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AND VOLUME OF MELTING IN HALIDE SALTS**

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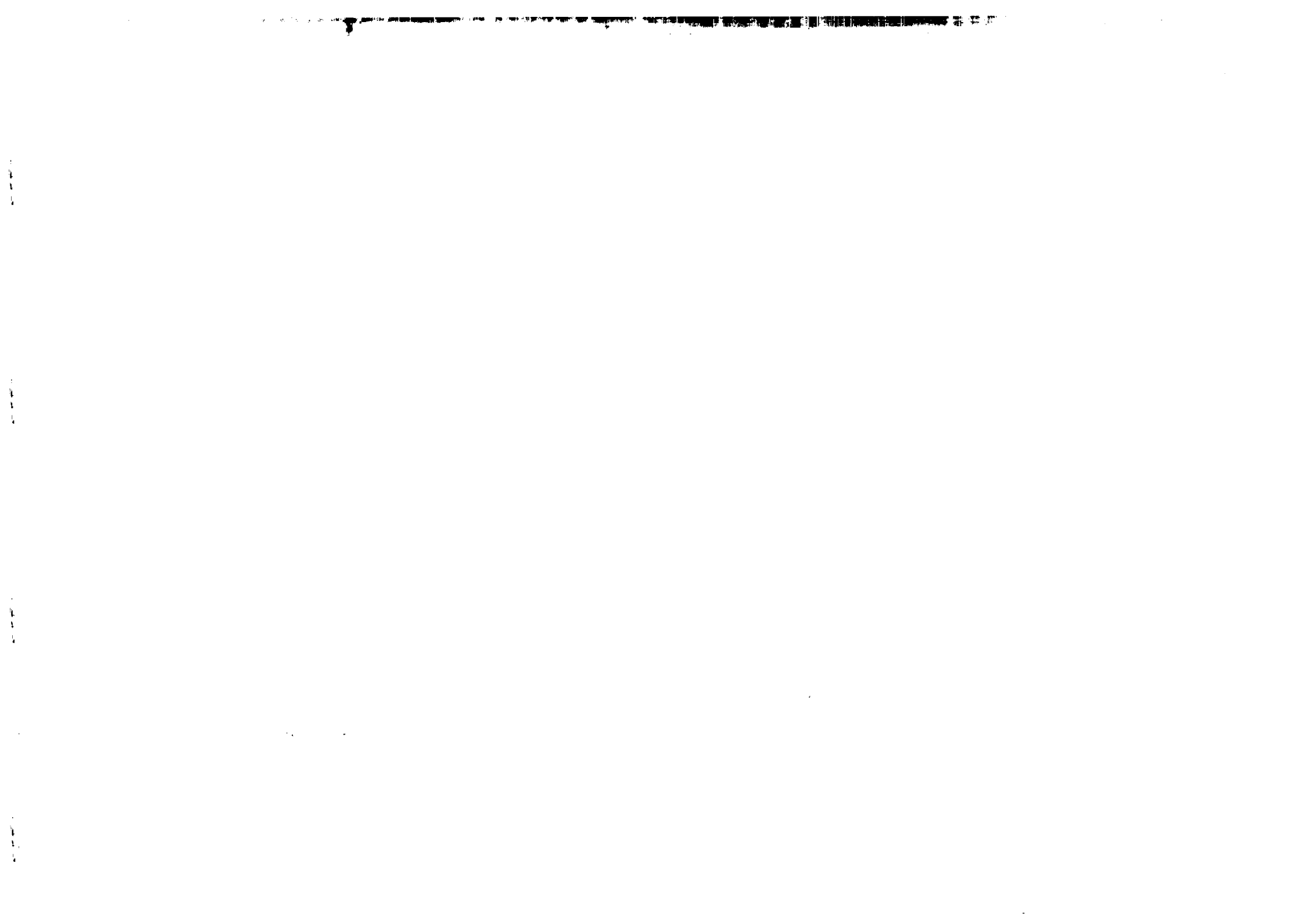


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AND VOLUME OF MELTING IN HALIDE SALTS**

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Abstract

Melting parameters and transport coefficients in the melt are collated for halides of monovalent, divalent and trivalent metals. A number of systems show a deficit of entropy of melting relative to the linear relationships between entropy change and relative volume change on melting that are found to be approximately obeyed by a majority of halides. These behaviours are discussed on the basis of structural and transport data. The deviating systems are classified into three main classes, namely (i) fast-ion conductors in the high-temperature crystal phase such as AgI, (ii) strongly structured network-like systems such as ZnCl₂, and (iii) molecular systems melting into associated molecular liquids such as SbCl₃.

1. Introduction

There has been for a number of years a continued interest in studying the structure of molten salts with the main help of neutron and X-ray diffraction techniques. Most of this work on monovalent and divalent metal halides, and the related theoretical and computer simulation studies, have been reviewed by Rovere and Tosi (1986), McGreevy (1987) and Enderby and Barnes (1990) (see also McGreevy and Pusztai 1990). Similar studies of trivalent metal halides, after the early work of Triolo and Narten (1978) on molten SbCl_3 and of Ichikawa and Matsumoto (1981) on molten BiI_3 , have only recently been undertaken in a systematic way (Howe, Price and Saboungi 1990; Saboungi, Price, Scarnhorn and Tosi 1991; Mochinaga, Iwadata and Fukushima 1991). Alternative melting mechanisms and liquid structure types have been recognized from the available structural data on a limited number of trichlorides, with the help of macroscopic melting parameters and transport coefficients in the melt and in correlation with the character of the chemical bonding (Tosi, Pastore, Saboungi and Price 1991).

