Phase Star Correlations for Salt Systems in Melts

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Using a regression analysis it was found that the following correlations exist for the phase stars (crystallization trees) of ternary and ternary reciprocal salt systems in melts: i, between the melting temperature and the composition of the eutectic mixtures and ii, between the melting enthalpy of the eutectic composition and its melting temperature.

The concept of *phase stars* (eutectic stars or crystallization trees) was devised by Academician N. S. Kurnakov[1] and developed by A. G. Bergman and N. S. Dombrovskaya.[2–4] In terms of model ideas about phase transitions in molten salt systems we may propose the following definition: the phase star (crystallization tree) is an oriented graph the centre of which is the invariant (eutectic) point of a given system, the beam vertices are the invariant (eutectic) points of subsystems having lower dimensions and the ribs show the crystallization direction [Figure 1(*b*)]. Usually the melting temperature or crystallization temperature of the eutectic salt mixture is indicated in the graph vertices. For example, for the ternary system shown in Figure 1(*a*) three crystallization fields together with three border curves, along which they cross in pairs, form the phase star (the crystallization tree) with a vertex at the ternary eutectic point E. The graph dimensionality is equal to the subsystem dimensionality from which the compositions simulated by the graph vertices are taken. In our case these are the binary systems due to which the star is two-dimensional.

The revelation of the phase star is the final stage in the construction of the composition-property diagram, including melting diagrams. During the investigation of physical properties of eutectic compositions phase stars have not been used to date. A first attempt is presented here. The goal of this work is a more fundamental investigation of phase stars in order to determine the correlation between all characteristics which may be revealed using this model.

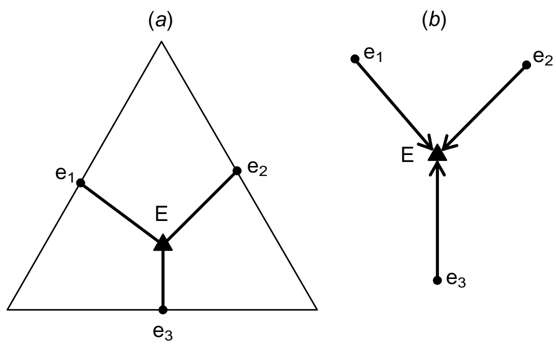

Figure 1 Phase diagram for the ternary eutectic system A,B,C//X (*a*) and its phase star (crystallization tree) (*b*).

Two aspects are studied:

(1) The correlation between the melting temperature and the composition of the eutectic mixtures in ternary reciprocal systems.

(2) The correlation between the melting temperature and melting enthalpy of the eutectic compositions in ternary and ternary reciprocal systems.

Equation (1)[5] is used:

$$r = \frac{\sum_{i=1}^{n} x_i/y_i - \frac{1}{n}\sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{\sqrt{\sum_{i=1}^{n} x_i^2 - \frac{1}{n}\left(\sum_{i=1}^{n} x_i\right)^2}\sqrt{\sum_{i=1}^{n} y_i^2 - \frac{1}{n}\left(\sum_{i=1}^{n} y_i\right)^2}} \qquad (1)$$

where r is the correlation coefficient under the linear approximation and n is the number of pairs of the values x_i and y_i involved in the calculation.

The confidence interval K for the correlation coefficient r at the significance level P% was determined from equation (2):

$$K_{\max,\min} = \frac{1-r}{1+r}\exp[\pm 2U(P)/\sqrt{n-3}\,] \qquad (2)$$

where the plus sign in the exponent exp relates to the maximum value of K, the minus sign relates to the minimum value and the function $U(P)$ takes the meanings as follows:

P(%)	98	95	90	80
$U(P)$	2.326	1.960	1.645	1.282

Twelve ternary reciprocal systems were analysed during the solution of the first problem; experimental data for these were taken from reference books.[6–8] The irreversible reciprocal systems are selected with two ternary eutectics; their melting diagram has the shape shown in Figure 2. The correlation coefficients are calculated for salts AY and BX representing a stable salt pair, the products of the double-exchange reaction proceeding in the system:

$$AX + BY \rightarrow AY + BX$$

The melting temperature of the binary and ternary eutectic

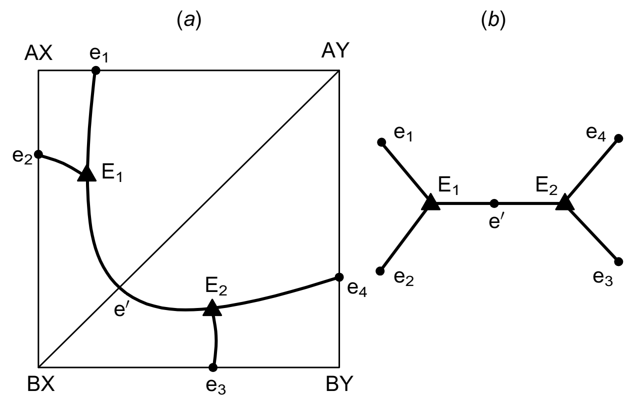

Figure 2 Phase diagram for the ternary irreversible-reciprocal system A,B//X,Y (*a*) and its phase star (crystallization tree) (*b*).

is taken as meaning y in equation (1) and the content of the salt in the corresponding eutectic mixture is taken as x (in mol%). For the salt AY they are e_1, e_2, E_l, e′, E_2 and for the salt BX they are e_2, E_1, e_3, e_4, e′ and E_2. The results of the calculation are given in Table 1.

