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**THE  $\text{Na}^+$ ,  $\text{K}^+/\text{CN}^-$ ,  $\text{I}^-$  BINARY SYSTEMS**Milan DRÁTOVSKÝ<sup>a</sup>, Bohumír GRÜNER<sup>b</sup>, Ivan HORSÁK<sup>c</sup> and Jiří MAKOVIČKA<sup>c</sup><sup>a</sup> *Department of Inorganic Chemistry, Charles University, 128 40 Prague 2*<sup>b</sup> *Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 250 68 Řež and*<sup>c</sup> *Computer Laboratory, Charles University, 128 40 Prague 2*

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The phase diagram of the KCN–KI binary system was measured and the published phase diagrams of the KCN–NaCN, NaI–KI and NaCN–NaI systems were verified and completed. The systems form solid solutions with minima on the liquidus and solidus curves. The solid solutions in the KCN–KI system probably have a high segregation temperature, close to the solidus curve. For the four binary systems the experimental points were fitted with liquidus and solidus curves either by applying smoothing spline functions or by using two different models. The results obtained are discussed.

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This work is a preparatory study for the measurement and correlation of the phase diagram of the  $\text{Na}^+$ ,  $\text{K}^+/\text{CN}^-$ ,  $\text{I}^-$  ternary reciprocal system. This ternary system may find use as a relatively low-melting medium for investigating selective reductions of some elements and their compounds in salt melts while masking other elements in their iodo or cyano complexes.

From among the binary systems, the KCN–NaCN system has been completely described<sup>1</sup>. As to the KI–NaI system, only the liquidus curve and the solid solution segregation temperature (about 365°C) have been reported<sup>1</sup>. For the NaCN–NaI system, the diagram of the solidus and liquidus curves (without experimental points) and the positions of the minima on these curves have been given<sup>2</sup>. The phase diagram of the KCN–KI system has not been published.

Since these binary systems form solid solutions with minima on the solidus and liquidus curves, they offer an opportunity for testing the various methods for the calculation of these curves<sup>3–5</sup>. The method which will prove most successful then may be applied to the correlation of the phase diagram of the ternary reciprocal system from the phase diagrams of the binary systems.

**EXPERIMENTAL**

*Chemicals.* All chemicals used were of reagent grade purity (Lachema, Brno, and Spolana, Neratovice). NaI and KI were dried at 150°C for 2 h. The cyanides were freed from carbonates in a nitrogen stream. From KCN solutions, carbonate was precipitated with an equivalent

amount of  $\text{Ba}(\text{OH})_2$ , and KCN was separated from KOH by concentration of the solution in a vacuum rotary evaporator followed by fractional crystallization, making use of the different solubility of the two substances<sup>6</sup>. The dry purified chemical contained  $97.0 \pm 0.4\%$  KCN. NaCN was first fused to decompose the red substances arising from the polymerization of hydrogen cyanide, a saturated solution of NaCN was then prepared and  $1\% \text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$  was added in order to prevent polymerization of HCN (refs<sup>7,8</sup>). Sodium carbonate separated from the saturated solution in 24 h. The solution was filtered and evaporated in a vacuum rotary evaporator at  $40-50^\circ\text{C}$ , the vapour pressure being additionally reduced by cooling the receiver to  $-80^\circ\text{C}$ . The purified chemical contained  $98.5 \pm 0.2\%$  NaCN.

The tabulated values<sup>9</sup> of the thermodynamic constants of the pure components were used in the calculations.

*Chemical analysis.* Purity of the alkali iodides and cyanides was verified by argentometric titrations and melting point measurements.