Recourse to macroscopic thermodynamic and transport data has previously been made to infer gross structural characters of many melts, in particular by Ubbelohde (1978), and also to characterize the solid electrolyte state of fast-ion conductors as an ion-disordered phase (O'Keefe and Hyde 1976). The aim of the present work is to bring this approach to a quantitative level for the halides of monovalent, divalent and trivalent metals.

To this end we examine for these systems the validity of an approximate linear relationship between the entropy change ΔS and the volume change ΔV on melting, such as was first noticed for argon and sodium under pressure by Stishov, Makarenko, Ivanov and Nikolaenko (1973) and empirically established for a range of metals by Lasocka (1975). For such monatomic systems ΔS is found to extrapolate in the limit $\Delta V \rightarrow 0$ to the value $R \ln 2$. This limiting value has been alternatively interpreted as arising from the localization of shear modes on melting (Tallon 1982a) or from topological line defects in the liquid (Rivier and Duffy 1982). In the extended form proposed by Tallon and Robinson (1982) for polyatomic

systems, the relationship reads

$$\Delta S = n R \ln 2 + \alpha B_T \Delta V, \quad (1)$$

where n is the number of components in a formula unit, α the coefficient of thermal expansion and B_T the isothermal bulk modulus. Tallon (1982b) has discussed on the basis of (1) the abnormally low values of the entropy of melting for superionic SrCl_2 and CaF_2 , from the data of O'Keefe and Hyde (1976).

Aside from the intrinsic fundamental interest in the limiting value of the entropy of melting for $\Delta V \rightarrow 0$, the relationship (1) becomes practically useful by virtue of the fact that the Grüneisen parameter $\gamma = \alpha B_T V / C_V$ and the heat capacity C_V take similar values for similar systems in corresponding states. To the extent that the quantity $\alpha B_T V$ at liquid-solid coexistence does not vary widely from system to system within a given family of salts, equation (1) implies an approximate linear relationship between the melting parameters ΔS and $\Delta V/V$, extrapolating for $\Delta V/V \rightarrow 0$ to values in the ratios 2 : 3 : 4 for monovalent, divalent and trivalent metal halides. This prediction turns out to be approximately verified by a majority of the salts that we consider.

There are nevertheless found to be a number of exceptions to this broad empirical fact, which are mostly represented by systems whose measured ΔS lies well below the value predicted from the known $\Delta V/V$. As we shall see, the systems showing a "melting entropy deficit" include not only superionic conductors, but also strongly structured glass-formers and systems melting into associated molecular liquids. This identification will be strengthened by discussing the entropy-volume relationship in correlation with the ionic conductivity σ and shear viscosity η of the melt at freezing and with the type of crystal structure in the high-temperature solid phase, and by taking advantage of liquid structure data whenever possible and appropriate.

2. The entropy - volume relationship

The data that we have been able to collate refer to 21 monohalides, 24 dihalides and

18 trihalides, with a predominance of chlorides. The systems that we have chosen cover to a large extent all the systems in these families for which data on ΔS and on the molar volume V_m of the liquid phase at the melting temperature T_m are available in the literature. The data on ΔS and T_m that we have adopted are from Barin and Knacke (1973), Barin, Knacke and Kubaschewski (1977), Pankratz (1984) and Chase *et al.* (1985), while the data on V_m are from Janz (1988) and from Igarashi and Mochinaga (1987). However, for many of these systems the value of the molar volume of the solid at melting does not seem to be known. We have followed Igarashi and Mochinaga (1987) in assuming that the difference between V_m and the molar volume V_{RT} of the solid at room temperature provides a reasonable and presumably upper estimate for the volume change on melting. The quantity that we indicate in the following as $\Delta V/V$ is accordingly taken as $(V_m - V_{RT})/V_m$. This choice is likely to lead to an underestimate of the average slope and to an overestimate of the intercept in a test of the presumed relationship between ΔS and $\Delta V/V$. Excluding the case of $AlCl_3$, to which we shall return later, the quantity $(V_m - V_{RT})/V_m$ reaches at most the value 0.3 in the systems that we consider, and we believe that the inaccuracy involved in our use of V_{RT} to assess the magnitude of the relative volume change on melting does not have major consequences for our purposes. One should, of course, also bear in mind the intrinsic fluctuations that may be expected in the value of $\alpha_B V_m$ from salt to salt, as well as the likely inaccuracies in the available values of V_m and ΔS .

The data on T_m , ΔS and $\Delta V/V$ are collected in tables 1, 2 and 3 for monohalides, dihalides and trihalides, respectively. In each table the various systems have been ordered first according to increasing values of the chemical activity parameter χ_M proposed by Pettifor (1986) for the metal, and then for a given metal in the order from the fluoride to the iodide. This ordering introduces a correlation with the character of the chemical bonding, crudely corresponding to increasing weight of covalency *versus* ionicity as one proceeds downwards within each table. Pettifor (1986) has exhaustively demonstrated and discussed the correlations between his chemical activity scale and the types of crystal structure of compounds with $A_m B_n$ stoichiometry at low temperature. In the present connection the

crystal structure of main interest is that of the solid at melting, which is included in tables 1-3 from information given in Structure Reports as well as in the books of Wyckoff (1964) and Wells (1990). As we shall see, the systems showing a deficit of entropy of melting fall into well defined pockets within the ordering of systems that we have adopted.

Tables 1-3 present also the values of the transport coefficients σ and η in the melt at freezing, from the compilation by Janz (1988). These will be useful in the later discussion.

