On the Unusual Premelting Phenomenon of Potassium Thiocyanate Crystal

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Recently, Ubbelohde et al.[1] have published a series of papers on the unusual premelting effect of potassium thiocyanate crystal and concluded the rapid homophase increase of lattice defects as the melting point is approached. Quite independently,we have studied the transition phenomenon of this crystal in relation to that found in ammonium thiocyanate[2]. During the course of the differential thermal analysis of potassium thiocyanate we can not detect any such a tendency of premelting found by them, so we have reexamined the existence of the effect by use of the methods of dilatometric and d. c. conductivity measurements.

The sample (special grade, Wakō Pharmaceutical Co.) used were purified three times by fractional recrystallization from aqueous solution and then dried at 150°C under high vacuum (10^{-5} mmHg) for several hours after packing the sample in the glass-made dilatometer. Mercury was employed as a confining liquid, since it was confirmed that the mercury did not react with the sample even above the melting point. The results obtained are shown in Fig. 1 and in Table I in which the data by Ubbelohde and others are also given for comparison. For the d. c. conductivity measurement the specimen purified in the same way

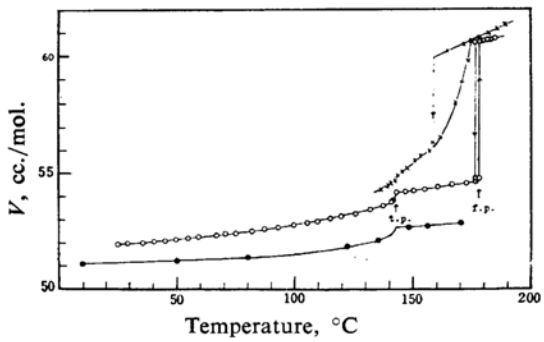

Fig. 1. The molar volume versus temperature curves of KSCN.
× Ubbelohde et al.
○ Present authors
● Yamada et al. (by X-ray method)

1) D. W. Plester, S. E. Rogers and A. R. Ubbelohde, *Proc. Roy. Soc.*, A235, 469 (1956); E. Rhodes and A. R. Ubbelohde, ibid., A251, 156 (1959); Idem, *Trans. Faraday Soc.*, 55, 1705 (1959).

2) M. Sakiyama, H. Suga and S. Seki, presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

TABLE I. VOLUME PARAMETERS OF KSCN

	Present authors	Ubbelohde and others
V_L	60.6	60.6±0.1
V_S	54.7	57.5
ΔV_f	5.9	3.1
$\Delta V_f/V_S$ (%)	10.8	5.4
V_t	54.13	54.7
$\Delta V_t/V_t$ (%)	1.53	0.36
ΔV_t	0.83	—
$V_{25°}$ (by flotation)	51.92*(51.3**)	51.92
t. p.	142.7°C	141.4°C
f. p.	178.45°C	175.1°C
α_S (high temp. phase)	2.6×10^{-4}	1.27×10^{-3}
α_L (low temp. phase)	3.91×10^{-4}	4.86×10^{-4}

V_L=molar volume of liquid at freezing point.
V_S=molar volume of solid at freezing point.
V_t=molar volume of solid at transition point.
ΔV_f=change in volume on melting.
ΔV_t=change in volume at transition point.
$V_{25°}$*=molar volume measured at 25°C by Ubbelohde et al.
** molar volume at ca. 10°C calculated from the dimensions of the unit cell[3].
(molar volumes are in cc./g. formula weight)

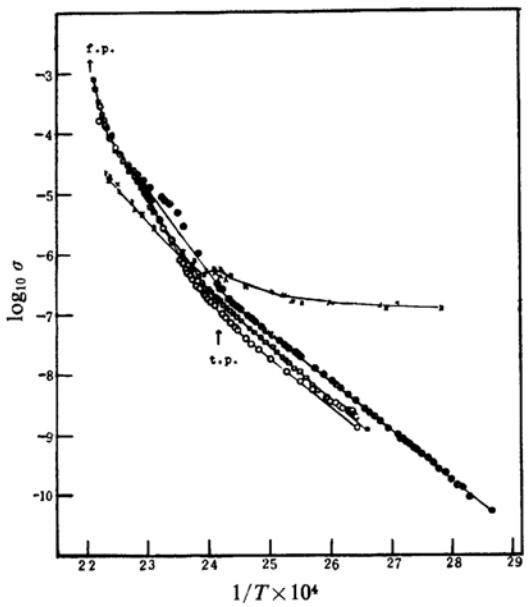

Fig. 2. The d. c. conductivity versus $1/T$ curves and their empirical equations of KSCN.
× Ubbelohde et al.
$\sigma_L=1\times10^{-3}\times\exp(-6.6/RT)$
$\sigma_H=3\times10^{14}\times\exp(-47.2/RT)$
⊙ Our results
$\sigma_L=2\times10^{12}\times\exp(-36.1/RT)$
$\sigma_H=1\times10^{25}\times\exp(-59.5/RT)$
○ $\sigma_L=3\times10^{10}\times\exp(-33.3/RT)$
$\sigma_H=6\times10^{16}\times\exp(-44.0/RT)$
□ $\sigma_L=2\times10^{11}\times\exp(-34.3/RT)$
$\sigma_H=3\times10^{19}\times\exp(-49.2/RT)$
σ_L: d. c. conductivity for low temperature phase
σ_H: d. c. conductivity for high temperature phase

as mentioned above was used in the shape of disk tablet (weight : 100 mg. ; diameter : 13 mm. ; thickness : 1 mm.). The conductivity versus $1/T$ relationships and empirical equations derived are shown in Fig. 2 together with the results by Ubbelohde et al.

From the results of our dilatometric study it is found that the volume changes abruptly at the melting point with almost no hysteresis effect in the cooling direction, standing in remarkable contrast to the case by Ubbelohde et al., and that our data are in good harmony with the thermal expansion determined with the X-ray method by Yamada et al[3]. who kindly measured the temperature dependence of the unit cell dimensions in accordance with our request. The fact that we obtained much larger activation energy (~35 kcal./mol.) for the d. c. conductivity at lower temperature region seems to indicate that our sample involves less impurities and is also in parallel with the dilatometric data. Detailed descriptions of the experimental procedures and discussion will be published in due course.

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3) Y. Yamada, H. Suga and T. Watanabe, presented at the 7th Annual Meeting of the Society of Applied Physics, Japan, 1960.