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Differentiation of the Fourfold Mutual System Na, K // Cl, NO_3, MoO_4 and Phase Complex of Its Stable Secant Triangle $NaCl-KNO_3-Na_2MoO_4$

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***Abstract*—Based on the graph theory, the fourfold mutual system Na, K // Cl, NO_3, MoO_4 was differentiated taking into account the complex formation ($NaKMoO_4$, $K_5Cl(NO_3)_4$, $Na_3Cl(MoO_4)$) and the inner secants ($KNO_3-Na_3ClMoO_4$, $K_6Cl(NO_3)_5-Na_3ClMoO_4$). For the first time, the complex of the three-component system $NaCl-KNO_3-Na_2MoO_4$, being its stable triangle, was studied using a set of physicochemical methods (visual-polythermal analysis (VPA), differential thermal analysis (DTA), X-ray phase analysis (XRP)).**

Keywords—fourfold mutual system, composition-property diagram, differentiation, chloride, nitrate, molybdate, sodium, potassium

I. INTRODUCTION

Due to the complex of properties (low melting point, thermal stability up to 4000 °C, low corrosion activity, high electrical conductivity, good thermal conductivity, low viscosity) melts, containing nitrates and molybdates of alkali metals, are widely used in metallurgy and power engineering as heat-accumulating materials, as part of electrolytes for electrochemical oxidation of metals, etc. [1, 2]. The introduction of halides (chlorides and fluorides) into nitrate-molybdate systems makes it possible to ensure thermal and thermodynamic stability of melts in a wider temperature range with relatively low corrosion activity, since the melts of halides are very aggressive and subject to pyrohydrolysis [3]. In this respect, it seems relevant to study their joint behavior, "composition-property" and "property-property" diagrams in two- and more component systems, as well as to search for methodological approaches to the formation and study of complex systems in order to develop new materials with given properties.

The purpose of this study is to differentiate the fourfold mutual system Na, K // Cl, NO_3, MoO_4 using the method of partitioning of n-dimensional diagrams of composition systems with complexation based on incidence matrices, graph theory and Boolean algebra [4-6], to identify phase unit blocks (Febov), to confirm the phase tree using the XRD method and thermal analysis of its stable secant triangle.

II. METHODS AND MATERIALS

The studies were carried out using the VPA and DTA methods [8, 9]; in platinum crucibles, the temperature gauge was a Pt-Pt/Rh thermocouple. To record the DTA curves, an installation based on the electronic automatic potentiometer KSP-4 with a voltage amplifier F-116/1 was used. The installation was calibrated according to phase transition temperatures of individual salts and their eutectic mixtures recommended in [9].

The X-ray phase analysis of initial salts and formed compounds was carried out on a DRON-2.0 diffractometer ($Cu_\alpha K$, λ=0.154 nm,

nickel filter) [10]. The samples for X-ray phase analysis were annealed at 150 °C for 60 hours, followed by quenching. The measurement limits made 2.108 imps/sec, time constant – 2, J=15 mA, and =30 kV. Phase compositions were identified according to the Hiller tables [11] and ASTM card files [12]. The accuracy of X-ray phase study made 0.1 wt.%.

Salts of the following classifications were used: "ACS" – KCl, "CP" – $NaNO_3$, "AR" – Na_2MoO_4. All compositions are expressed in mole percent and temperatures – in degrees Celsius.

III. RESULTS

Differentiation of the Na, K // Cl, NO_3, MoO_4 system was carried out on the basis of information on its limiting systems using the geometric and thermodynamic aspects [13].