The ΔS and $\Delta V/V$ data in tables 1-3 have been used to construct the diagram shown in figure 1. Here, the monohalides are represented by empty and filled circles, the dihalides by empty and filled squares and by filled lozenges, and the trihalides by empty and filled triangles. For each family of salts the empty symbols in figure 1 mark those systems whose entropy and volume change appear to be approximately consistent with a linear entropy-volume relation. The best fits to these data are shown by the straight lines in figure 1. They are given by the following equations:

for monohalides,

$$\Delta S/R = 2.2 \ln 2 + 4.9 \Delta V/V ; \quad (2)$$

for dihalides,

$$\Delta S/R = 3.9 \ln 2 + 7.8 \Delta V/V ; \quad (3)$$

for trihalides,

$$\Delta S/R = 5.0 \ln 2 + 12.4 \Delta V/V . \quad (4)$$

The significance of the deviations of the intercepts in (2)-(4) from the values proposed in (1) will be discussed in the next section, bearing in mind the inaccuracies in our analysis that we have stressed earlier in this section. Clearly, (2)-(4) approximately imply a single relationship between the entropy change per particle and the relative volume change.

The full symbols in figure 1 represent instead the systems showing a clear deficit in the entropy of melting relative to the above "norms". They will be the object of specific discussion in the following section. We shall also discuss there the case of $NiCl_2$, which is represented in figure 1 by the symbol X.

3. Discussion

(a) Monovalent metal halides

The Pettifor parameter χ_M clearly separates in table 1 the alkali halides from the less closely ionic halides of silver, copper and thallium and from indium monochloride. The latter compound transforms before melting into the layer-type yellow-TII structure. All these systems in the liquid state have similar values of ionic conductivity and shear viscosity, of typical magnitude for loosely coordinated ionic melts whose main structural characteristics arise from excluded volume effects and from relative Coulomb ordering of the two component species (see for example Rovere and Tosi 1986).

The entropy and volume change data for all the alkali halides in table 1, as well as those for AgCl, TlBr, TlI and InCl, have been used to obtain the empirical relationship between ΔS and $\Delta V/V$ which is given for monohalides in (2). Among these systems, only RbBr shows a deviation from (2) that may be significant. The deviation that we find for the intercept in (2) from the value $2 \ln 2$ given in (1) is certainly not significant. The value of the slope in (2) is in approximate agreement with that estimated by Tallon and Robinson (1982) from high-temperature crystal data.

AgI, AgBr and CuCl, in order of increasing $\Delta V/V$, are shown in figure 1 by filled circles. AgI is a well-known superionic conductor in its high-temperature crystal phase, while in AgBr and CuCl before melting the ionic conductivity attains values of magnitude similar to those shown for melts in table 1. The deficit in entropy of melting that may be attributed to these salts is clearly related to the fact that the entropy of the crystal is abnormally increased before melting by the disordering of the cationic component.

We stress again that the essence of the above comments on superionic conductors is not new, since it is already contained in the discussions given by O'Keefe and Hyde (1976) and by Tallon (1982b). Our brief discussion of monohalides nevertheless serves to set the scene for the following discussion of polyvalent metal halides.

(b) Divalent metal halides

The dihalides in table 2 span a wide range of the Pettifor parameter χ_M and a variety of crystal structures. Among them three types of systems deserve specific attention:

- (i) the fast-ion conductors BaCl₂, SrCl₂ and SrBr₂;
- (ii) the network-structured compounds ZnCl₂, BeF₂ and BeCl₂;
- (iii) the molecular crystals HgCl₂, HgBr₂ and HgI₂.

The fast-ion conducting state is attained through a structural phase transition in BaCl₂ and SrBr₂, in analogy with AgI, while SrCl₂ shows a continuous rapid increase in the ionic conductivity on the approach to melting. The latter behaviour is in a way similar to that of AgCl and CuCl, except that a superionic transition temperature can be assigned to SrCl₂ by virtue of a prominent peak in its heat capacity. This allows an assessment of the increase of entropy associated with the disordering of the anions in the high-temperature solid (O'Keefe and Hyde 1976). Naturally, SrCl₂, SrBr₂ and BaCl₂ (marked in order of increasing $\Delta V/V$ by filled squares in figure 1) show a deficit of entropy of melting relative to the "norm" for dihalides in (3). The entropy of melting of these dihalides is actually comparable in magnitude to that of the fast-ion conducting monohalides, only one sublattice remaining in both cases well ordered in the crystal near melting (Tallon 1982b).

Turning to the second group of dihalides that we have singled out above, the crystal structures of ZnCl₂ and BeF₂ are 3D networks of corner-sharing tetrahedral units centered on the metal ions, while the same local coordination in BeCl₂ leads through edge sharing to the chain-like "fibrous SiS₂" crystal structure. Both BeF₂ and ZnCl₂ can be brought into a glassy state by rapid cooling from the melt. From the available transport data in table 2, these systems in the melt have extremely low ionic conductivity and extremely high viscosity. BeF₂, ZnCl₂ and BeCl₂, in order of increasing $\Delta V/V$, are marked in figure 1 by filled lozenges. Clearly, they all show a very large deficit of entropy of melting relative to the "norm" for dihalides in (3).

As is known experimentally for ZnCl₂ from neutron diffraction measurements

(Biggin and Enderby 1981a), the melting process not only preserves the local structure of the crystalline state, in the form of a very stable tetrahedral coordination of the metal ions by chlorines, but also yields a melt in a state of intermediate range order. The latter is most clearly manifested by a first sharp diffraction peak (FSDP) in the partial liquid structure factors at scattering wave number near 1 \AA^{-1} , the FSDP being particularly prominent in the Zn - Zn partial structure factor. The suggestion coming from our analysis is that melting into a strongly structured liquid with intermediate range order does not absorb the full "normal" amount of entropy. The deficit in the entropy of melting should in such a case be expected to be gradually made up as the structure of the melt loosens up on further heating in the liquid state. It would be interesting to examine whether this suggestion may also apply to other glass-forming and strongly structured liquids.