*Differential thermal analysis.* The heating and cooling DTA curves were recorded on two instruments. The one was an OD-120 Derivatograph (MOM, Budapest), enabling, in addition to the DTA and TA curves, also the curve of weight changes with increasing temperature to be recorded; this was employed to establish the volatility of the substances, cyanides in particular, above their melting temperatures. The other apparatus used, set up at the Department of Inorganic Chemistry, Charles University in Prague<sup>10</sup>, was equipped with a compensation attachment for elimination of the effect of ambient temperature changes, and interfaced to a TZ 4601 recorder (Laboratorní přístroje, Prague). The temperatures and the DTA parameters were occasionally compared with the values read on an MT 100 digital voltmeter. Samples and reference substance ( $\text{Al}_2\text{O}_3$ ) were accommodated in corundum crucibles. Samples containing alkali cyanide were covered with a thin layer of  $\text{Al}_2\text{O}_3$  to prevent the cyanide melt from creeping up. The measurements were performed under dry nitrogen. The heating rate was  $5 \text{ deg min}^{-1}$ , cooling was spontaneous. Substances were used in amounts of 0.6 or 0.7 g. The peak temperatures were read following ICTA Recommendations<sup>11</sup>. The multiply measured phase transformation temperatures for a given sample did not vary more than by  $\pm 8^\circ\text{C}$ . The temperatures and their differences were measured by using Ni-NiCr thermocouples calibrated over the  $300-680^\circ\text{C}$  region by means of the  $\text{KClO}_4$  (s-s), Cd (s-l), Zn (s-l),  $\text{PbCl}_2$  (s-l),  $\text{K}_2\text{SO}_4$  (s-s) and  $\text{K}_2\text{CrO}_4$  (s-s) phase transformations<sup>9,11</sup>.

*X-ray diffraction measurements.* The Debye-Scherrer method was used. The measurements were carried out on a Mikrometa 2 instrument (Chirana, Prague) in a Siemens-Halske chamber using  $\text{CuK}_\alpha$  radiation (154.184 nm, nickel filter).

Experimental data processing was accomplished on an HP 9845A desk-top computer using our own programs, set up in BASIC.

## RESULTS AND DISCUSSION

Experimental points of the liquidus and solidus curves for the KCN-KI, NaCN-NaI, and NaI-KI binary systems were derived from the heating and cooling curves. Fig. 1 shows the measured experimental points for the KCN-KI system, Figs 2 and 3 show combinations of our experimental data with the published data<sup>1,2</sup> for the NaCN-NaI and NaI-KI systems, and Fig. 4 shows published data<sup>1</sup> for the NaCN-KCN system. The shapes of the liquidus and solidus curves indicate that the four

systems form completely miscible solid solutions. The cooling curves of some of the samples of the KCN-KI system, below the solidus temperature, exhibit hints of thermal effects at temperatures about 500°C, which may be ascribed to segregation

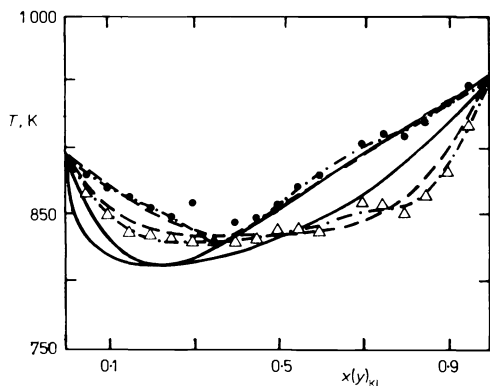


FIG. 1

Phase diagram of the KCN-KI binary system. ● Experimental points of the liquidus curve, △ experimental points of the solidus curve; - · - · - curve 1, - - - - curve 2, — curve 3

