Molten Mixtures of KCNS with Alkali Halides*

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Eutectic compositions and temperatures in potassium thiocyanate mixtures with Li chloride and bromide, and with Na, K, Rb, Cs chlorides, bromides and iodides were determined. A detailed investigation performed on the accessible portion of the liquidus area of the system K^+, Na^+/CNS^-, Cl^- allowed to state the existence of five crystallization regions and three invariant points.

1) The present paper is part of an investigation we are performing on systems type K^+, Me^+/CNS^-, X^-, and concerns the mixtures of potassium thiocyanate with 14 alkali halides, as well as further remarks on the reciprocal ternary system formed with sodium and potassium thiocyanates and chlorides, formerly examined by OPARINA and DOMBROVSKAYA [1].

2) C. Erba RP, Merck or Schuchardt thiocyanates and halides were used. In particular, Merck potassium thiocyanate at our disposal, after having been recrystallized from water, dried under vacuum and submitted to a thermal shock, melted at 176 °C; Merck NaCNS, dried under vacuum at ~150 °C, melted at 307.5 °C.

Temperatures were taken by means of Chromel-Alumel thermocouples, checked by comparison with a NBS certified Pt resistance thermometer. The visual method employed was described elsewhere [2].

3) The liquidus curves of the KCNS + alkali halide systems were investigated from pure thiocyanate to x_{KCNS} values varying between 0.96 and 0.92. The results are summarized in Fig. 1, where the ideal curves, concerning a number of branches rich in thiocyanate (r.i.t.-branches) and diverging from the experimental ones enough to avoid confusion in the picture, are also drawn for comparison.

Within the examined composition range, each system exhibited a eutectic, the coordinates of which are reported in Tab. 1.

The experimental and ideal r.i.t.-branches of the K(CNS, Cl) and (KCNS + NaCl) systems lay so close that they (within the limits of the experimental fluctuations) nearly overlapped, while a considerable negative deviation from ideality was put into evidence for the (KCNS + LiCl) r.i.t.-branch. For the corresponding bromides and iodides more or less negative deviations were always observed.

MeX	$x_{MeX,\,E}$	t_E (°C)
LiCl	0.033	166.7
LiBr	0.043	163.5
NaCl	0.033_5	167.2
NaBr	0.045	163.8
NaI	0.061_5	158.8
KCl	0.031_5	171.9
KBr	0.045	170.0
KI	0.066_5	166.9
RbCl	0.031_5	170.9
RbBr	0.045_5	168.9
RbI	0.069	164.6
CsCl	0.030	168.3
CsBr	0.044_5	164.7
CsI	0.072	158.0

Table 1. Eutectics in molten mixtures of KCNS with alkali halides.

Concerning the mentioned Li, Na, K halides, for which no solubility in the solid state into KCNS is apparent, it may be concluded that the r.i.t.-branches negative deviations from ideality progressively increase with decreasing cation radii (or increasing cation polarizing power), and with increasing anion radii.

On the contrary, Rb halides noticeably dissolve into solid KCNS, which agrees both with our recent observations on the (KCNS + $RbNO_3$) system [3], and with the anomalously low freezing point depression found by RICCARDI et al. [4] in diluted solutions of RbCl into KCNS.

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[1] A. F. OPARINA and N. S. DOMBROVSKAYA, Zh. Neorg. Khim. **3**, 413 [1958].

[2] M. BRAGHETTI, D. LEONESI, and P. FRANZOSINI, Ric. Sci. **38**, 116 [1968].

[3] G. PIANTONI, M. BRAGHETTI, and P. FRANZOSINI, Ric. Sci., in press.

[4] R. RICCARDI and P. FRANZOSINI, Gazz. Chimica **92**, 386, 395 [1962].

A limited solubility in solid KCNS cannot be excluded even for Cs halides, for which the limiting values of the $\Delta T/m$ ratios are by 1 to 2 units lower than expected for solutes giving two particles foreign to the thiocyanate.

As previously observed for a number of analogous families of systems [5, 6], the eutectic composition is displaced towards higher x_{MeX} values when, Me being the same, Cl, Br, I are successively taken as X.

It is interesting to point out that the KCNS mixtures with Na, K, Rb, Cs chlorides, bromides and iodides, in spite of deviations from ideality, give eutectic compositions $x_{MeX,E}$ depending in an almost linear way from the differences $\Delta r = r_{Me^+} - r_{K^+}$ Å (see Fig. 2): with respect to the straight lines, Li halides eutectics lie towards lower x_{MeX} values.