In their high-temperature crystal structure HgCl_2 , HgBr_2 and HgI_2 are best viewed as molecular crystals composed of monomeric formula units having linear shape. Melting occurs into liquids with very low ionic conductivity and "normal" viscosity (see table 2), and accordingly these melts are commonly described as molecular liquids. We know of no structural investigation of the state of short and possibly intermediate range order in these melts. Their entropy and volume changes on melting appear to conform to the "norm" established for dihalides in (3). This empirical relation has been obtained from the data on all the dihalides in table 2, excluding only NiCl_2 and the superionic and strongly structured salts that we have discussed just above.

The systems which approximately obey (3) thus include, in addition to the molecular-type mercury dihalides, systems crystallizing in the 3D CaCl_2 and PbCl_2 -type structures as well as in the layer-type CdCl_2 and CdI_2 structures. These can all be described as formed from more or less distorted close packings of the halogens, inside which the metal ions occupy interstitial sites. In the PbCl_2 structure the metal ions have nine halogen neighbours at various distances, while in the CaCl_2 , CdCl_2 and CdI_2 structures they are in an octahedral-type coordination. From the transport data in table 2 it appears that all these salts have loose

ionic-type structures in the melt, with an extreme of low ionic conductivity and high viscosity reached in CdI_2 and PbBr_2 . The liquid structure has been studied by neutron diffraction in CaCl_2 (Biggin and Enderby 1981b) and MgCl_2 (Biggin, Gay and Enderby 1984, Day and McGreevy 1985). Remnants of 2D structural characters have been noticed in molten MgCl_2 .

There is considerable scatter of the representative points for the above dihalides in figure 1 around the best fit of the entropy-volume relationship given in (3). In particular, CdI_2 and PbBr_2 show fairly sizable negative deviations from it. In view of this scatter and of the discussion of our analysis already given in § 2, we believe that the difference between the value $3.9 \ln 2$ that we have obtained for the intercept in (3) and the value $3 \ln 2$ predicted in (1) is not significant.

As a final comment on dihalides, we remark that NiCl_2 (entered in figure 1 with the symbol X) shows a large excess of entropy of melting relative to the "norm". This salt at atmospheric pressure sublimes before melting, but can be brought to melting under some excess pressure (see the footnote to table 2). Neutron diffraction experiments on molten NiCl_2 by Newport, Howe and Wood (1985) have indicated that the local structure around the Ni ions changes on melting from sixfold to tetrahedral-type coordination. The behaviour of the entropy of melting for NiCl_2 may prelude to similar behaviours to be more commonly found in tetrahalides and higher halides.

(c) Trivalent metal halides

In obtaining the empirical entropy-volume relation (4) for trihalides we have included all the salts in table 3 except for AlBr_3 , AlI_3 , GaCl_3 , SbCl_3 and SbBr_3 . These five trihalides will be discussed together with BiCl_3 later in this section.

The other salts in table 3 crystallize in the 3D UCl_3 and PuBr_3 structures and in the layer-type AlCl_3 and FeCl_3 structures. These trihalide structures can be put in correspondence with the PbCl_2 structure and with the CdCl_2 - CdI_2 structures for dihalides. The UCl_3 structure is described as hexagonal, with each metal ion surrounded by six halogens on the corners of a trigonal prism and further coordinated by three coplanar

halogens at somewhat greater distance. One may construct this structure by first stacking into a chain monomeric formula units having the shape of trigonal pyramids with the metal ion at the apex, with the stacking requirement that the three halogens in the base of each pyramid should be equally shared between two metal ions to yield the trigonal prism around each metal ion. The chains should then be packed into a 3D structure so as to give three interchain metal-halogen bonds to each metal ion. The PuBr_3 structure may be similarly obtained by allowing for different lengths of interchain bonds. This structure appears to be of a transitional type between the UCl_3 and AlCl_3 structures, as is suggested by the structural phase transitions undergone with increasing temperature by DyCl_3 ($\text{PuBr}_3 \rightarrow \text{AlCl}_3$) and by GdCl_3 ($\text{PuBr}_3 \rightarrow \text{UCl}_3$). The AlCl_3 and FeCl_3 layer-type structures are built from somewhat distorted close packings of the halogens, within which the metal ions occupy suitable interstitial sites with octahedral-type coordination.

The limiting value of the empirical entropy-volume relation in (4) for $\Delta V \rightarrow 0$ is rather well determined by the values of ΔS for YCl_3 and DyCl_3 , which both have an extremely small volume change on melting (Igarashi and Mochinaga 1987). It thus appears that the discrepancy between the value of the intercept in (4) and that proposed in (1) for trihalides may be real. The transport coefficients for YCl_3 and DyCl_3 in the melt (see table 3) have typical values for trihalides with a relatively loose ionic structure. The available data on the liquid structure of YCl_3 , as obtained from neutron diffraction experiments (Saboungi *et al.* 1991), show that the melting process preserves the essentially octahedral coordination of the metal ions and that this local structure, though quite stable as compared with that of strongly ionic dihalide melts such as SrCl_2 , has a much shorter average lifetime than that of a strongly structured melt such as ZnCl_2 . This is also evident from a comparison of the transport coefficients in these melts (see tables 2 and 3). The presence of intermediate range order in molten YCl_3 is revealed by a FSDP at scattering wave number near 1 \AA^{-1} (Saboungi *et al.* 1991). However, Coulomb interactions suffice to yield this structural feature in a purely ionic model of molten trihalides, and only the detailed topology of the intermediate range order is determined by more complex contributions to the potential energy function of

the melt (Tosi *et al.* 1991).

