alkali halides is a formidable experimental project. However, some density measurements by Kirshenbaum *et al.*[7] have been extrapolated to estimate critical data for NaCl and KCl. Using their results, one obtains the following:

	T_c (°K)	V_c (cm^3/mole)	$(a_0^2/T_c V_c) \times 10^{20}$ (mole/cm^{0}K)	$\kappa_c a_0$
NaCl	3400 ± 200	266 ± 60	0.062 ± 0.02	2.7 ± 0.4
KCl	3200 ± 200	415 ± 150	0.054 ± 0.03	2.5 ± 0.5

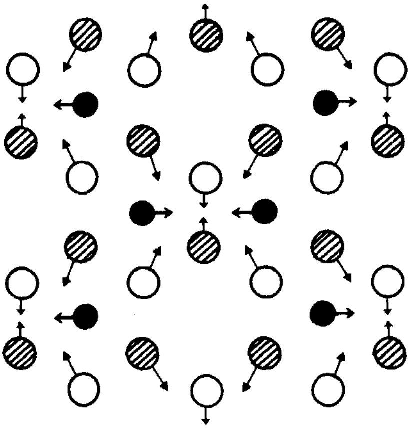
It is satisfactory that from this data the critical point is characterized by the ratio of a_0 to the Debye–Huckel screening length being about 3, to within the errors given by Kirshenbaum *et al.* This is to be compared with a ratio of 9 at the normal boiling point.

To summarize, boiling points at atmospheric pressure, for the alkali halide family, obey the relation (2.1). Provided corresponding states arguments apply, the critical volume and temperature are related to the molecular equilibrium spacing a_0 by Eq. (2.6), the constant being the same for the whole series of alkali halides. We feel it should occasion no surprise that a_0 enters the formulae at the critical point when one is dealing with ionic liquids and molecular vapours for $T < T_c$. As T_c is approached, we anticipate that both ionic species and molecules will be present.

3 MELTING OF AlCl$_3$

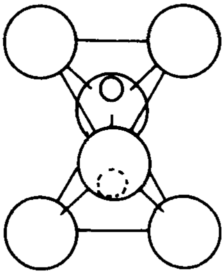
Having discussed the boiling and critical behaviour of ionic materials in rather general terms, we now turn to deal in some detail with the specific case of the melting of $AlCl_3$. As discussed below this phase transition is from an ionic solid to a molecular liquid.

That the solid is ionic is clear from the X-ray diffraction determination of its structure by Ketelaar *et al.*[8] The atomic arrangement is as shown in Fig. 1a, and the structure of the molecule[9] Al_2Cl_6 is as in Fig. 1b. This molecule is the basic unit in the molten molecular phase, as demonstrated by X-ray studies of the melt.[10]



(a)

FIGURE 1a Plane projection of the $AlCl_3$ structure (from Ketelaar *et al.*, Ref. 8). The shaded and open circles represent the chlorine ions at $z = \pm 1/4$. The solid circles indicate positions of Al atoms. The arrows denote chlorine ion displacements required to allow formation of Al_2Cl_6 molecules from this ionic structure.



(b)

FIGURE 1b Structure of the Al_2Cl_6 molecule in the vapour phase. Large circles represent chlorine atoms. Small circles denote aluminium atoms.

3.1 PROPOSAL OF SOFT PHONON MODES IN SOLID $AlCl_3$

As to the solid structure, this is layer-like. That the bonding within a layer is ionic is seen from the fact that each Al ion shares three pairs of halogen ions with three Al neighbours. Within each layer, it is possible to recognize those displacements of the halogen ions which would lead to formation of an Al_2Cl_6 molecular solid. These displacements are depicted by the arrows in Figure 1a.

Consider the expansion of the ionic solid lattice. It would seem that, at some lattice parameter in excess of the equilibrium value, it wil become energetically favourable for each Al ion to satisfy its own valence requirements by appropriating a halogen ion from each of the two pairs that it shares with neighbouring Al ions, rather than continuing to share these pairs with them as at equilibrium.

