

## Entropies and Melting Points of Univalent Nitrates

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The entropies of the univalent nitrates are discussed in relation to those of the corresponding halides. It is shown that the latter class of compounds have entropies at room temperature which depend systematically upon the ionic radii, and that the values for the nitrates are consistent with appreciable contributions from librational oscillations of the nitrate group. Entropy changes at solid state and melting transformations in the univalent nitrates are considered, and there is shown to be little alteration in the activity of the nitrate group at the melting point, except in the case of  $\text{LiNO}_3$ . In contrast with the conclusions of other authors, it is found that the relatively low melting points of univalent nitrates do not arise from high values of entropy of fusion due to the formation of association complexes in the melt. It is suggested instead that the resonant properties of librating nitrate groups may be responsible for producing abnormally low values for the heats of fusion.

Ionic compounds containing complex ions have potentially available degrees of freedom, which, by reason of their thermal activation, may contribute appreciably to the total value of the entropy function. A comparison of the entropies of nitrates with those for compounds having spherically symmetric anions, may be used in identifying contributions of this kind, and since the univalent halides are in some respect comparable to the corresponding nitrates, and have been widely studied, they form a suitable basis for comparison.

The values of entropy for the univalent nitrates and halides at  $298.15^\circ\text{K}$  ( $S_{298.15}$ ) are shown in Fig. 1. Values for lithium, rubidium, and cesium nitrates are unfortunately not available at present. The data are positioned in the diagram according to the ionic radius of the anion for a coordination number of six, except in the case of  $\text{NO}_3^-$ , which is tentatively allocated the thermochemical radius found by Yatsimirskii<sup>3</sup> (1.89 Å), since other radii given by this author accord well with those determined crystallographically. The straight lines in the diagram are drawn for halides having a common cation, the lines for  $\text{Cs}^+$  ( $r = 1.69$  Å), and  $\text{NH}_4^+$  ( $r = 1.48$  Å) being omitted for the benefit of clarity.

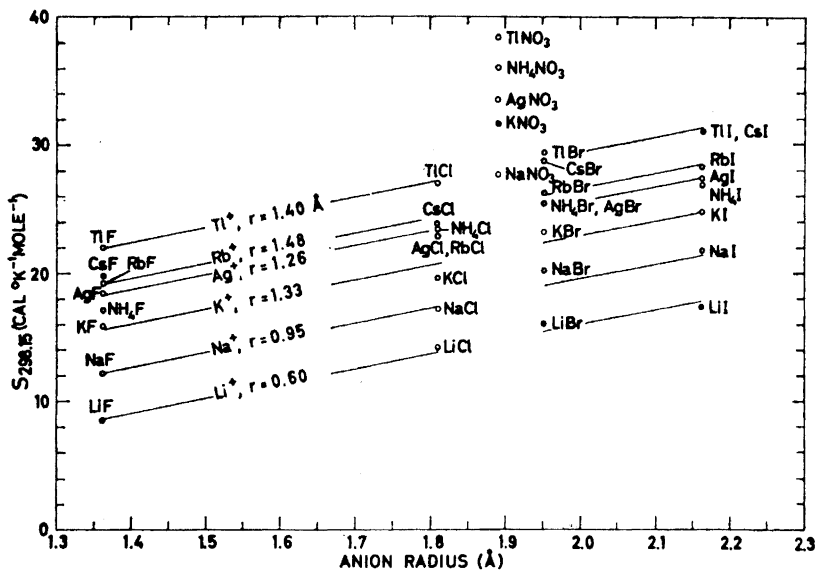


Fig. 1. Entropies at 298.15°K for univalent nitrates and halides as a function of anion radius. The values for the cesium halides are taken from Landolt-Börnstein,<sup>1</sup> other values from Kelley and King.<sup>2</sup>

The diagram shows that, for the halides, the entropy increases linearly with anion radius ( $r_a$ ) for a given cation, while a change of cation displaces the line parallel to the entropy axis, but leaves the slope unchanged at a value  $\Delta S_{298.15}/\Delta r_a = 11.7 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1} \text{ \AA}^{-1}$ . (For brevity,  $\text{cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$  is written as eu in the remainder of the text).