The representative points of the UCl_3 and PuBr_3 -type trihalides, as well as those of BiCl_3 and SbI_3 , cluster in the central region of the linear entropy-volume relationship for trihalides in figure 1. Leaving again BiCl_3 aside for the moment, the available data on transport coefficients for these salts in the melt indicate rather loose ionic-type liquid structures, except for SbI_3 . This latter salt, which actually shows a fairly sizable positive deviation from (4), would be an interesting case for microscopic structural study. The liquid structure of several rare-earth trichlorides has been studied by X-ray diffraction and Raman scattering by Mochinaga *et al.* (1991). Their data show that the local coordination of the metal ion in the melt is of octahedral type, suggesting that the relatively high values of ΔS and $\Delta V/V$ in these salts as compared with YCl_3 and DyCl_3 may be related to the change in local structure that occurs on melting in UCl_3 -type salts as compared with AlCl_3 -type ionic materials. Mochinaga *et al.* propose from the analysis of their X-ray diffraction data that the first-neighbour distance between metal ions in these melts is about 5 \AA . Such a value also results from a liquid structure calculation for a trihalide within a purely ionic model (Pastore, Akdeniz and Tosi 1991).

The range of $\Delta V/V$ covered by trihalides in figure 1 is very wide, terminating with AlCl_3 at $\Delta V/V = 0.47$. While the established crystal structure of AlCl_3 is the same as that of YCl_3 and DyCl_3 , molten AlCl_3 has been characterized, from X-ray diffraction studies (Harris, Wood and Ritter 1951), as a molecular liquid of dimeric Al_2Cl_6 units having the shape of two tetrahedra joined by sharing an edge. The melt combines an extremely low ionic conductivity with a low viscosity (see table 3), suggesting that the intermolecular correlations in the liquid may be rather weak. We feel that molten AlCl_3 should be an interesting case for a microscopic structural investigation by neutron diffraction, with specific reference to its neutron diffraction pattern in the FSDP region of scattering wave number as compared with molten AlBr_3 (see the discussion of the latter melt given later in this section). We should also point out in this connection, and with reference to the very large value of $\Delta V/V$ for AlCl_3 ,

that it may be accidental that the representative point of this salt falls in figure 1 on the line given by (4). Taking the volume of the solid as that at melting rather than at room temperature would still not shift this point by a major amount, but our choice of referring ΔV to the volume of the liquid rather than to that of the solid is important in determining where AlCl_3 lies in our diagram.

The remaining six trihalides in table 3, namely AlBr_3 , AlI_3 , GaCl_3 , BiCl_3 , SbCl_3 and SbBr_3 , all have solid-state structures in which separate molecular units can be recognized. These are (i) the AlBr_3 and GaCl_3 structures, which are formed by arranging into layers dimeric units having the shape of two tetrahedra sharing an edge (as already mentioned for the Al_2Cl_6 molecular dimers above), and (ii) the BiCl_3 and SbCl_3 structures, which are 3D packings of chains obtained by stacking monomeric formula units having the shape of trigonal pyramids. The stacking differs from that described earlier in this section for the UCl_3 and PuBr_3 structures in that the two triplets of halogens facing a metal ion within a chain are now at rather different distances from it.

As already mentioned, among these six systems BiCl_3 conforms to the entropy-volume relation given in (4). By comparison with the other five molecular-type trihalides, molten BiCl_3 has an appreciable ionic conductivity and a rather high viscosity (see table 3). A neutron diffraction study of molten BiCl_3 by Saboungi and Price (unpublished) indicates a melt with an ionic-type structure, characterized by a fairly stable local coordination of the halogens around the metal ions and by a faint trace of intermediate range order. The liquid structure of BiCl_3 appears in fact to be qualitatively similar to that of BiI_3 , as reported by Ichikawa and Matsumoto (1981). The latter compound crystallizes in the layer-type FeCl_3 structure and has an ionic conductivity in the melt similar to that of BiCl_3 (Janz 1988).

To the other five molecular-type trihalides, namely AlBr_3 , AlI_3 , GaCl_3 , SbCl_3 and SbBr_3 , we have attributed a deficit in the entropy of melting, their representative points being shown as filled triangles in figure 1. The liquid structure of SbCl_3 , as studied by neutron and X-ray diffraction by Triolo and Narten (1978) and discussed by Johnson, Narten, Thiessen and Triolo (1978), can be described as arising from discrete monomeric units with strong

intermolecular correlations leading to an associated molecular liquid with a distorted octahedral arrangement of chlorines around metal ions, as would result from stacking monomeric units in an umbrella configuration. Neutron diffraction and Raman scattering studies of molten AlBr_3 by Price, Saboungi and Grimsditch (unpublished) demonstrate that the liquid consists of Al_2Br_6 units and shows a prominent FSDP in its diffraction pattern. The viscosity of molten AlBr_3 is larger than that of AlCl_3 by one order of magnitude (see table 3) and the molar volumes of these two melts near freezing are essentially the same (Janz 1988), notwithstanding the difference in sizes between the two halogens. It would clearly be interesting to examine quantitatively in these molecular liquids the relationship between a FSDP in the neutron diffraction pattern and the intra and intermolecular correlations.

We suggest that a deficit in the entropy of melting for the molecular-type trihalides may be associated with the residual ordering which is preserved in the melt near freezing, though through the preservation of molecular units as basic constituents and of strong intermolecular correlations rather than through a network-like structure as in BeF_2 and ZnCl_2 . The difference in behaviours that seems to emerge between the molecular-type trihalides and the molecular-type mercury dihalides discussed in § 3(b) probably arises from the differences in number of constituents and shape of the molecular units leading to different types of intermolecular correlations. On the other hand, it appears that BiCl_3 undergoes a more substantial structural change on melting. A closer stacking of monomeric units would allow strong interactions with relatively fast exchanges of the chlorines, as suggested by the relatively high values of η and σ .