4) The topology of the accessible portion of the reciprocal ternary system K^+, Na^+/CNS^-, Cl^- as outlined ten years ago by OPARINA and DOMBROVSKAYA [1], though not uncorrect in its main features, required refinishing. In particular, the mentioned authors identified only four crystallization regions (that is "... the NaCNS field, ... the KCNS field, ... the field of continuous solid solutions (Na,K)Cl, which breaks below 400° into two fields of limited solid solutions ..."), while a fifth region belonging to the compound [n KCNS·NaCNS] (where n is probably 3, and whose existence was recently pointed out by ourselves [3]), escaped their attention.

In order to draw a more correct map of the liquidus area, we investigated 14 offdiagonal cuts, whose projections are shown in the upper portion of Fig. 3, and whose characteristics are summarized in Tab. 2. We also took data from Tab. 1 concerning the West side and the Northeast-Southwest diagonal (stable diagonal [1]) of the map, and data by PIANTONI et al. [3] and by SINISTRI et al. [5] concerning the South and East sides, respectively.

Sections of six significant offdiagonal cuts are shown in Fig. 4: the discontinuities at the ends of the short nearly isothermal intermediate branches observed both along cuts I to III, and along the (K, Na)CNS liquidus curve [3] enabled us to fix the East and West boundaries of the fifth crystallization region, whose Northern limits are drawn through the discontinuities observed along cuts VI and VII. Cut IV (not intersecting the mentioned region) exhibits a profile far different from cuts I to III.

On the basis of all mentioned data, a map was drawn (lower portion of Fig. 3), where the isotherms at 140, 160, ..., 240 °C and the curves of simultaneous crystallization are shown. The projections of the latter on the West and South sides (Fig. 5) allowed us to single out the coordinates of the three invariant points A, B, C (Tab. 3). In the figure, F and G represent the two only invariant points (a transition one and a eutectic one, respectively) reported by OPARINA and DOMBROVSKAYA [1].

In order to check the accuracy of our map, we measured the melting temperatures of mixtures cor-

Cut	Composition of the starting mixture (in mole)		Added component	x_{ac}	Characteristic points t °C	x_{ac}	t °C
I	KCNS + KCl	99 : 1	NaCNS	0.244	133.5	0.262	133
II		65.60 : 1		0.244	133	0.265	132.5
III		49.01 : 1		0.249	132	0.265	132
IV		39.02 : 1		0.224	137	0.320	156
V		31.26 : 1		0.182	145	0.385	178
X		19 : 1		0.128	163	0.500	213.5
XI		12.30 : 1		0.140	204	0.607	238
XII		8.99 : 1		0.153	233	—	—
XIII	KCNS + NaCNS	19 : 1	NaCl	0.036_5	160	—	—
XIV		9 : 1		0.038_0	153	—	—
VI		3.10 : 1		0.014_6	132.5	—	—
VII	KCNS + NaCNS	2.82 : 1	KCl	0.015_0	132.5	—	—
VIII		1 : 1		0.023_8	208.5	—	—
IX		1 : 3		0.037_0	261	—	—

Table 2. Offdiagonal cuts in the system K^+, Na^+/CNS^-, Cl^-. x_{ac}: molar fraction of the added component.

[5] C. SINISTRI, P. FRANZOSINI, and M. ROLLA, Ric. Sci. **35** (II-A), 681 [1965].

[6] G. PIANTONI, D. LEONESI, M, BRAGHETTI, and P. FRANZOSINI, Ric. Sci. **38**, 127 [1968].