The analysis of information on fusibility diagrams of the face elements of the system under study showed that: binary in-($NaKMoO_4$ (S_1), $K_5Cl(NO_3)_4$ (S_2)) and congruently melting ($Na_3Cl(MoO_4)$ (D)) formed in Na, K / K // MoO_4, K // Cl, NO_3 and Na // CI, MoO_4, respectively, indicate the presence of complexation processes that must be considered when differentiating (Fig. 1); stable diagonals of the ternary mutual systems Na, K // NO_3, MoO_4, Na, K // Cl, NO_3 and Na, K // Cl, MoO_4 are three pairs of salts KNO_3-Na_2MoO_4, NaCl-KNO_3 and KCl-Na_2MoO_4, respectively, which differentiate the fourfold mutual system Na, K // Cl, NO_3, MoO4 into two tetrahedrons (Fig. 1), for which there are two internal intersecting triangles: Na_2MoO_4-KCl-KNO_3; Na_2MoO_4-NaCl-KNO_3.

Taking the above into account it was revealed that the initial data on the differentiation of face elements entered into the simplified incident matrix (Table 1), where the top rows contain the least connected vertices (components), are characterized by a large number of zeros.

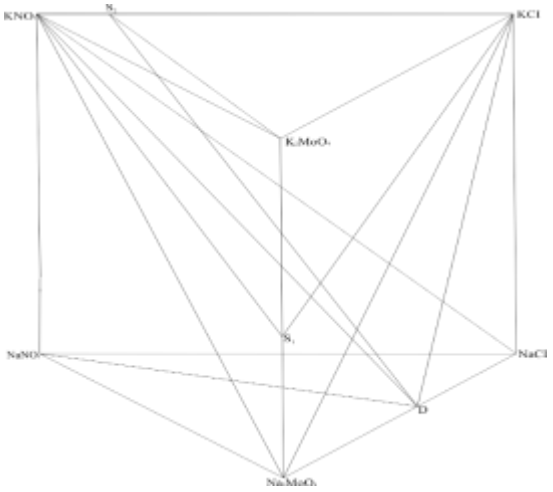

Fig. 1. Prism of compositions of the fourfold mutual system Na, K // Cl, NO_3MoO_4, where: S_1 -$Na_2MoO_4 \cdot K_2MoO_4$; S_2-$K_5Cl(NO_3)_4$; D -Na_3ClMoO_4.

By constructing a rational matrix, the number of factors in the logical equation is reduced. The connection between the vertices in the matrix is indicated as 1, its absence – as 0. On its basis, a logical equation is formed, which is solved by successively multiplying the factors in accordance with the Boolean algebra rules and the laws of absorption [3, 5]. In this case, when solving the equation, the set of graphs (k-n), i.e. phase unit blocks (FUBs), where k – number of vertices of the composition polyhedron, n – component of the system, which indicates internal intersections.

TABLE I. RATIONAL MATRIX OF INCIDENTIONS OF THE SYSTEM Na, K // CI, NO_3, MoO_4

vertices	K_2MoO_4 X_1	NaCl X_4	$NaNO_3$ X_5	S_1 X_8	D X_9	KCl X_3	KNO_3 X_6	S_2 y	$NaNO_3$ X_2
K_2MoO_4		1	1	1	1	1	1	1	0
NaCl			1	1	1	1	1	1	0
$NaNO_3$				1	0	0	1	0	1
S_1					1	0	0	0	1
D						1	0	0	1
KCl							0	1	0
KNO_3								1	0
S_2									0
$NaNO_3$									

Their search was carried out according to the method [4, 13], i.e. from among the bonds designated in the aggregate k-n+1, those relations were revealed, the addition of which to the initial rational matrix will eventually allow the system to be partitioned into Phoebe. For this, a pairwise subtraction of k-n+1 – vertex graphs was carried out, then all two-vertex graphs were written out and the possibilities of their realization were checked, for which they were entered into the original adjacency matrix and the solution was repeated. As a result of the check, two additional internal cutters KNO_3-Na_3ClMoO_4 and $K_6Cl(NO_3)_5$-Na_3ClMoO_4 (Fig. 1) were identified in the system, the feasibility of which was confirmed by XRP. Having wtitten the missing vertices from each graph, we obtained the desired set of stable complexes, i.e. Phoebus of this system. The Phoebus set (tetrahedra), whose stable character is confirmed by XFP, was used to compose the tree of phases (Fig. 2). The tree of phases is characterized as linear, consisting of 10 tetrahedra connected by 9 triangles, in each of which one of the vertices is represented by a binary compound D (Fig. 2).