It may be useful in concluding this section to add a brief summary of some main points in the foregoing discussion of trihalides. These show a variety of melting mechanisms, namely (i) ionic-to-ionic (for example in YCl_3 and in the rare-earth chlorides), (ii) ionic-to-molecular (AlCl_3), (iii) molecular-to-ionic (BiCl_3), and (iv) molecular-to-molecular (for example in SbCl_3 and AlBr_3). Only for the latter type of melting mechanism do we find some evidence for a deficit in the entropy of melting.

4. Concluding remarks

By examining the relationship between entropy and volume of melting for halides, we have found that both strongly structured network-type dihalides and molecular-type trihalides have an "abnormally" low entropy of melting. This property is associated with strong remnants in the melt of the order which is present in the high-temperature solid. The deficit in melting entropy will be compensated on further heating of the melt leading to further structural loosening. In the course of the discussion, we have singled out several compounds which seem to be worthy of microscopic structural studies in the molten state.

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References

- Barin, I & Knacke, O. 1973 *Thermodynamic Properties of Inorganic Substances*. Springer.
- Barin, I, Knacke, O. & Kubaschewski, O. 1977 *Thermodynamic Properties of Inorganic Substances - Supplement*. Springer .
- Biggin, S. & Enderby, J. E. 1981a *J. Phys. C: Solid State Phys.* **14**, 3129-3136.
- Biggin, S., and Enderby, J. E. 1981b *J. Phys. C: Solid State Phys.* **14**, 3577-3583.
- Biggin, S., Gay, M. & Enderby, J. E. 1984 *J. Phys. C: Solid State Phys.* **17**, 977-985.
- Chase, M. W., Davies, C. A., Downey, J. R., Frurip, D. J., McDonald, R. A. & Syverud, A. N. 1985 *J. Phys. Chem. Ref. Data* **14**, Suppl. 1.
- Day, S. E. & McGreevy, R. L. 1985 *Phys. Chem. Liquids* **15**, 129-136.
- Enderby, J. E. & Barnes, A. C. 1990, *Repts. Progr. Phys.*, **53**, 85-179.
- Harris, R. L., Wood, R. E. & Ritter, H. L. 1951 *J. Am. Chem. Soc.* **73**, 3150-3155.
- Howe, M. A., Price, D. L. & Saboungi, M. L. 1990 *Proc. Symp. Molten Salts*. The Electrochemical Society.
- Igarashi, K. & Mochinaga, J. 1987 *Z. Naturforsch.* **42a**, 777-778.
- Ichikawa, K. & Matsumoto, T. 1981 *Phys. Lett. A* **83**, 35-38.
- Janz, G. J. 1988 *J. Phys. Chem. Ref. Data* **17**, Suppl. 2.
- Johnson, E., Narten, A. H., Thiessen, W. E. & Triolo, R. 1978 *Faraday Disc. Chem. Soc.* **66**, 287-295.
- Lasocka, M. 1975 *Phys. Lett.* **51A**, 137-138.
- McGreevy, R. L. 1987 *Solid State Phys.* **40**, 247-325.
- McGreevy, R. L. & Pusztai, L. 1990 *Proc. R. Soc. Lond.* **A430**, 241-261.
- Mochinaga, J., Iwadate, Y. & Fukushima, K. 1991 *Mat. Science Forum* **73-75**, 147-152.
- Newport, R. J., Howe, R. A. & Wood, D. N. 1985 *J. Phys. C: Solid State Phys.* **18**, 5249-5257.
- O'Keefe, M. & Hyde, B. G. 1976 *Phil. Mag.* **33**, 219-224.

Pankratz, L. B. 1984 *Thermodynamic Properties of Halides - Bull. 674*. U.S. Bureau of Mines.

Pastore, G., Akdeniz, A. & Tosi, M. P. 1991 *J. Phys.: Cond. Matter* in press.

Pettifor, D. G. 1986 *J. Phys. C: Solid State Phys.* **19**, 285-313.

Rivier, N. & Duffy, D. M. 1982 *J. Phys. C: Solid State Phys.* **15**, 2867-2874.

Rovere, M. & Tosi, M. P. 1986 *Repts. Progr. Phys.* **49**, 1001-1081.

Saboungi, M. L., Price, D. L., Scamehorn, C. & Tosi, M. P. 1991 *Europhys. Lett.* **15**, 283-288.

Stishov, S. M., Makarenko, I. N., Ivanov, V. A. & Nikolaenko, A. M. 1973 *Phys. Lett.* **45A**, 18.

Tallon, J. L. 1982a *Phys. Lett.* **87A**, 361-364.

Tallon, J. L. 1982b *Solid State Commun.* **42**, 243-245.

Tallon, J. L. & Robinson, W. H. 1982 *Phys. Lett.* **87A**, 365-368.

Triolo, R. & Narten, A. H. 1978 *J. Chem. Phys.* **69**, 3159-3162.

Tosi, M. P., Pastore, G., Saboungi, M. L. & Price, D. L. 1991 *Physica Scripta* in press.

Ubbelohde, A. R. 1978 *The Molten State of Matter*. Wiley.

Wells, A. F. 1990 *Structural Inorganic Chemistry*. Oxford University Press.

Wyckoff, R. W. G. 1964 *Crystal Structures*, vol. 1. Interscience.

