THE MELTING MECHANISM OF THE ALKALI THIOCYANATES

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INTRODUCTION

The melting of a solid always implies a transition from a state of comparatively high order to one of comparative disorder. A measure of the increase of disorder or randomization on melting is given by the Boltzmann relationship

$$S_f = R \ln W_L / W_S,$$

where W_S and W_L represent the number of independent ways of realizing the arrangements of solid and melt respectively and S_f is the entropy of fusion. Each new kind of disorder which occurs on passing from the crystal to the melt involves a new mechanism of randomization on melting. Ubbelohde[1] has summarized the different ways of randomization in the transition from the solid to the melt as positional, orientational, vibrational and configurational randomization. Other terms, which in certain cases can make large contributions to the entropy of fusion, are those due to the presence of mesomorphic states and the formation of association complexes in the melt[2]. Treating these increases of disorder as independent and additive, S_f becomes to a first approximation:

$$S_f = S_{positional} + S_{orientational} + S_{vibrational} + S_{configurational} + S_{association} + \ldots.$$

Generally, in an ideal case the melting point is sharp and it is assumed that the free-energy curves for the liquid and solid phases are completely independent. In certain cases, however, this is not strictly true and there are changes in slope of the free energy curve of the solid state before the two curves intersect[3]. This phenomenon is known as " homophase premelting " and occurs whenever the structures of the two phases are very similar (e.g. the crystalline paraffins)[2].

This paper is concerned with the melting mechanism of the alkali thiocyanates which are a group of low melting ionic salts such as:

$$\text{LiSCN, m.p. } 237°\text{C}; \quad \text{NaSCN, m.p. } 305°\text{C}; \quad \text{KSCN, m.p. } 177°\text{C};$$
$$\text{RbSCN, m.p. } 195°\text{C}$$

The following sections review the available experimental evidence with regard to the melting mechanism of these salts and a theory is put forward to account for their very low melting points.

THERMODYNAMIC PARAMETERS

The potassium salt is the most stable of the alkali thiocyanates, decomposition starting at approximately 250°C in the melt. Lithium thiocyanate decomposes on heating in the solid state and sodium thiocyanate decomposes on melting. *Table 1* compares the melting points, entropies, heats of fusion and volume changes for the sodium and potassium thiocyanates, nitrates and chlorides. The entropies of fusion of all these salts are approximately the same, but the latent heats of fusion (H_f) of the salts with spherically symmetrical anions (halides) are nearly twice as large as those for the salts with the irregularly shaped anions (nitrates and thiocyanates). The increase in the heat content of a salt on fusion is primarily due to the increased randomness of motion of its constituents (i.e. positional randomization) which depends on the volume increase on fusion.

Table 1. Thermodynamic parameters

Salt	Ref.	T_f (°C)	H_f (kcal/mole)	S_f (e.u.)	$\Delta V_f/V_s$ (%)
NaCl	4	800	7·20	6·7	30·0
KCl	4	769	6·42	6·16	23·0
NaNO₃	4	308	3·85	6·63	11·0
KNO₃	4	333	2·57	4·25	—
NaSCN	5	310	—	—	7·2
KSCN	5	177	3·39	7·56	5·4

The alkali halides show large volume changes on fusion, whereas for the other salts the volume change is small. Since T_f (the temperature of fusion) is also small, particularly for potassium thiocyanate, and $T_f = H_f/S_f$ there must be additional modes of entropy uptake for potassium thiocyanate on melting, other than that caused purely by positional randomization. The
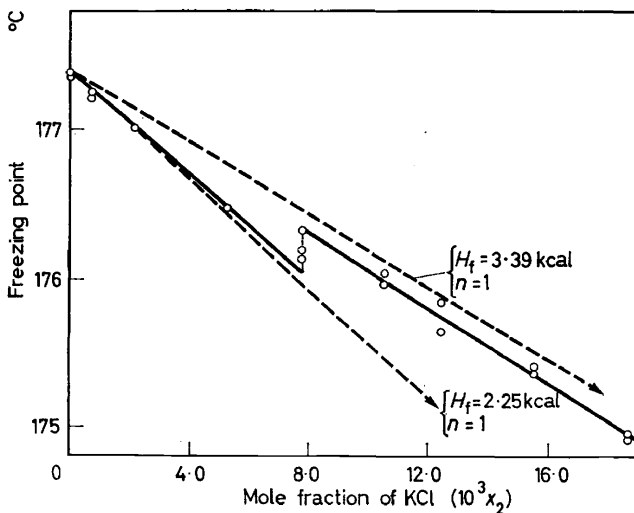

Figure 1. Depressions of freezing point of KSCN by KCl

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dilational changes with temperature for potassium thiocyanate are of great interest[5]. These indicate that marked homophase pre-melting occurs in this compound. The small overall change in volume on melting suggests a randomization mechanism which involves the rearrangement of a proportion of the ions into association complexes in the melt which do not require a large increase in volume.

A literature search also revealed that there were marked discrepancies in the values of H_f determined cryoscopically and calorimetrically[6]. Recent research in these laboratories has been directed to evaluating, by precision cryoscopic methods, the latent heat of fusion of potassium thiocyanate[6]. The results shown (*Figure 1*) can be interpreted if there is a transition in this salt in the immediate neighbourhood of the melting point. The dilatometric results suggest that this transformation is continuous, and that it occurs in the previously observed pre-melting region.