For a given crystal structure, increases in ionic radius and mass may be expected to increase the entropy by reducing the frequencies of the normal lattice modes of vibration of the crystal. According to the Debye approximation, this corresponds to a reduction in the characteristic temperature ( $\theta_D$ ), and thus a more rapid initial increase of heat capacity with temperature. From Fig. 1, it is seen that the relationship between entropy and anion radius is in fact linear for the halides, and the dependence may, moreover, be extended to the form of an additivity rule for both anion and cation radii, if silver and thallium are assigned the pseudo-radii 1.5 and 1.8 Å, respectively. Expressed analytically, the additivity rule takes the form,

$$\dot{S}_{298.15} = -14.6 + 11.7(r_a + r_c) \quad (1)$$

It is noteworthy that the above additivity rule is independent of coordination number, since tetrahedral, octahedral, and cubic coordinations are to be found among the crystal structures of the halides; indicating that the distribution curves for the lattice frequencies are similar in these structures. Potassium fluoride and lithium bromide, which have similar values of entropy ( $S_{298.15} = 15.9$ , and  $16.0 \text{ eu}$ ) and sums of radii ( $r_a + r_c = 2.69$ , and  $2.55 \text{ \AA}$ ) may

be taken as examples of the operation of the rule. Since the relative molecular masses (and hence also the reduced masses) differ substantially for these compounds, it is seen that ionic mass as an independent parameter does not appreciably influence the value of  $S_{298.15}$ .

Ammonium nitrate has an  $S_{298.15}$ -value which is approximately 12 eu above the line connecting the values for the corresponding halides, while those for the other nitrates are  $9.7 \pm 0.5$  eu higher than the lines for the appropriate halides. The entropies of the nitrates are not consistent with those of the halides, since an arbitrary adjustment of the effective  $\text{NO}_3^-$  radius to bring the nitrates in line with the halides would require a value  $> 2.7 \text{ \AA}$ .

On the basis of the data in Fig. 1, likely values of  $S_{298.15}$  for  $\text{LiNO}_3$ ,  $\text{RbNO}_3$ , and  $\text{CsNO}_3$  may be predicted to be 24.5, 34.5, and 36.5 eu, respectively.

In obtaining a theoretical expression for the entropy of a univalent nitrate crystal, it is noted that, excepting  $\text{NH}_4\text{NO}_3$ , no transformations have been detected calorimetrically below room temperature. Thus the transitions discovered by means of electrical measurements<sup>4</sup> involve only small entropy increments. The electrical measurements also show that there is no extensive freedom of ionic movement at room temperature and exclude therefore the possibility of communal entropy arising from that source.

Measurements on the infrared absorption and Raman spectra<sup>5,6</sup> of nitrates at liquid helium, liquid nitrogen, and room temperatures, have yielded the following frequencies of libration of the anion (in  $\text{cm}^{-1}$ ):  $\text{NaNO}_3$  (32 and 185),  $\text{TlNO}_3$  (25?),  $\text{AgNO}_3$  (30?),  $\text{CsNO}_3$  (25),  $\text{RbNO}_3$  (15 and 30). Representative of the frequencies of vibration for the six degrees of internal freedom of the nitrate group is that of the symmetrical stretching mode,  $\nu = 1068 \text{ cm}^{-1}$ .<sup>6</sup>

Neglecting entropy increments due to phase and order-disorder transformations, a simple expression for the entropy function for one mole of a univalent nitrate salt may be derived by regarding the crystals as consisting of a Debye solid comprising  $N$  ion-pairs for the lattice, together with two (or more) Einstein solids representing the additional librational and internal vibrational properties of the  $N$  nitrate groups. The respective degrees of freedom correspond to  $N$  librators and  $6N$  harmonic oscillators. Since the lower frequency lattice modes have the greater influence upon the entropy function at sufficiently low temperatures, an operative Debye temperature ( $\theta_D$ ) may be deduced from the low frequency lattice resonances found by means of infrared spectroscopy. Similarly, infrared measurements provide the basis for assigning the Einstein temperatures ( $\theta_E$ ) appropriate to the librators and harmonic oscillators. Thus, the total entropy at the temperature  $T$  may be written approximately as follows,

$$S_T = \sum_{i=1}^3 f_i R \int_0^T \frac{F_i(T/\theta_i)}{T} dT \quad (2)$$

where the constant  $f_i$  is the number of degrees of freedom corresponding to the Debye or Einstein function  $F_i$ .