Table 1. Physical properties of some monovalent metal halides

Salt	χ_M	Structure ^a	T_m (K)	ΔS_m (cal K ⁻¹ mol ⁻¹)	$\Delta V/V^b$	σ ($\Omega^{-1}\text{cm}^{-1}$)	η (cp)
CsCl	0.25	NaCl	918	5.29	0.30	1.1	1.6
CsBr	0.25	CsCl	909	6.20	0.30	0.80	1.8
RbCl	0.30	NaCl	988	4.45	0.24	1.5	1.4
RbBr	0.30	NaCl	953	3.88	0.19	1.1	1.6
KCl	0.35	NaCl	1045	5.98	0.23	2.2	1.1
KBr	0.35	NaCl	1007	6.06	0.23	1.6	1.2
KI	0.35	NaCl	954	6.02	0.22	1.3	1.4
NaCl	0.40	NaCl	1074	6.30	0.28	3.6	1.0
NaBr	0.40	NaCl	1020	6.15	0.27	2.9	1.2
NaI	0.40	NaCl	934	6.08	0.25	2.2	1.2
LiF	0.45	NaCl	1121	5.77	0.32	8.6	1.9
LiCl	0.45	NaCl	883	5.28	0.27	5.7	1.5
LiBr	0.45	NaCl	823	5.12	0.27	4.7	1.7
LiI	0.45	NaCl	742	4.72	0.23	3.9	2.1
AgCl	1.18	NaCl	728	4.26	0.13	3.7	2.3
AgBr	1.18	NaCl	703	3.12	0.14	2.9	3.5
AgI	1.18	β -AgI	831	2.70	0.071	2.3	3.6
CuCl	1.20	Wurtzite	696	2.43	0.16	3.7	4.1
TlBr	1.56	CsCl	733	5.35	0.20	0.82	2.2
TlI	1.56	CsCl	715	4.92	0.17	0.53	2.6
InCl	1.60	yellow TlI	498	4.42	0.11	0.85	--

^a Crystal structure of high temperature solid phase.

^b Relative difference $(V_m - V_{RT})/V_m$ between the volume V_m of the liquid at T_m and the volume V_{RT} of the solid at room temperature.

Table 2. Physical properties of some divalent metal halides

Salt	χ_M	Structure ^a	T_m (K)	ΔS_m (cal K ⁻¹ mol ⁻¹)	$\Delta V/V^b$	σ ($\Omega^{-1}\text{cm}^{-1}$)	η (cp)
BaCl ₂	0.50	CaF ₂	1235	3.09	0.19	2.0	3.8
BaBr ₂	0.50	PbCl ₂	1130	6.87	0.13	1.2	--
SrCl ₂	0.55	CaF ₂	1146	3.44	0.11	2.0	3.7
SrBr ₂	0.55	CaF ₂	930	2.60	0.13	0.83	--
CaCl ₂	0.60	CaCl ₂	1045	6.44	0.043	2.0	3.4
CaBr ₂	0.60	PbCl ₂	1015	6.85	0.074	1.4	--
MnCl ₂	0.945	CdCl ₂	923	9.76	0.21	1.5	--
FeCl ₂	0.99	CdCl ₂	950	10.81	0.26	3.0	--
NiCl ₂	1.09	CdCl ₂	1304 ^c	14.16	0.25	--	--
MgCl ₂	1.28	CdCl ₂	980	9.74	0.28	1.0	2.2
MgBr ₂	1.28	CdI ₂	984	9.55	0.30	0.69	5.4
HgCl ₂	1.32	HgCl ₂	554	9.11	0.21	3x10 ⁻⁵	1.6
HgBr ₂	1.32	HgBr ₂	514	8.33	0.11	1x10 ⁻⁴	2.5
HgI ₂	1.32	HgBr ₂	530	8.55	0.17	1x10 ⁻⁴	3.0
CdCl ₂	1.36	CdCl ₂	841	9.04	0.16	1.9	2.5
CdBr ₂	1.36	CdCl ₂	841	9.47	0.23	1.1	2.9
CdI ₂	1.36	CdI ₂	661	7.49	0.22	0.20	17.
ZnCl ₂	1.44	ZnCl ₂	570	4.09	0.14	1x10 ⁻³	4x10 ³
BeF ₂	1.50	β -Crystobalite	825	1.36	0.02	--	6x10 ⁸
BeCl ₂	1.50	SiS ₂	688	2.98	0.20	2x10 ⁻⁴	--
PbCl ₂	1.80	PbCl ₂	771	6.78	0.16	1.5	4.6
PbBr ₂	1.80	PbCl ₂	644	6.12	0.17	0.63	8.0
PbI ₂	1.80	CdI ₂	683	8.20	0.08	0.44	--
SnCl ₂	1.84	PbCl ₂	520	6.73	0.14	0.76	--

^a Structure of high temperature crystal phase.

^b Relative difference $(V_m - V_{RT})/V_m$ between the volume V_m of the liquid at T_m and the volume V_{RT} of the solid at room temperature.

^c At $p = 2.5$ atm. Under standard pressure NiCl₂ sublimes at 1260 K, with an entropy change of 42.7 cal K⁻¹ mol⁻¹.