TRANSPORT PROPERTIES

Viscosity and conductivity measurements in molten potassium and sodium thiocyanates indicate that the transport properties of these salts are anomalous when compared with those for the alkali halides.

Table 2. Migration parameters of melts[5]

Salt	$10^3 \, \sigma_1/T_f$	E_η (kcal/mole)	E_σ (kcal/mole)	E_η/E_σ
NaCl	3·30	9·40	1·54	6·11
KCl	2·04	7·83	2·30	3·40
NaSCN	1·15	4·70	4·74	0·99
KSCN	0·34	5·72	5·85	0·98
NaNO₃	1·69	3·85	2·02	1·91
KNO₃	1·05	4·41	2·85	1·55
KHSO₄	0·10	11·95	6·2	1·93

Table 2 shows that the ratio σ_1/T_f (σ_1 is the conductivity of the melt just above the melting point) is much smaller for the low-melting salts. This, again, is evidence in favour of the formation of association complexes in molten thiocyanates. Also, at temperatures considerably above the melting point the ratio E_η/E_σ (E_η = energy of activation for viscous flow; E_σ energy of activation for conduction in the melt) approaches unity for the low melters. This can be explained if E_σ refers to large clusters of ions, such as occur in associated melts. Plester *et al.*[5] also found that E_η is greater for potassium thiocyanate at temperatures close to the melting point than at higher temperatures. On the other hand, E_η for potassium chloride remains contant. If association complexes do occur in the melt one would expect a greater number near the freezing point, which would explain the higher initial value of E_η.

In transport measurements in the solid phase, there is a complex temperature dependence. A plot shows the usual upper and lower slopes for the curve with changes at the crystal transition temperature (142°C). Near the freezing point there is a steep rise in conductivity which corresponds to the pre-melting region found in volume measurements[5].

CRYSTALLOGRAPHIC AND OPTICAL PROPERTIES

The crystallography of the thiocyanates is rather complex[7], but it can be assumed that the SCN⁻ion is linear with the following bond distances[8]: S—C 1·61Å and C—N 1·17Å. Klug has evaluated the crystal structure of potassium thiocyanate at 25°C; the SCN⁻ions lie in parallel planes[9]. In view of the reported volume changes and crystal transition at 142°C for this salt, the high-temperature crystal structure is probably different; however, it is most likely to be one of increased symmetry.
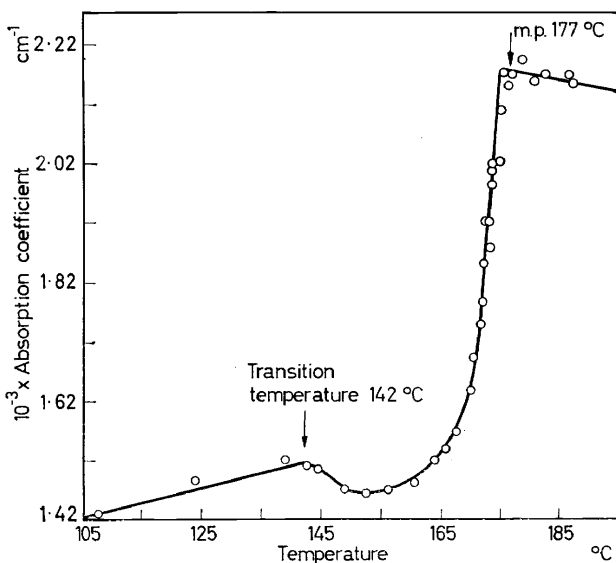

Figure 2. Ultra-violet absorption coefficient of KSCN at 2300Å

Recently the melting transition of potassium thiocyanate has been studied by ultra-violet absorption spectroscopy, which provides a means of studying environmental changes with temperature[10]. Both E_{max} and absorption coefficient curves (*Figure 2*) confirm homophase pre-melting for this salt, since marked changes in these parameters are observed before the melting point is reached. Evidence for the formation of association complexes in molten potassium thiocyanate is given by the marked rise in the value of the maximum absorption coefficient, compared with that found for salts which show simple positional randomization on melting (*e.g.* LiI).

PROPOSED MELTING MECHANISM OF THE ALKALI THIOCYANATES

The evidence so far available indicates that a number of modes of randomization are available when the alkali thiocyanates melt.

As in all ionic salts, positional randomization of the constituent ions is important for potassium thiocyanate, and orientational randomization also plays a part. However, it is unlikely that orientational randomization for SCN⁻ is complete, since the volume increase on fusion is too small to permit

free rotation. Viscosity, conductivity and spectroscopic measurements all point to the existence of association complexes or ion-pairs in the melt. The formation of association complexes would add a considerable term to the entropy of fusion without materially affecting the heat of fusion. This is confirmed by the low latent heat of fusion of potassium thiocyanate. The thiocyanates, in particular the potassium salt, show large pre-melting effects in the solid immediately below the melting point. This suggests that there is extensive formation of co-operative flaws in the crystalline state[11]. Such extensive flaw formation would tend to increase the disorder of the solid state, leading to a higher energy content for the solid close to the melting point, which will eventually result in a smaller heat of fusion. The apparent crystal transition found in the cryoscopic measurements also indicates that the solid state is very disordered close to the melting point.

Summarizing, it may be said that positional and orientational randomization occur on melting the thiocyanates and that there are also important contributions from the formation of association complexes in the melt and pre-melting in the solid.

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