The necessary displacements of the Cl ions to bring this about are precisely those shown by the arrows in Figure 1a.

If such a lattice expansion were carried out, with assumed force laws, we anticipate that the phonon spectrum of the ionic crystal would herald the approach of a phase transition to a molecular crystal by a particular phonon mode becoming soft. However, we caution that a description of the force laws in purely ionic terms does not contain the electronic re-distribution which is to be expected in the formation of the Al_2Cl_6 molecule. Such redistribution will naturally work in a direction to assist the phonon softening.

Thus, we anticipate that as the temperature of the ionic solid $AlCl_3$ is raised, a marked change in the phonon mode corresponding to the deformation depicted in Figure 1a will occur. In principle, the instability this phonon softening heralds could be to a solid molecular phase. Presumably, in this material, a proper account of the thermal vibrations will lead to a vanishing small range of stability of the weakly bound molecular solid. We stress that the weakness of these binding forces is due to the effective screening of the Al ions by the neighbouring Cl^- ions in the Al_2Cl_6 molecule. It is also worth noting that solid $AlBr_3$ has a different structure from $AlCl_3$. Already in the solid, the lattice can be viewed as composed of Al_2Br_6 molecules.

This is the point at which we must comment on the conditions under which transitions from an ionic condensed phase to a molecular phase are favoured. It seems clear, for the halogen anions, that it is polyvalent cations that afford favourable circumstances for the molecular phase to be formed. This is because, to satisfy the local valence requirements of the polyvalent cation, the number of nearest neighbours in the molecule equals the cation valency. Thus, in the ionic-molecular phase change, the coordination number changes less severely than for monovalent cations.

The unfavourable energetics involved in reducing the coordination is counteracted by the fact that the anion-cation distance will be reduced when the molecule is formed, and at the same time the anions can be polarized up to the formation of a partially covalent bond. That there is an effect of polarizability is illustrated by the differences we pointed out above between solid $AlCl_3$ and solid $AlBr_3$ and also between the alkaline earth fluorides and chlorides on the one hand and their bromides and iodides on the other. We proceed to illustrate in the next section, using the example of the mercury halides, the effects of polarizability which arise when the polyvalent cation itself has weakly bound *d*-electrons.

4 STRUCTURAL TRANSITION IN HgI_2

The possibility of an ionic-molecular solid-solid transition was referred to above in the discussion of the melting of $AlCl_3$. Though our prime interest here is in melting and boiling it is noteworthy that such an ionic-molecular solid transition has actually been observed in HgI_2.

The ionic form of the solid (red HgI_2) is tetragonal, each Hg ion being surrounded tetrahedrally by four equivalent I ions. The Hg–I separation is 2.78 Å.[11,12] In contrast, the high temperature solid structure (yellow HgI_2) is of layer type. In this structure, only two I ions remain at the distance 2.78 Å, while four other nearest neighbors of a Hg ion are at the larger distance of 4.11 Å. The interpretation of these facts is that largely covalent HgI_2 molecules are formed in the transition, and remain intact in the molecular crystal phase.

We anticipate again that, as the temperature is increased, the appropriate phonons of red HgI_2 will soften, although an elementary ionic force field will not be adequate to describe the transition quantitatively.

The high temperature phase of HgI_2 has the same structure as $HgBr_2$. Although the structure of $HgCl_2$ has different symmetry, in all these cases the solid is built from molecules. X-ray diffraction studies of the chloride and the bromide[13] have shown that the molecules have a linear configuration in the solid state. This leads to residual intermolecular interactions which are stronger than van der Waals binding because the molecules carry a quadrupole moment.