In literature there is no information on all binary and triple systems that are included in the prism of system compositions. In this study, the phase complex of its stable cutting triangle NaCI-KNO_3-Na_2MoO_4, which according to thermodynamic and geometric aspects, combines two elements of the phase tree (Fig. 1), has been experimentally studied since it includes compound D.

3.1. Thermal analysis of a three-component system NaCl-KNO_3-Na_2MoO_4

The fusibility diagrams of two binary systems (NaCl-Na_2MoO_4, NaCl-KNO_3) included in face elements of the system under study have been studied previously (Table 3). Their phase diagrams are characterized by eutectic and peritectic processes of nonvariant equilibrium, which is caused by the formation of congruent (Na3CI (MoO4) and incongruently melting (NaCl·KNO_3) binary compounds, being cationic and cation-anionic complexes, respectively.

According to the results of thermal analysis, we found that in the KNO_3-Na_2MoO_4 system, only eutectic phase formation processes are implemented (Table 3), therefore, the melting diagram is presented by two crystallization fields belonging to initial components. To construct the liquidus surface of the NaCl-KNO_3-Na_2-MoO_4 system, in the composition triangle reflecting its fusibility diagram, we carried out a thermal analysis of phase-formation processes using ten internal sections (I-X, Fig. 3), based on the results of which the crystallization fields of initial and binary compounds were outlined (NaCl·KNO_3, $Na_3Cln(MoO_4)$). Experimental data on their points of intersection with monovariant lines, obtained by thermal analysis of the compositions of these sections, are shown in Table 4.

TABLE II. ELEMENTS OF DIFFERENTIATION OF FOURFOLD MUTUAL SYSTEM Na, K // Cl, NO_3, MoO_4

Reactive Associations (RA) (metastable complexes)	Phase unit blocks (FUBs)	
	Set of vertices identified by solving a logical equation	*Stable complexes*
$X_1\ X_2\ X_3\ X_4\ X_8$	$X_5\ X_6\ X_7\ X_9$	$NaNO_3$ –KNO_3 –K_2ClNO_3-D
$X_1\ X_2\ X_3\ X_5\ X_8$	$X_4\ X_6\ X_7\ X_9$	NaCl –KNO_3 –K_2ClNO_3- D
$X_1\ X_2\ X_3\ X_7\ X_8$	$X_4\ X_5\ X_6 X_9$	NaCl –KNO_3 –KNO_3-D
$X_1\ X_2\ X_4\ X_5\ X_8$	$X_3\ X_6\ X_7\ X_9$	KCl –KNO_3 –K_2ClNO_3-D
$X_1\ X_2\ X_5\ X_6\ X_8$	$X_3\ X_4\ X_7\ X_9$	KCl –NaCl –K_2ClNO_3-D
$X_1\ X_3\ X_4\ X_5X_8$	$X_2\ X_6\ X_7\ X_9$	Na_2MoO_4 –KNO_3 –K_2ClNO_3-D
$X_1\ X_3\ X_4\ X_7\ X_8$	$X_2\ X_5\ X_6\ X_9$	Na_2MoO_4 –$NaNO_3$ –KNO_3-D
$X_1\ X_3\ X_5\ X_6\ X_8$	$X_2\ X_4\ X_7\ X_9$	Na_2MoO_4 –NaCl –K_2ClNO_3-D
$X_1\ X_3\ X_5\ X_7X_8$	$X_2\ X_4\ X_6\ X_9$	Na_2MoO_4 –NaCl –KNO_3 –D
$X_1\ X_4\ X_5\ X_6\ X_8$	$X_2\ X_3\ X_7\ X_9$	Na_2MoO_4 –KCl –K_2ClNO_3-D