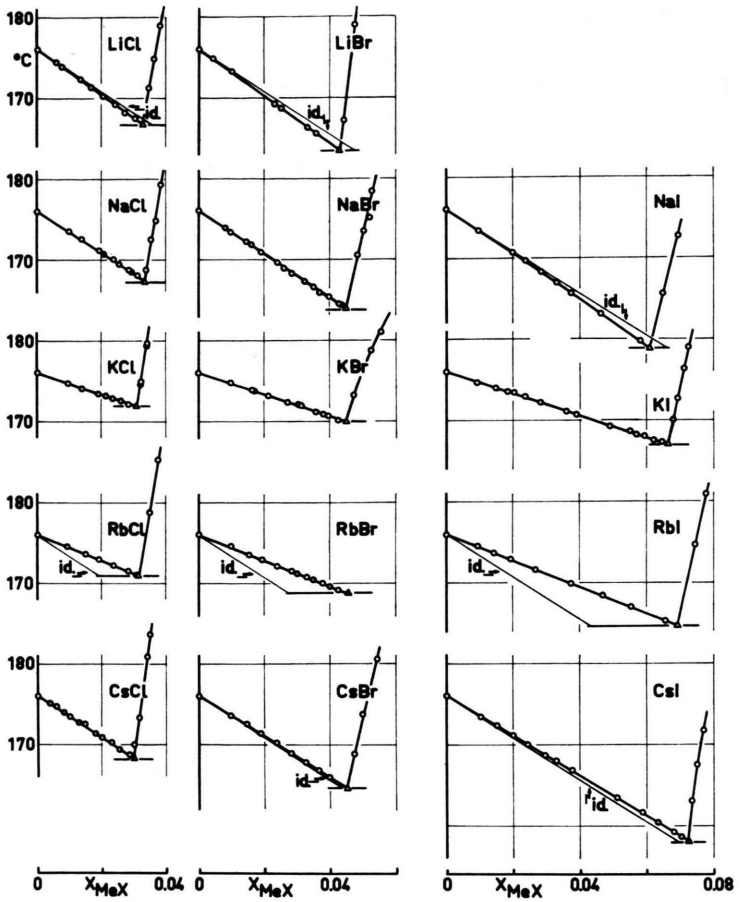


Fig. 1. Liquidus curves of systems type KCNS+MeX (thick curves). For a number of branches rich in thiocyanate, ideal (thin) curves, calculated according to SINISTRI and FRANZOSINI [7] ($\Delta H_{f,KCNS}=3.07$ kcal/mole [4]) are also drawn. As for KCNS+RbBr, because of the poor reliability of solid-liquid equilibrium temperatures taken in mixtures less rich in thiocyanate than the eutectic, the eutectic coordinates were singled out with the help of eutectic deposition temperatures measured in non-eutectic mixtures. - Concerning KCNS+K(Cl, Br, I), DINGEMANS [8] formerly found $x_{MeX,E}$ values equal to 0.0317, 0.0487 and 0.0655, respectively: the agreement with our data (Tab. 1) is satisfactory.

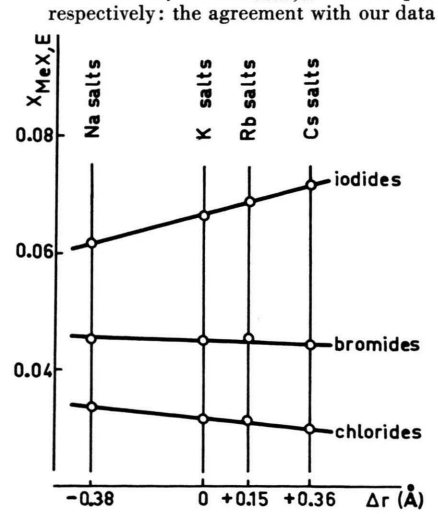


Fig. 2. Eutectic compositions as a function of the differences $\Delta r=(r_{Me^+}-r_{K^+})$ Å; cationic radii by JANZ [9].

[7] C. SINISTRI and P. FRANOSINI, Ric. Sci. **33** (II-A), 419 [1963].
[8] P. DINGEMANS, Rec. Trav. Chim. Pays-Bas **58**, 559 [1939].
[9] G. J. JANZ, Molten Salts Handbook, Academic Press, New York 1967, p. 1.