Taking as example  $\text{NaNO}_3$ , infrared resonances ranging from 71 to 217  $\text{cm}^{-1}$  have been identified as corresponding to lattice vibrations.<sup>7</sup> From these, a weighted average of 100  $\text{cm}^{-1}$  has been used to obtain  $\theta_D = 150^\circ\text{K}$ . This value is consistent with the low temperature portion of the heat capacity

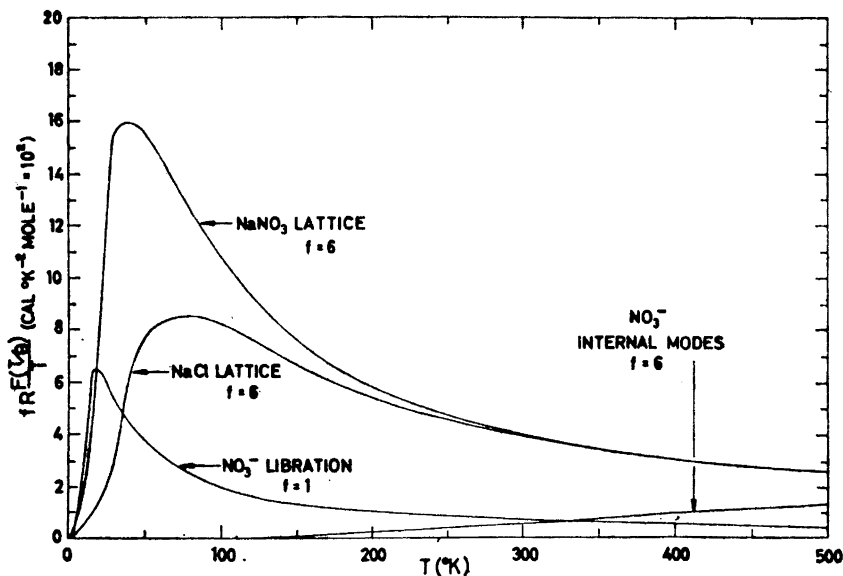


Fig. 2. The function  $fR \frac{F(T/\theta)}{T}$  versus  $T$ . The number of degrees of freedom  $f$  are shown for each contribution.

curve for  $\text{NaNO}_3$  given by Sokolov and Schmidt.<sup>8</sup> The characteristic Einstein temperatures for the dominant libration and internal vibration of the nitrate group are 46 and 1500°K, respectively.

The integrand of eqn. 2 with the above values substituted for the characteristic temperatures is plotted in Fig. 2, to show the relative importance of the contributions from the lattice, librational, and internal modes of vibration. Also included in the diagram for comparison is the corresponding function for the NaCl lattice ( $\theta_D = 281^\circ\text{K}$ ,  $25 < T < 664^\circ\text{K}$ <sup>9</sup>). By comparing the areas under the curves, it is seen that in  $\text{NaNO}_3$  at room temperature, there is an appreciable contribution to the entropy from libration of  $\text{NO}_3^-$ , and a much smaller amount from its internal vibrations. It is also seen that the value of  $\theta_D$  assigned to the  $\text{NaNO}_3$  lattice results in a considerably greater entropy than for NaCl. Graphical integration of the functions, yields the following values for the respective entropies, the figures in brackets are the literature values shown in Fig. 1.