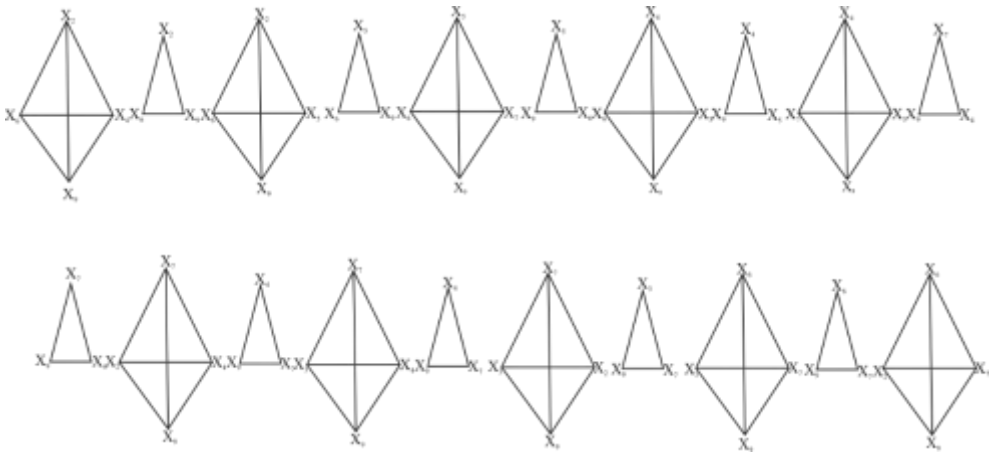

Fig. 2. Phase tree of fourfold mutual system Na, K // Cl, NO_3, MoO_4.

TABLE III. NVP CHARACTERISTICS OF THE NACL -KNO_3-NA_2MOO_4 SYSTEM ESSENTIAL LIMITS

System	*NVP*	*Composition, mol.%**	*t, °C*	*Crystallizing phases*	*References*
NaCl-Na_2MoO_4	e	26	606	Na_2MoO_4, Na_3ClMoO_4)	[13]
	e	48.8-50	624	Na_3ClMoO_4), NaCl	
NaCl-KNO_3	e	12	310	KNO_3, NaCl·KNO_3	[13]
	p	32	390	NaCl·KNO_3, NaCl	
KNO_3-Na_2MoO_4	e	97	312	KNO_3, Na_2MoO_4	Studied by us

* The composition is indicated for the first component of the system in column 1.

TABLE IV. INTERSECTION CHARACTERISTICS OF INTERNAL CUTS OF THE NaCl-KNO_3-Na_2MoO_4 SYSTEM

No.	*Initial composition, mol.%*	*Composition, mol.%*	*t, °C*	*Crystallizing phases*
I	$3Na_2MoO_4$-$97KNO_3$	NaCl		
		4	234	KNO_3, Na_2MoO_4, NaCl·KNO_3
		15	300	Na_3ClMoO_4), NaCl·KNO_3
		21	318	Na_3ClMoO_4), NaCl·KNO_3, NaCl
II	$10Na_2MoO_4$-$90KNO_3$	10	270	Na_2MoO_4, Na_3ClMoO_4)
		25	385	Na_3ClMoO_4), NaCl
III	$20Na_2MoO_4$-$80KNO_3$	12	359	Na_2MoO_4, Na_3ClMoO_4)
		30	460	Na_3ClMoO_4), NaCl
IV	30 Na_2MoO_4-$70KNO_3$	13	439	Na_2MoO_4, Na_3ClMoO_4)
		35	497	Na_3ClMoO_4), NaCl
V	$45Na_2MoO_4$-$55KNO_3$	13	470	Na_2MoO_4, Na_3ClMoO_4)
		37	534	Na_3ClMoO_4), NaCl
VI	$60Na_2MoO_4$-$40KNO_3$	13	500	Na_2MoO_4, Na_3ClMoO_4)
		40	559	Na_3ClMoO_4), NaCl
VII	$75Na_2MoO_4$-$25KNO_3$	14	533	Na_2MoO_4, Na_3ClMoO_4)
		43	590	Na_3ClMoO_4), NaCl
VIII	$90Na_2MoO_4$-$10KNO_3$	23	575	Na_2MoO_4, Na_3ClMoO_4)
		48	606	Na_3ClMoO_4), NaCl
IX	4NaCl-$97KNO_3$	Na_2MoO_4		
		3	234	KNO_3, Na_2MoO_4, NaCl·KNO_3
X	25NaCl-$75KNO_3$	3	318	Na_3ClMoO_4), NaCl·KNO_3
		30	445	Na_2MoO_4, Na_3ClMoO_4)