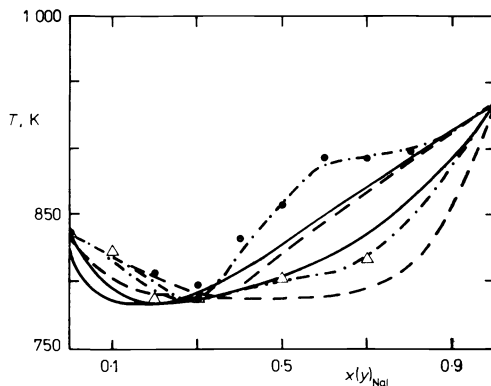


FIG. 2

Phase diagram of the NaCN-NaI binary system. Points and curves as in Fig. 1

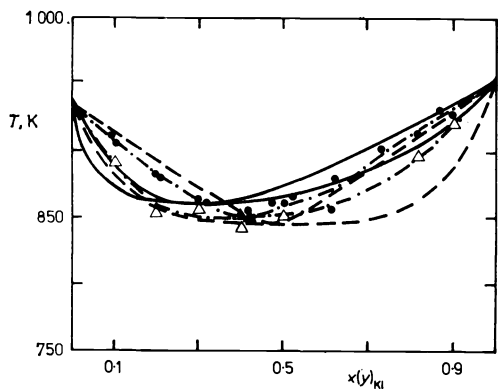


FIG. 3

Phase diagram of the NaI-KI binary system. Points and curves as in Fig. 1

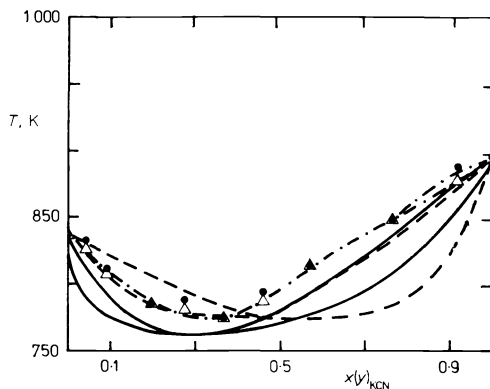


FIG. 4

Phase diagram of the NaCN-KCN binary system. Points and curves as in Fig. 1

of the solid solutions. The fact that segregation of solid solutions of the four binary systems takes place above ambient temperature is also borne out by X-ray diffractograms, which for samples cooled to ambient temperature invariably indicated the presence of the two components and not of the solid solution.

The experimental points in the four diagrams were fitted with cubic splines<sup>12</sup> (curves 1) in a manner such that the curves passed through the melting points of the pure components and through the common minimum of the liquidus and solidus curves. The concentration and temperature coordinates of the minima on the liquidus and solidus curves so obtained are given in Table I under the heading „Curve 1“. The curves labelled 2 and 3 in Figs 1–4 were calculated following two different physical models.

Curves 2 were calculated by using the model of regular liquid and solid solutions<sup>3</sup>, based on the following simple expression for the excess Gibbs energy of mixing:

$$\Delta G^l = (A/R) x(1 - x) \quad (1)$$

or

$$\Delta G^s = (B/R) y(1 - y), \quad (2)$$

where  $x$  and  $y$  are the mole fractions of a component in the liquid and solid phases, respectively,  $R$  is the gas constant and  $A$  and  $B$  are constants. Provided that these relations are obeyed, the liquidus and solidus curves are described by the equations

$$\ln(1 - x) + (A/T) x^2 - \ln(1 - y) - (B/T) y^2 = (\Delta h_1^f/R) (1/T_1^f - 1/T) \quad (3)$$

for component 1, and

$$\ln x + (A/T) (1 - x)^2 - \ln y - (B/T) (1 - y)^2 = (\Delta h_2^f/R) (1/T_2^f - 1/T) \quad (4)$$

TABLE I

Parameters (mole fraction of component AC/temperature, °C) of the minima of the liquidus and solidus curves

AC-BC system	Curve 1	Curve 2	Assumption		
			a)	b) (curve 3)	c)
KCN-KI	0.65/558	0.635/562	0.50/572	0.78/540	0.77/453
NaCN-NaI	0.70/515	0.65/516	0.57/540	0.80/510	0.76/436
NaI-KI	0.58/577	0.52/572	0.37/595	0.70/586	0.69/499
NaCN-KCN	0.63/502	0.55/501	0.37/497	0.70/489	0.67/390

for component 2. Here  $\Delta h_i^f$  and  $T_i^f$  are changes in the melting enthalpy and melting temperatures, respectively, of the pure component  $i$ . Since Eqs (3) and (4) are transcendent with respect to  $x$  and  $y$ , the iterative approach had to be applied to their solving. Thus, the model has two adjustable parameters (the constants  $A$  and  $B$ ); the shape of the liquidus and solidus curves, however, is sensitive particularly to their difference ( $A - B$ ), and the position of the common minimum of the two curves (for  $x = y$ ) depends on this difference solely, hence, on a single adjustable parameter. Curves 2 in Figs 1–4, which optimally correspond to the experimental points distribution, were obtained by iterative refinement of  $A$  and  $B$ . The positions of the minima of these optimum curves are given in Table I under the column heading „Curve 2“. Since only one adjustable parameter is available for the calculation of the position of the minimum, it cannot be brought to a perfect agreement with the experimental value. The  $B$  value was estimated to  $B = 1\,500$  K for all the systems as a compromise. Lower values result in a decrease in the distance between the liquidus and solidus curves, whereupon the fit grows poorer, whereas higher  $B$  values bring about changes in the shape of the phase diagram such that a type corresponding to incomplete miscibility of the components emerges. For parameter  $A$ , values of 600 K (KCN–KI), 450 K (NaCN–NaI), 300 K (NaI–KI) and 700 K (NaCN–KCN) were used.