$$\begin{aligned} \text{NaNO}_3: S_{\text{latt}} &= 24.0 \text{ eu} \\ S_{\text{lib}} &= 5.8 \text{ eu} \\ S_{\text{int}} &= 0.5 \text{ eu} \\ \hline S_{298.15} &= 30.3 \text{ eu} \quad (27.6 \text{ eu}) \end{aligned}$$

$$\text{NaCl: } S_{298.15} = 17.0 \text{ eu} \quad (17.33 \text{ eu})$$

The calculated entropies at room temperature are in satisfactory agreement with those obtained experimentally, indicating the model to be substantially

correct, consistent with a lack of appreciable anomalous contributions to the entropy of  $\text{NaNO}_3$  below room temperature. In the case of  $\text{NaNO}_3$ , a better degree of agreement would be obtained by using a somewhat higher value for  $\theta_D$ , as may be required by a more detailed knowledge of the actual distribution of lattice frequencies in the crystal. The regularity of the entropies of the other nitrates represented in Fig. 1 shows that these are also normal, and possibly include only such small increments as have been detected in  $\text{NH}_4\text{NO}_3$  at the transition below room temperature. The entropy of the latter compound clearly includes additional contributions due to modes of cation vibration.

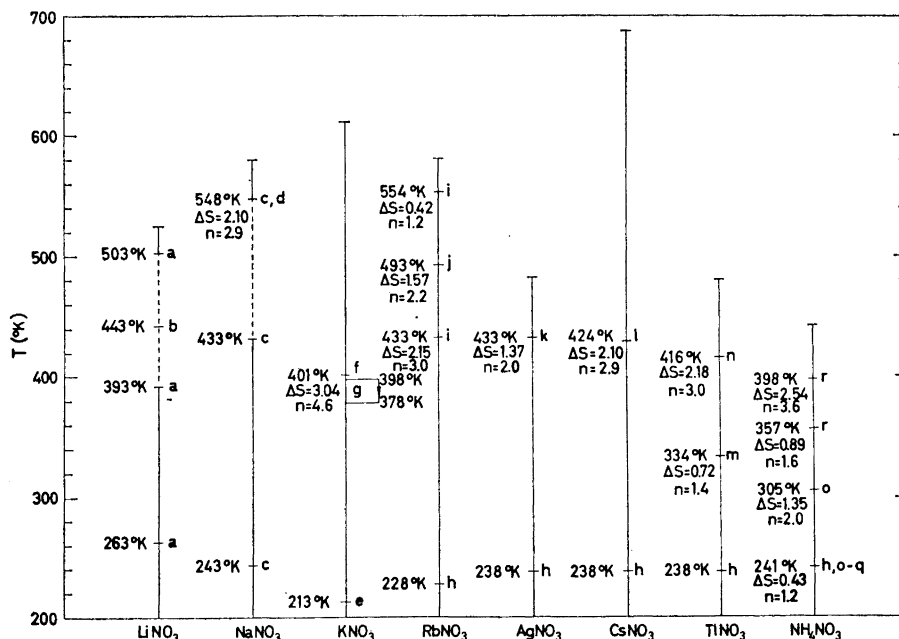


Fig. 3. Solid state transition temperatures in the univalent nitrates. Entropy increments  $\Delta S$  (in eu) are given together with corresponding values of the disorder parameter  $n$ . Transformation ranges of temperature are indicated by broken lines. References: *a* Fermor and Kjekshus,<sup>10</sup> *b* Rhodes and Ubbelohde,<sup>11</sup> *c* Fermor and Kjekshus,<sup>12</sup> *d* Strømme,<sup>13</sup> *e* Fermor and Kjekshus,<sup>14</sup> *f* Sokolov and Schmidt,<sup>15</sup> *g* Borchert,<sup>16</sup> *h* Fermor and Kjekshus,<sup>4</sup> *i* Mustajoki,<sup>17</sup> *j* Arell and Varteva,<sup>18</sup> *k* Arell,<sup>19</sup> *l* Mustajoki,<sup>20</sup> *m* Landolt-Börnstein,<sup>1</sup> *n* Arell and Varteva,<sup>21</sup> *o* Stephenson *et al.*,<sup>22</sup> *p* Kamiyoshi and Yamakami,<sup>23</sup> *q* Brown and McLaren,<sup>24</sup> and *r* Steiner and Johnston.<sup>25</sup>