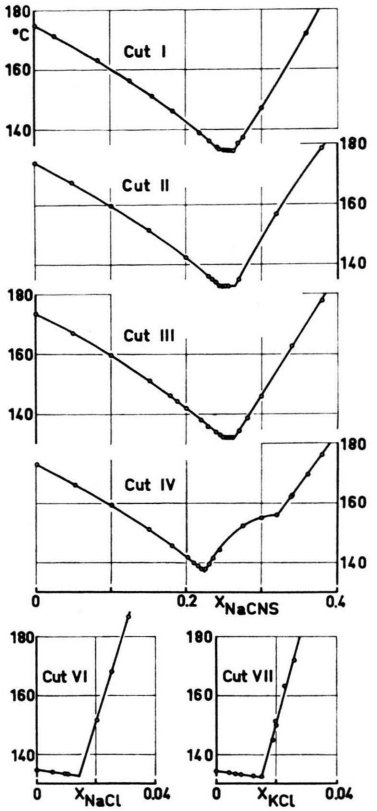
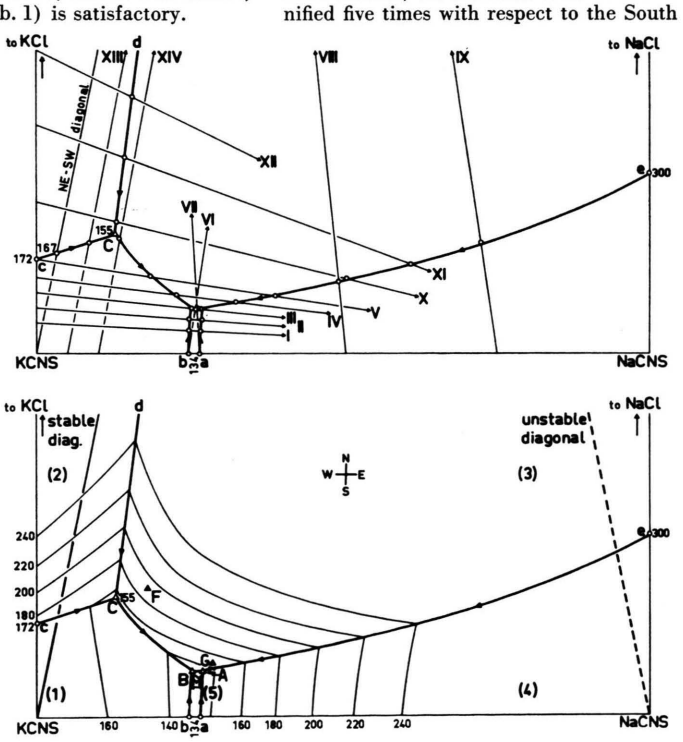


Fig. 4. Some significant offdiagonal cuts (explanation in text).

Fig. 3. Map of the system K^+, Na^+/CNS^-, Cl^- (explanation in text). In order to make details more evident, the East and West sides are magnified five times with respect to the South one.



Point	Composition (mole%)		t °C	References
A	KCNS	73.4_0	132	this paper
	NaCNS	25.0_8		
	NaCl	1.5_2		
B	KCNS	75.2_0	132	this paper
	NaCNS	23.2_8		
	NaCl	1.5_2		
C	KCNS	87.3_0	155	this paper
	NaCNS	8.7_8		
	NaCl	3.9_2		
F	KCNS	82.25	152	Ref. 1
	NaCNS	13.5		
	NaCl	4.25		
G	KCNS	71.7	126	Ref. 1
	NaCNS	26.5		
	NaCl	1.8		

Table 3. Crosspoints of the co-crystallization curves in the system K^+, Na^+/CNS^-, Cl^-.

responding, as for compositions, to A, B, C, F, G. The first one melted at 132.1°, the second at 132.3°, the third at 154.9 °C, that is in a good agreement with the values selected through extrapolation from our co-crystallization curves (see Tab. 3); whereas the fourth and fifth mixtures melted respectively at 189.0° and 145.6 °C, that is according to what expected on the basis of our map, even if at considerably higher temperatures than found by OPARINA and DOMBROVSKAYA [1].

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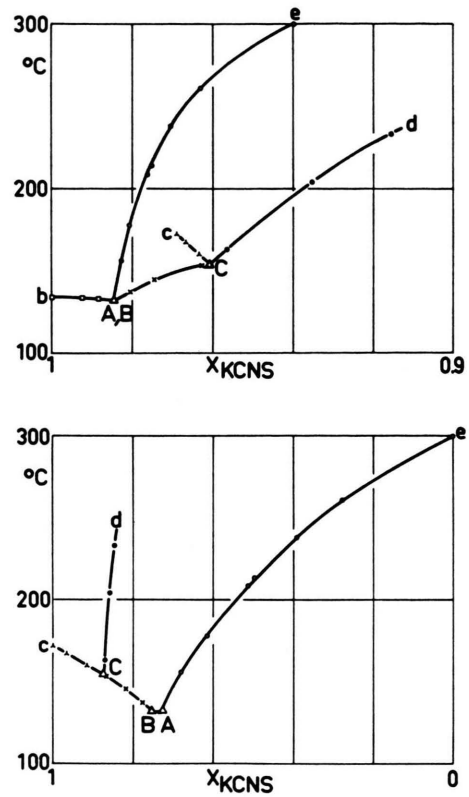

Fig. 5. Projections of the co-crystallization curves on the West (upper portion of the picture) and South (lower portion) sides of the map.