Parameter  $B$  can also serve to calculate the temperature peak of segregation of the solid solutions, viz. by means of the formula  $T_{\max} = B/2$ . Given  $B = 1\,500$  K, we have  $T_{\max} = 750$  K ( $\approx 480^\circ\text{C}$ ), which is in a fairly good agreement with the experimental values for the NaI–KI and KCN–KI systems, which are  $365^\circ\text{C}$  (ref.<sup>1</sup>) and about  $500^\circ\text{C}$ , respectively, taking into account the low sensitivity to the parameter  $B$  and high uncertainty in the determination of the segregation temperatures.

Curves 3 in Figs 1–4 were calculated following another physical model, which does not involve adjustable parameters<sup>4</sup>. For two uni-univalent electrolytes with a common ion to form solid solutions with an extremum on the liquidus and solidus curves, at least one of the two components must behave differently in liquid and solid solutions, and also the two components must exhibit mutually different behaviour either in liquid or in solid solutions<sup>4,5</sup>. In the case of liquidus and solidus curves exhibiting a minimum, this difference must rest in a higher degree of dissociation or a lower degree of association of the component in the liquid solution as compared to the solid solution<sup>4</sup>.

For each of the studied binary systems with a common ion, equations are derived assuming one of the three following variants:

- a) dissociation of the lower-melting component in the liquid phase,
- b) dissociation of the higher-melting component in the liquid phase,
- c) dissociation of the higher-melting component in the liquid phase and association of the lower-melting component to the 2nd degree in the solid phase.

The van't Hoff reaction isobar can be used:

$$K_i/K_i^0 = \exp [(\Delta h_i^f/R) (1/T_i^f - 1/T)], \quad (5)$$

where  $K_i$  and  $K_i^0$  are the equilibrium constants for the  $i$ -th component between the liquid and solid phases in solutions and in the pure state, respectively.

By way of example, we shall demonstrate the procedure for assumption *b*). The equilibria between the liquid and solid phases can be written as



for the lower-melting component, and



for the higher-melting component. Based on this, the mole fractions of the species (labelled by square brackets) are as follows:

liquid phase of the pure component AC:

$$[(AC)^{0,l}] = 1; \quad (6)$$

solid phase of the pure component AC:

$$[(AC)^{0,s}] = 1; \quad (7)$$

liquid phase of the pure component BC:

$$[B^{0,l}] + [C^{0,l}] = 1 \quad (8a)$$

$$[B^{0,l}] = [C^{0,l}] = 1/2 \quad (8b)$$

$$2[B^{0,l}] = 1; \quad (8c)$$

solid phase of the pure component BC:

$$[(BC)^{0,s}] = 1; \quad (9)$$

liquid solution:

$$[(AC)^l] + [B^l] + [C^l] = [(AC)^l] + 2[B^l] = 1; \quad (10)$$

solid solution:

$$[(AC)^s] + [(BC)^s] = 1. \quad (11)$$

Inserting Eqs (6)–(11) into Eq. (5) with regard to schemes (A) and (B) we obtain

$$K_{AC}/K_{AC}^0 = \{[(AC)^l]/[(AC)^s]\} / \{[(AC)^{0,l}]/[(AC)^{0,s}]\} = \\ = [(AC)^l]/[(AC)^s] = M \quad (12)$$

$$K_{BC}/K_{BC}^0 = \{[B^l]^2/[(BC)^s]\} / \{[B^{0,l}]^2/[(BC)^{0,s}]\} = \\ = 4 [B^l]^2/[(BC)^s] = Q, \quad (13)$$

where

$$M = \exp [(\Delta h_{AC}^f/R) (1/T_{AC}^f - 1/T)] \quad (14)$$

$$Q = \exp [(\Delta h_{BC}^f/R) (1/T_{BC}^f - 1/T)]. \quad (15)$$

By solving the four equations (10)–(13), the four unknown mole fractions of the species [(AC)<sup>l</sup>], [(AC)<sup>s</sup>], [B<sup>l</sup>] and [(BC)<sup>s</sup>] are expressed as functions of *M* and *Q*, and the results are inserted in Eqs (16)–(19) for the mole fractions of the components in the liquid and solid solutions:

$$x_{AC} = [(AC)^l] / \{[(AC)^l] + [B^l]\} = 2 [(AC)^l] / \{1 + [(AC)^l]\} \quad (16)$$