The solid state transformations which are known to occur above 200°K in the univalent nitrates are summarized in Fig. 3, where the transformation temperatures and entropy increments (where known) are given. Also included in the diagram are the corresponding values of  $n$ , calculated from the equation.

$$n = \exp(\Delta S/R) \quad (3)$$

Newns and Staveley<sup>26</sup> have pointed out that at a number of transformations in salts containing polyatomic ions, the entropy increments may be understood largely upon the basis of the appearance of an  $n$ -fold degree of disorder in the higher temperature phase. It is assumed that entropy increments due to changes in volume and vibration frequencies are relatively small. In the several cases where  $n \approx 2$ , for example, the transition may be expected to involve a twofold disorder of orientation of the nitrate group between two metastable spatial or orientational positions which are crystallographically different.

Other causes of entropy change at transitions are provided by alterations in vibrational frequencies (including the appearance of new degrees of freedom), changes in lattice potential and volume, and the communal entropy which is provided by freedom of positional interchange of ions, the latter being more characteristic of the molten and gaseous phases. The entropy change per mole of binary salt which results from a shift of frequency from  $\nu_1$  to  $\nu_2$  is given<sup>9</sup> by

$$\Delta S_\nu = 6R \ln \nu_1/\nu_2 \quad (4)$$

while the full extent of the communal entropy is  $R$  per mole for a given species of ion.

The recrystallization properties of apparently all of the univalent nitrates, together with their comparatively low electrical resistivities in the high temperature forms, are indicative of high rates of diffusion. An indication of comparatively large cation mobility has also been obtained from NMR experiments<sup>27</sup> in the case of  $\text{NaNO}_3$ . In the latter investigation, the movement of  $\text{Na}^+$  ions through the lattice at a rate of more than  $10^3$  jumps per second was deduced from the width of the central line in the quadrupole split NMR spectrum above  $549^\circ\text{K}$ .

The question arises as to whether an appreciable amount of communal entropy is associated with these mobile cations. Siegel<sup>28</sup> suggested that above the critical temperature, each disordered nitrate group has an aragonite rather than a calcite coordination with the neighbouring sodium ions. As shown in Fig. 3, however, the measured entropy value corresponds to a value of  $n = 2.9$ , compared with the value  $n = 2$  which would result from a twofold disorder of interchange between aragonite positions of the nitrate group. Strømme<sup>13</sup> has shown that there is a statistical distribution between two twofold disordered non-equivalent sets of positions of the nitrate group in the lattice. On the basis of this evidence he obtains a theoretical entropy change of 1.9 eu, which allows a possible maximum of only 0.2 eu for the communal entropy of mobile cations.

Inspection of the entropy of fusion data ( $\Delta S_f$ ) for univalent nitrates and halides (Fig. 4), shows that, except for  $\text{LiNO}_3$  and  $\text{RbNO}_3$ , the values for the nitrates lie within the spectrum of those for the halides; thus demonstrating a consistency between the two classes of compound which was shown to be lacking in the values of  $S_{298.15}$ . Thus, apart from  $\text{LiNO}_3$ , the entropies of fusion of the univalent nitrates do not exceed those for a similar class of compounds with spherically symmetric anions, and it is deduced therefore