It follows from Table 1 that a correlation between the melting temperature and the eutectic composition for some systems is absent. Inclusion of the saddle eutectic e′ into the calculation influences the values of the correlation coefficient r. The largest value of r is recorded in the systems with a strict phase diagram symmetry relative to stable and metastable diagonals, and with similar values of melting

Table 1 Correlation between melting temperature and eutectic composition in the crystallization trees of ternary reciprocal systems.[a]

System	Salt		r_{AY}		r_{BX}	
	AY	BX	I	II	I	II
Ba,Na//Cl,NO_3	NaCl	$Ba(NO_3)_2$	0.9983	0.9532	0.9977	0.9351
Ba,Na//Cl,SO_4	$BaSO_4$	NaCl	0.1712	0.9753	0.9924	0.9952
Ba,Na//Br,NO_3	NaBr	$Ba(NO_3)_2$	0.9888	0.8524	0.9611	0.9192
Ca,Na//Cl,SO_4	$CaSO_4$	NaCl	0.9123	0.9123	0.6715	0.7896
Cs,Na//Cl,F	NaF	CsCl	0.9942	–	0.9979	–
K,Na//Cl,F	NaF	KCl	0.9903	0.9979	0.1512	0.4299
K,Li//Br,F	LiF	KBr	0.2450	–	0.9884	–
Li,Na//ClO_4,NO_3	$NaClO_4$	$LiNO_3$	0.8248	0.7932	0.9112	0.9591
Na,Rb//Cl,I	NaCl	RbI	0.9168	0.8539	0.6872	0.5134
Na,Rb//Cl,F	NaF	RbCl	0.9999	0.9401	0.6044	0.9663
Na,Sr//Br,NO_3	NaBr	$Sr(NO_3)_2$	0.9506	0.9065	0.9986	0.8372
Na,Tl//Cl,SO_4	Na_2SO_4	TlCl	0.9832	0.9747	0.9342	0.9351

[a] I, without taking into calculation the saddle eutectic; II, taking into consideration the saddle eutectic.

temperature and ternary eutectic point composition. For example, the ideally symmetric system Cs,Na//Cl,F (Figure 3) with the following characteristics of the invariant points: E_1 482 °C, 33.5% NaCl, 4% NaF, 62.5% CsCl; E_2 438 °C, 2% NaF, 48.5% CsF, 49.5% CsCl. In addition, the location and the steepness of the isotherms in such diagrams testify to the high rate of irreversibility of the ternary reciprocal system accompanied as a rule by a large value for the thermal effect of the exchange reaction (for example, for the system Cs,Na//Cl,F it is 52.426 kJ mol^{-1}).

The absence of the correlation may mean either non-ideal behaviour of the salt in the melt or an incorrect experiment. The presence of the correlation allows us to use the crystallization tree for the prognosis of the eutectic mixture properties. Such a possibility was tested taking as an example the correlation between melting temperature and melting enthalpy[9] of the salt eutectics. The results are given in Table 2. Such correlations exist in almost all ternary and ternary reciprocal systems tested. The presence of the correlation allows us to perform an approximation according to two variables and to derive the regression equation (3)

$$y = b_0 + b_1 x_1 + b_2 x_2 \tag{3}$$

from which – knowing one of the variables x_1 and x_2 and the values of the property y – we can find the value of the other. Given two known values we may find a third unknown value.

Thus, the crystallization tree (phase star) can be used for the calculation of the melting enthalpies of the eutectic salt mixtures and for the selection of a composition of appropriate heat content for different practical applications.

Table 2 Correlation between melting temperature and melting enthalpy in the crystallization trees of ternary and ternary reciprocal systems.

System	r
Li//Cl,NO_3,SO_4	0.9964
K,Li,Na//F	0.9962
Li//Cl,F,OH	0.9946
K,Mg,Na//Cl	0.9912
K,Li//Cl,SO_4 (Li_2SO_4–LiCl–KCl)	0.8840
Li,Na//Cl,NO_3 ($LiNO_3$–NaCl–$NaNO_3$)	0.9921

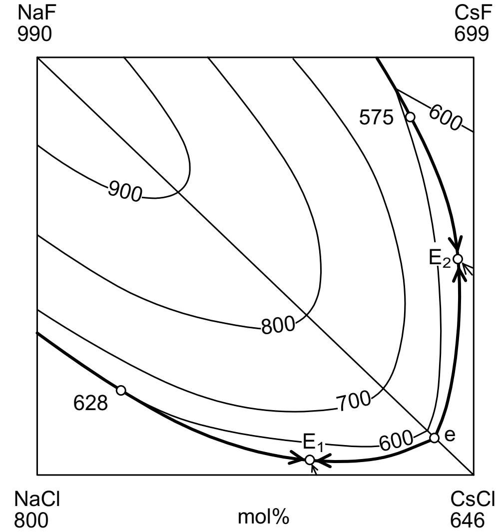

Figure 3 Melting diagram for the ternary reciprocal system Cs,Na//Cl,F.[8]

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Received: Moscow, 26th April 1995
Cambridge, 27th June 1995; Com. 5/02736E