perature of 150° C, a hydrogen carrier gas velocity of 50 ml./min, a sample size of 0.1 μ l., and a hot-wire conductivity detector.

The relative retention volumes of isomers are given in Table 1. It should be noted that with increasing sample size the elution peaks become asymmetric and the separation factors decrease. In spite of these circumstances it was possible to perform, under proper conditions and column size, preparative separation of 20- μ l. samples of 2,4,6-trichloroheptane and isolation of pure stereo-isomers.

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Relationship between Volume Change on Fusion and the Volume of Defect Formation in Ionic Crystals

THE molar volume change on fusion of an ionic compound, ΔV_{fusion} , is relatively easy to determine. It may be found directly, by observing the change in length of a column of fused salt in a capillary when this is cooled through the freezing temperature, or indirectly by measuring the freezing point of the salt as a function of pressure and applying the Clapeyron–Clausius equation. The literature now contains reliable values of ΔV_{fusion} for the common inorganic salts^{1,2}.

It is well known that ionic solids may contain defects of the Schottky (vacant site) or Frenkel (interstitial ion) type, and that migration of these defects gives rise to diffusion and electrical conductance in the solids. Since the individual defects in an ionic crystal bear an excess charge relative to the undistorted lattice, the condition of electrical neutrality requires that a given crystal must contain at least two types of defect bearing opposite excess charge. For each cation vacancy in a stoichiometric crystal containing ions of non-variable valency, there must be either an anion vacancy or an interstitial cation elsewhere in the crystal. In a particular compound, one or other of these possibilities usually predominates; for example, the alkali halides are known to contain cation and anion vacancies³, and the silver halides mainly cation vacancies and interstitial cations⁴. In CaF_2 , the complementary defects are anion vacancies and interstitial anions⁵.

The molar volume of formation of defects, $\Delta V_{\text{form.}}$, is defined as the volume increase associated with the formation of one mole of each of the complementary defects in an initially perfect crystal. $\Delta V_{\text{form.}}$ is relatively difficult to determine experimentally; values are at present available only for KCl, NaCl, AgBr and KNO_3 (refs. 6–8). It is found from the isothermal pressure coefficient of the electrical conductivity of the crystal; measurements must be carried out on the pure substance, and also on a sample into which additional defects have been introduced by adding traces of divalent cations⁶. It has been found that, for crystals containing vacant cation and anion sites in equal numbers, $\Delta V_{\text{form.}}$ is about 1.5 times the molar volume of the salt, whereas for silver bromide $\Delta V_{\text{form.}}$ is only about 0.5 times the molar volume. The magnitude of $\Delta V_{\text{form.}}$ relative to the molar volume of the solid, V_s , therefore gives an indication of the types of defect predominant. (If there were no distortion of the

crystal lattice around each defect, $\Delta V_{\text{form.}}$ would equal V_s for crystals containing anion and cation vacancies, and would be zero for crystals containing cation vacancies and interstitial cations.)

The purpose of this communication is to point out that there appears to be a proportionality between $\Delta V_{\text{form.}}$ and ΔV_{fusion} for all crystals, irrespective of the types of defect present in the solid (Table 1).

Table 1

Salt	V_s , just below m.p.	ΔV_{fusion}	$\Delta V_{\text{form.}}$	$\Delta V_{\text{fusion}}/\Delta V_{\text{form.}}$
KCl	41.60	7.2	67	0.11
NaCl	30.2	7.5	43	0.18
AgBr	31.1	2.5	16	0.16
KNO_3	52.5	1.73	11	0.16

(all volumes in ml.mole⁻¹)

The ratio $\Delta V_{\text{fusion}}/\Delta V_{\text{form.}}$ is formally equal to the degree of defect formation (that is, the fraction of lattice sites vacant, or fraction of interstitial sites occupied) which would have to occur in the solid in order to produce a volume change equal to ΔV_{fusion} . It is seen that $\Delta V_{\text{fusion}}/\Delta V_{\text{form.}}$ lies in the range 0.15 ± 0.04 for the four salts for which data exist. The X-ray diffraction work carried out by Levy *et al.*⁹ on fused alkali halides showed that the average co-ordination number in salts having the rock-salt structure falls from six to about five on fusion. If this change were brought about by introduction of defects into the crystalline solid, the degree of defect formation required would be about 0.17. This is suggestively close to the figures in the last column of Table 1, and leads me to propose the following rules:

(1) The fusion of an ionic crystal is equivalent to the introduction of disorder into the crystalline lattice to the extent of 15 ± 4 per cent.

(2) The defects introduced on fusion are of the same type as those already present in the crystal below its melting point.

Thus, fused silver halides may be thought of as containing an approximately intact bromide lattice, with 85 per cent of the silver ions occupying normal sites and the remaining 15 per cent on interstitial sites, while fused alkali halides have approximately the rock-salt lattice each with 15 per cent of the cation and anion sites vacant. These pictures are approximate in so far as the vestiges of lattice structure which remain in the melt are insufficient to impart the property of rigidity.

The converse of the above rules may be written:

(3) Those ionic compounds for which $\Delta V_{\text{fusion}}/0.15$ is less than about one-half of the molar volume have cation vacancies and interstitial cations, or anion vacancies and interstitial anions, as predominant defects in the solid. Those compounds for which $\Delta V_{\text{fusion}}/0.15$ is about 1.5 times the molar volume contain predominantly cation vacancies and anion vacancies.

This third rule may be the most useful of the three, because it enables us to predict the type of defect present in a solid from a knowledge of its volume change on fusion. This quantity is relatively easy to determine, whereas the determination of $\Delta V_{\text{form.}}$ (on which conclusions as to type of defect have usually been based) requires the difficult and painstaking measurement of the pressure coefficient of the electrical conductivity.

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