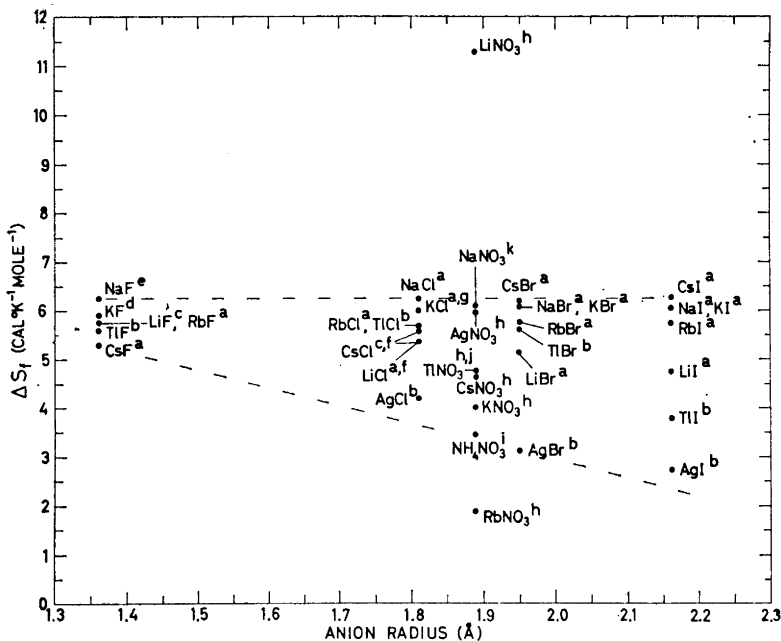


Fig. 4. Entropies of fusion  $\Delta S_f$  for univalent nitrates and halides as a function of anion radius. References: *a* Dworkin and Bredig,<sup>29</sup> *b* Landolt-Börnstein,<sup>1</sup> *c* Douglas and Dever,<sup>30</sup> *d* Johnson and Bredig,<sup>31</sup> *e* Kelley,<sup>32</sup> *f* Bogacz and Trzebiatowski,<sup>33</sup> *g* Douglas,<sup>34</sup> *h* Kleppa and McCarty,<sup>35</sup> *i* Keenan,<sup>36</sup> *j* Rolla *et al.*,<sup>37</sup> *k* Janz *et al.*<sup>38</sup>

that the rotational activity of the nitrate group is, in general, not appreciably altered at the melting point.

Each class of compounds having a common anion, *i.e.* fluorides, chlorides, nitrates, bromides, and iodides, is seen to include a member with  $\Delta S_f$  equal or close to the boundary value of 6.25 eu (3.15  $R$ ) which is drawn as a broken line in the figure. Although rather striking, the limiting value may be fortuitous, in view of the variety of factors influencing  $\Delta S_f$  (*e.g.* vibrational frequencies, free volume, communal interchange, *etc.*). The phenomenon is of interest, however, and will be investigated further.

The value of  $\Delta S_f$  (11.3 eu) in  $\text{LiNO}_3$  results from the activation of additional degrees of freedom in this compound, and although too large to be accounted for on a simple disorder model, the amount is less than has been given for free rotation of the nitrate group (25 eu<sup>39</sup>). Although electrical measurements on  $\text{LiNO}_3$  suggest that there is considerable activity of the anion close to the melting point, the anion rotation may be more inhibited than in  $\text{NaNO}_3$  owing to a greater degree of locking of the nitrate groups in the former more compact compound, as indicated by the structural parameters.<sup>40</sup>

Rubidium nitrate is anomalous in having a low value of  $\Delta S_f$  (1.9 eu) which is more typical of metals than ionic compounds. The anomaly appears