Table 3. Physical properties of some trivalent metal halides

Salt	χ_M	Structure ^a	T_m (K)	ΔS_m (cal K ⁻¹ mol ⁻¹)	$\Delta V/V^b$	σ ($\Omega^{-1}\text{cm}^{-1}$)	η (cp)
YCl ₃	0.66	AlCl ₃	994	7.56	0.0045	0.39	--
DyCl ₃	0.685	AlCl ₃	924	6.61	0.0032	0.44	4.2
GdCl ₃	0.69	UCl ₃	875	11.12	0.21	0.34	--
NdCl ₃	0.6975	UCl ₃	1032	11.63	0.18	0.60	2.7
NdBr ₃	0.6975	PuBr ₃	955	11.34	0.21	0.27	--
PrCl ₃	0.70	UCl ₃	1059	11.43	0.17	0.94	3.3
CeCl ₃	0.7025	UCl ₃	1090	11.80	0.17	1.1	--
LaCl ₃	0.705	UCl ₃	1131	11.49	0.16	1.3	6.7
LaI ₃	0.705	PuBr ₃	1051	12.58	0.23	0.43	--
UCl ₃	0.735	UCl ₃	1110	10.00	0.11	1.1	--
AlCl ₃	1.66	AlCl ₃	466	18.14	0.47	5x10 ⁻⁷	0.36
AlBr ₃	1.66	AlBr ₃	371	7.26	0.17	1x10 ⁻⁸	2.4
AlI ₃	1.66	(AlBr ₃) ^c	464	8.19	0.19	2x10 ⁻⁶	2.8
GaCl ₃	1.68	GaCl ₃	351	7.84	0.17	2x10 ⁻⁶	1.8
BiCl ₃	2.04	BiCl ₃	507	11.20	0.18	0.38	41.
SbCl ₃	2.08	SbCl ₃	346	8.96	0.17	2x10 ⁻⁴	2.4
SbBr ₃	2.08	SbCl ₃	368	9.51	0.19	3x10 ⁻⁵	3.9
SbI ₃	2.08	FeCl ₃	444	12.28	0.14	2x10 ⁻⁴	--

^a Structure of high temperature crystal phase.

^b Relative difference $(V_m - V_{RT})/V_m$ between the volume V_m of the liquid at T_m and the volume V_{RT} of the solid at room temperature.

^c Presumed crystal structure (Wells 1990). The vapour phase consists of Al₂I₆ molecules.

Figure legend

Figure 1. Relations between entropy of melting ΔS (in $\text{cal K}^{-1} \text{mol}^{-1}$) and relative volume change $\Delta V/V = (V_m - V_{RT})/V_m$ for halides of monovalent, divalent and trivalent metals. The monohalides are represented by empty and filled circles, the dihalides by empty and filled squares and by filled lozenges, and the trihalides by empty and filled triangles. The symbol X marks NiCl_2 . The straight lines represent best fits obtained for assumed linear relationships between ΔS and $\Delta V/V$, from the locations of the empty symbols for each family of salts.

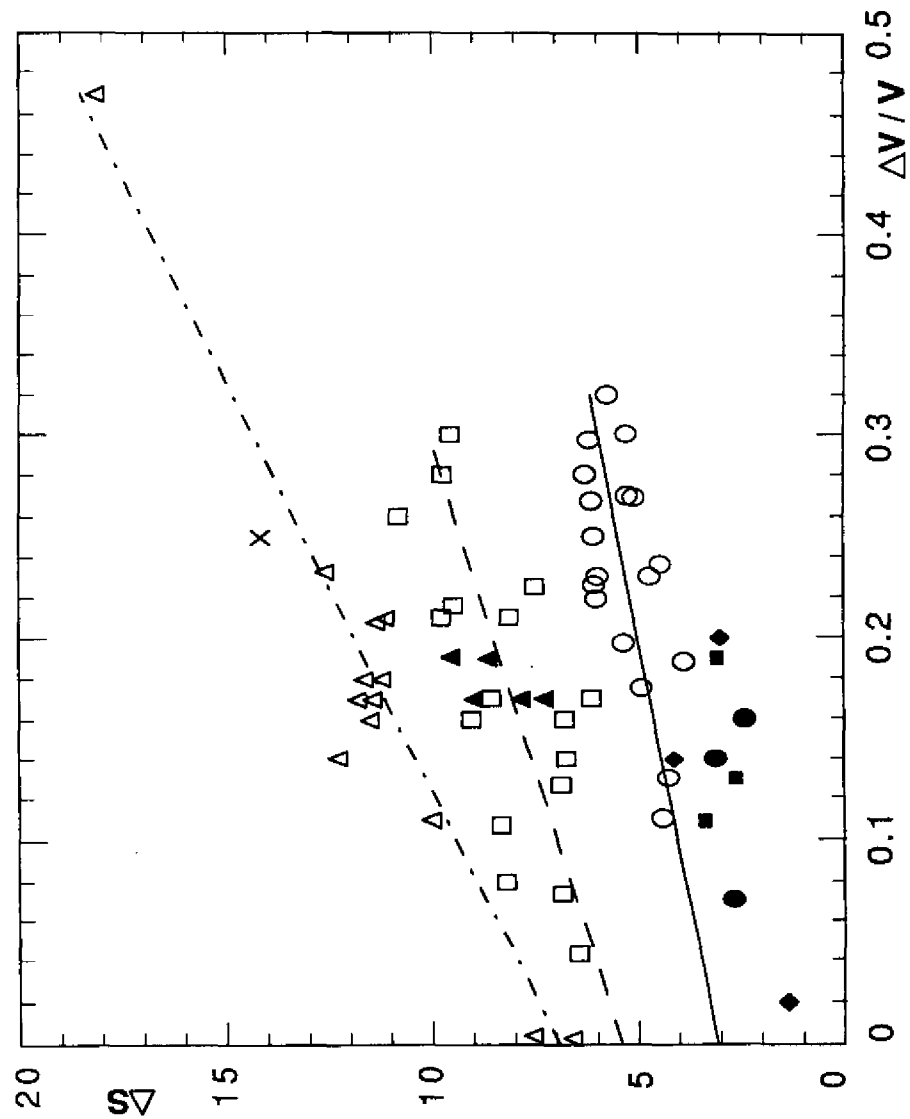


Fig.1