$$x_{BC} = [B^l] / \{[B^l] + [(AC)^l]\} = [B^l] / \{1 - [B^l]\} \quad (17)$$

$$y_{AC} = [(AC)^s] / \{[(AC)^s] + [(BC)^s]\} = [(AC)^s] \quad (18)$$

$$y_{BC} = [(BC)^s] / \{[(BC)^s] + [(AC)^s]\} = [(BC)^s]. \quad (19)$$

In this manner the equations for the liquidus and solidus curves are obtained in the forms

$$x_{AC} = \frac{2 \{M - 0.5Q \pm [0.25Q^2 - MQ(1 - M)]^{1/2}\}}{2M - 0.5Q \pm [0.25Q^2 - MQ(1 - M)]^{1/2}} \quad (20)$$

$$x_{BC} = \frac{0.5Q \mp [0.25Q^2 - MQ(1 - M)]^{1/2}}{2M - 0.5Q \pm [0.25Q^2 - MQ(1 - M)]^{1/2}} \quad (21)$$

$$y_{AC} = \{M - 0.5Q \pm [0.25Q^2 - MQ(1 - M)]^{1/2}\} / M^2 \quad (22)$$

$$y_{BC} = \{M(M - 1) + 0.5Q \mp [0.25Q^2 - MQ(1 - M)]^{1/2}\} / M^2. \quad (23)$$

Each *x* or *y* has two values at a given temperature: one is lower and the other is higher than as corresponds to the position of the minimum on the liquidus and solidus curves. Within the temperature region between the melting temperature of the higher-melting component and the temperature of the minimum, the two

values are both real or one of them is beyond the range of physical reality. Naturally, we have  $x_{AC} + x_{BC} = y_{AC} + y_{BC} = 1$ .

Eqs (20)–(23) can be also derived by starting from the Le Chatelier–Schröder equation for solid solutions in the forms

$$a_{AC}^l/a_{AC}^s = M \quad (24)$$

$$a_{BC}^l/a_{BC}^s = Q, \quad (25)$$

where  $a_i^l$  and  $a_i^s$  are the activities of the  $i$ -th component in the liquid and solid solutions, respectively<sup>5</sup>. The activity  $a_{AC}^l$  is proportional to the mole fraction of the non-dissociated component, hence

$$a_{AC}^l = k_{AC}^l x_{AC} / (x_{AC} + 2x_{BC}) = k_{AC}^l x_{AC} / (2 - x_{AC}). \quad (26)$$

Activity  $a_{BC}^l$  is proportional to the product of the cation and anion fractions, hence

$$a_{BC}^l = k_{BC}^l x_{BC}^2 / (2x_{BC} + x_{AC})^2 = k_{BC}^l x_{BC}^2 / (1 + x_{BC})^2. \quad (27)$$

In solid solutions, the activities obey the simple relation

$$a_i^s = k_i^s y_i \quad (i = AC, BC). \quad (28)$$

The constants  $k_i^l$ ,  $k_i^s$  in Eqs (26)–(28) are determined using the boundary conditions

$$\lim_{x_i \rightarrow 1} a_i^l = 1 \quad (29)$$

$$\lim_{y_i \rightarrow 1} a_i^s = 1. \quad (30)$$

In this manner we obtain  $k_{BC}^l = 4$ ,  $k_{AC}^l = k_{AC}^s = k_{BC}^s = 1$ , and the system of equations for the liquidus and solidus curves (20)–(23) are obtained by inserting Eqs (26) to (28) into Eqs (24) and (25).

Similar systems of equations can be derived assuming the behaviour sub *a*) and sub *c*).

An overview of the positions of the minima on the liquidus and solidus curves, calculated for the binary systems, adopting assumptions *a*), *b*), *c*) is given in Table I. Values calculated applying assumption *b*) approach the experimental data most closely. The liquidus and solidus curves calculated according to assumption *b*) are labelled 3 in Figs 1–4. To attain a complete agreement of the position of the minimum with the experimental points, the equations would have to have two adjustable parameters. An attempt was therefore made to derive the liquidus and solidus curves



assuming partial dissociation of the components in liquid solution and to introduce the dissociation constants of the components as adjustable parameters in the equations. Too complex general equations of the 3rd and 4th orders, however, emerged, and we did not attempt to solve them. In a calculation correlation of the Na<sup>+</sup>, K<sup>+</sup>/I<sup>-</sup>, CN<sup>-</sup> ternary reciprocal system from the four binary systems, the equations given in this paper thus will have to be employed.

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