The projection of the liquidus surface of the system onto the KNO_3-Na_2MoO_4 side revealed that seven lines of monovariant equilibrium are closed at three nonvariant points (NVP), including one eutectic (E (234)) and two peritectic (P (270), P (318)) melting patterns (Fig. 3), compositions and melting points of which are confirmed by the DTA method and are shown in Table 5.

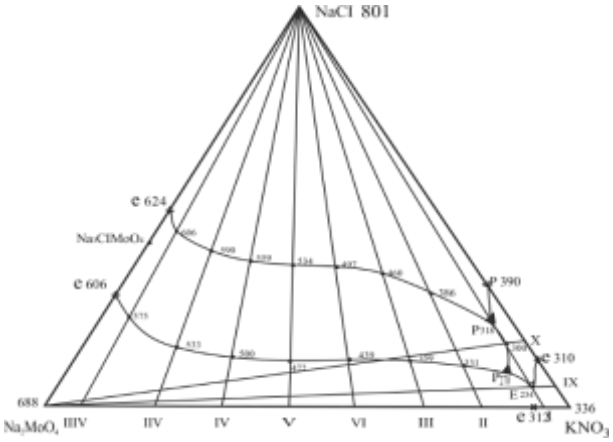

Fig. 3. Diagram of the NaCl-KNO_3-Na_2MoO_4 system composition: where: x → Δ ▲, eutectics and peritectic, implemented in binary and ternary systems; e, p, E, P – designations of double and triple eutectic and peritectic.

TABLE V. NVP CHARACTERISTICS OF THE NaCl-KNO_3-Na_2MoO_4 SYSTEM

System	*NVP*	*t, °C*	*Composition, mol.%*			*Crystallizing phases*
			NaCl	*KNO_3*	*Na_2MoO_4*	
NaCl-KNO_3-Na_2MoO_4	E	234	4	93	3	KNO_3, Na_2MoO_4, NaCl·KNO_3
	P	318	21	76	3	NaCl, Na_3ClMoO_4, NaCl·KNO_3
	P	270	10	85	5	Na_3ClMoO_4, Na_2MoO_4, NaCl·KNO_3

Thus, according to the results of differentiation of the fourfold mutual system Na, K // Cl, NO_3, MoO_4, two internal cross-sections (KNO_3-Na_3ClMoO_4, $K_6Cl(NO_3)_5$-Na_3ClMoO_4) were detected in the polyhedron of the system compositions and ten phase single units (Table 2) were defined, the totality of which is the tree of phases (Fig. 2). Thermal analysis of its secant triangle of the three-component system NaCl-KNO_3-Na_2MoO_4 was carried out, for which an experimental topological model of the phase diagram was designed (Fig. 3) and the nature, composition and temperature of nonvariant points (NVP) were determined (Table 5).

The results of the study may be used to develop medium-temperature phase transition heat accumulating materials, as well as melts – electrolytes for electrochemical processes [2, 15].

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