The melting of these materials is from molecular solid to molecular liquid, but with the presence of quadrupolar forces distinguishing the transition from, say, the melting of Ar. It appears in the liquid that, because of some residual ionic conductivity, there is the possibility of a fraction of $HgBr_2$, say, being dissociated to form $HgBr^+$ and $HgBr_3^-$ complexes.[14]

5 SUMMARY AND CONCLUSION

That molecular phase formation would lead to weak intermolecular interactions has been recognised for a long time. Such weak interactions clearly limit the temperature range of stability of condensed molecular phases. Numerous examples of this can be picked out from Table I, and in particular the behaviour of the Al and Hg halides immediately exemplifies this.

The most general consequences of ionic to molecular phase transitions occur on melting ionic materials. Though differences of detail can occur on melting alkali halides, and it is known that in the vapour phase of, for example, NaCl, some dimers are formed, the qualitative point is that a basic length determining the energetics of the vapour phase, through intramolecular ionic binding, is the equilibrium interionic spacing a_0. Equation (2.1) is a clear manifestation of this when the alkali halides boil. It would be of considerable interest if experiments near the critical point of the alkali halides could eventually be carried out to test, and if necessary to refine, our corresponding states generalization of Eq. (2.1). One remarkable consequence of this generalisation is that the product of critical temperature and volume ought to be proportional to the square of the interionic equilibrium separation in the appropriate alkali halide molecules. Extrapolation of the density measurements of Kirshenbaum *et al.*,[7] for NaCl and KCl, leads to results which are consistent with our prediction $a_0^2/T_c V_c$ = constant for the alkali halide family.

Solid-liquid and solid-solid ionic to molecular transitions depend much more on specific details of the two phases. Nevertheless, some qualitative criteria favouring transitions to molecular phases can be given: high cation valency and highly polarizable ions. These considerations are exemplified by $AlCl_3$, in which a transition from ionic solid to molecular liquid occurs, the molecules being Al_2Cl_6. But going from Cl to Br is, as we have seen, enough to change the structure of the solid to that of a molecular phase. In HgI_2, there is a solid-solid transition from ionic to molecular ordering as the temperature is raised. An experimental study of phonon modes as a function of temperature in solid $AlCl_3$ and red HgI_2 would be helpful in connection with the discussion given here of phase transitions in these materials.

References

1. G. J. Janz, *Molten Salts Handbook*, (Academic: New York, 1967).
2. A. R. Ubbelohde, The Molten State of Matter (Wiley: Chichester, 1978).
3. F. G. Edwards, J. E. Enderby, R. A. Howe, and D. I. Page, *J. Phys.*, **C8**, 3483 (1975).
4. E. W. J. Mitchell, P. F. J. Poncet, and R. J. Stewart, *Phil. Mag.*, **34**, 721 (1976).
5. F. G. Edwards, R. A. Howe, J. E. Enderby, and D. I. Page, *J. Phys.*, **C11**, 1053 (1978).

6. N. H. March and M. P. Tosi, to appear.
7. A. D. Kirshenbaum, J. A. Cahill, P. J. McGonigal, and A. V. Grosse, *J. Inorg. N. Chem.*, **24**, 1287 (1962).
8. J. A. Ketelaar, C. H. Macgillvary, and P. A. Renes, *Rec. Trav. Chim. Pays-Bas*, **66**, 501 (1947).
9. K. J. Palmer and N. Elliot, *J. Am. Chem. Soc.*, **60**, 1852 (1938).
10. R. L. Harris, R. E. Wood, and H. L. Ritter, *J. Am. Chem. Soc.*, **73**, 3150 (1951).
11. R. W. G. Wyckoff, *Crystal Structure*, (Interscience: New York, 1963).
12. G. J. Janz and J. D. E. McIntyre, *Ann. N.Y. Acad. Sci.*, **79**, 790 (1959).
13. W. Scholten and J. M. Bijvoet, *Zs. Krist.*, **103**, 415 (1941).
14. G. J. Janz and J. D. E. McIntyre, *J. Electrochem. Soc.*, **109**, 842 (1962).