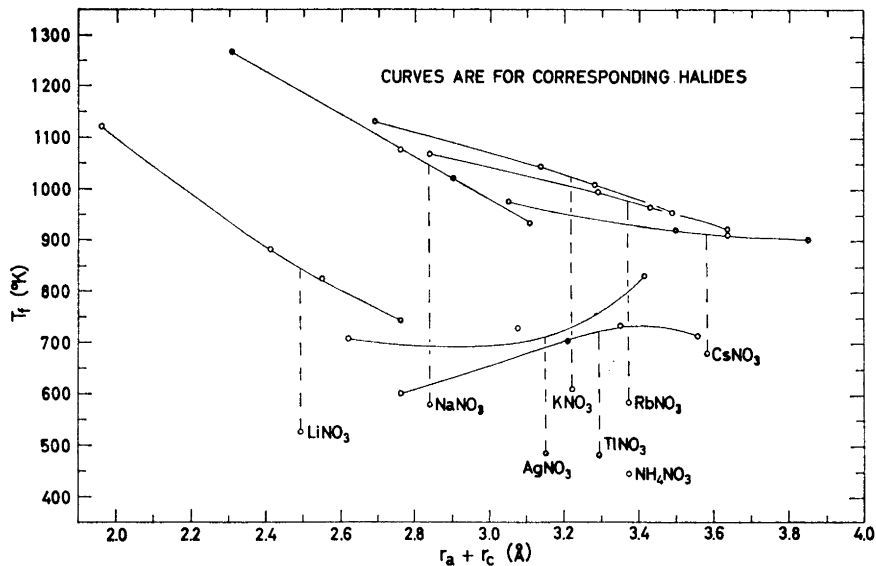


Fig. 5. Temperature of fusion  $T_f$  for the univalent nitrates and halides *versus* sum of anion and cation radii. The filled circle represents both AgBr and TlCl. The values of  $T_f$  are from the same sources as the data given in Fig. 4.

to be connected with the volume change on melting, since  $\text{RbNO}_3$  is exceptional in undergoing a slight decrease in volume on melting ( $\Delta V = -0.23\%$ ).<sup>41</sup>

The temperatures of fusion  $T_f$  of the univalent nitrates and halides are plotted *versus* the sum of the ionic radii of anion and cation ( $r_a + r_c$ ) in Fig. 5, where the latter compounds are left undesignated in order to avoid obscuring the diagram. A radius of 1.89 Å has been assigned to the  $\text{NO}_3^-$  ion, as before. Each group of halides has its associated curve connected to the result for the nitrate having the same cation, by means of a broken vertical line.

It is seen that for each nitrate,  $T_f$  lies below the appropriate halide curve by an amount which varies from 230°K for  $\text{AgNO}_3$  to 470°K for  $\text{NaNO}_3$ . Thus in terms of the heat of fusion  $\Delta H_f$  (where  $\Delta H_f = T_f \Delta S_f$ , independently of the mechanism of the fusion process) the relatively low values of  $T_f$  for the nitrates in conjunction with the normal values of  $\Delta S_f$  (excepting  $\text{LiNO}_3$ ) correspond to low values of  $\Delta H_f$ . This finding is in marked contrast with the conclusion of Davis *et al.*<sup>42</sup> and Ubbelohde,<sup>43</sup> who have suggested that low melting points in the nitrates arise from additional contributions to the entropy of the melt due to the formation of association complexes. The latter conclusion was based on values of  $\Delta S_f$  for chlorides alone, which differ substantially from those which were to be found in the literature at the time of writing, and since references given by the authors in this connection are incorrect, the origin of the misconception is not apparent.

An indication of the cause of relatively low values of  $\Delta H_f$  for nitrates is to be found in the results of resistivity and dielectric constant measurements.



Again taking as example  $\text{NaNO}_3$ , which deviates most from the corresponding curve for the halides, both resistivity and dielectric constant are anomalous at higher temperatures.<sup>12</sup> The marked increases in conductivity and dielectric constant which were observed, have been attributed to the disorder properties of the nitrate group. Because of the periodic rupturing of ionic bonds, and the propagation through the lattice of the associated disturbance in potential, the activity of the nitrate group increases the likelihood of structural faults and therefore promotes melting by reducing the mean bond strength and therefore reducing  $\Delta H_f$ .

The values of the melting points of univalent nitrates (and those of other compounds which are similar in having complex ions) may be partly determined by a resonance effect, in which periodic fluctuations in lattice potential emanating from a rotating or librating group cause sympathetic oscillations of other ions. The selective transfer of energy between the resonant groups and the lattice as a whole may be expected to result in a marked increase in ionic movement as the critical frequency becomes activated on raising the temperature. The corresponding increase in amplitudes of vibration stretches the cohesive bonds and thus promotes the break up of the lattice, and consequently its melting. Melting processes dominated by this mechanism, which may be referred to as *resonant melting*, are likely to occur when the resonant groups are tightly coupled, as for example when they approach each other closely in planar configurations. In those univalent nitrates which have structures of this type, the impossibility of obtaining cooperative meshing of a two dimensional array of rotators leads to out of plane movements of active groups, and consequently a large coefficient of thermal expansion perpendicular to the plane.

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