ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2018, Vol. 63, No. 5, pp. 675–681. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © E.M. Egorova, E.O. Ignat'eva, I.K. Garkushin, I.M. Kondratyuk, 2018, published in Zhurnal Neorganicheskoi Khimii, 2018, Vol. 63, No. 5, pp. 645–649.

PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Phase Equilibria of Three-Component Reciprocal System Na,K||I,MoO_4

E. M. Egorova*, E. O. Ignat'eva, I. K. Garkushin, and I. M. Kondratyuk

Samara State Technical University, Samara, 443100 Russia

**e-mail: dvoryanova_kat@mail.ru*

Received December 5, 2016

Abstract—The three-component reciprocal system Na,K||I,MoO_4 has been studied by differential thermal analysis (DTA). The compositions and melting temperatures have been determined, and the enthalpies of melting of eutectic mixtures measured. Phase equilibria in the system are described, and phase fields are demarcated.

DOI: 10.1134/S0036023618050194

Studies into phase equilibria and a search for invariant compositions in multicomponent salt systems are topical problems of contemporary materials science. The compositions corresponding to invariant equilibrium points are used as fusible electrolytes for chemical current sources and heat-accumulating materials [1, 2]. Halide systems involving oxygen-containing salts of s^1 elements, in particular, molybdates, are poorly studied as yet. The primary reason behind this is the complexity of experimental data interpretation due to numerous polymorphic transitions in sodium and potassium molybdates. On the other hand, the superposition of the thermal effects of polymorphic and eutectic transitions makes it possible to obtain a heat-accumulating material having a high value of the enthalpy of phase transition [3, 4]. Referring to foreign sources shows that the studies into salt mixtures are mainly directed to the theoretical calculations of thermodynamic, physical, and thermophysical characteristics without comprehensive studies of phase diagrams [5, 6]. Thus, an experimental investigation of halide systems involving s^1-element molybdates is very topical.

We have studied three-component reciprocal system Na,K||I,MoO_4 in order to elucidate the phase complex and to determine the alloy compositions corresponding to invariant equilibrium points. The experimental tool was differential thermal analysis (DTA) carried out on a standard design setup [7–9]. The initial reagents, which were of chemically pure grade (NaI and KI) or pure for analysis grade (Na_2MoO_4 and K_2MoO_4) were pre-dehydrated. The melting points of the reagents matched reference values [10, 11]. Platinum microcrucibles were used in experiments. The reference used was a freshly calcined Al_2O_3 sample. The sample size was 0.3 g. The compositions are expressed in equivalent percent.

The composition square of the three-component reciprocal system Na,K||I,MoO_4 is shown in Fig. 1. The two-component boundary systems were studied elsewhere: NaI–KI [12], Na_2MoO_4–K_2MoO_4 [13], NaI–Na_2MoO_4 [14], and KI–K_2MoO_4 [15]. Two of these two-component boundary binaries are eutectic melting systems. In system NaI–KI there is formed a continuous solid solution series with a minimum. System Na_2MoO_4–K_2MoO_4 is distinguished by the formation of incongruently melting compound D ($Na_2MoO_4 \cdot K_2MoO_4$), which influences the partition of the composition figure of the reciprocal system and its liquidus configuration.

For verifying the theoretical partition of the system, we experimentally studied diagonal section KI–Na_2MoO_4, whose T–x diagram is shown in Fig. 2. The composition and melting temperature of the quasi-binary eutectic were determined to be e_4 518°C, 35% KI and 65% Na_2MoO_4.

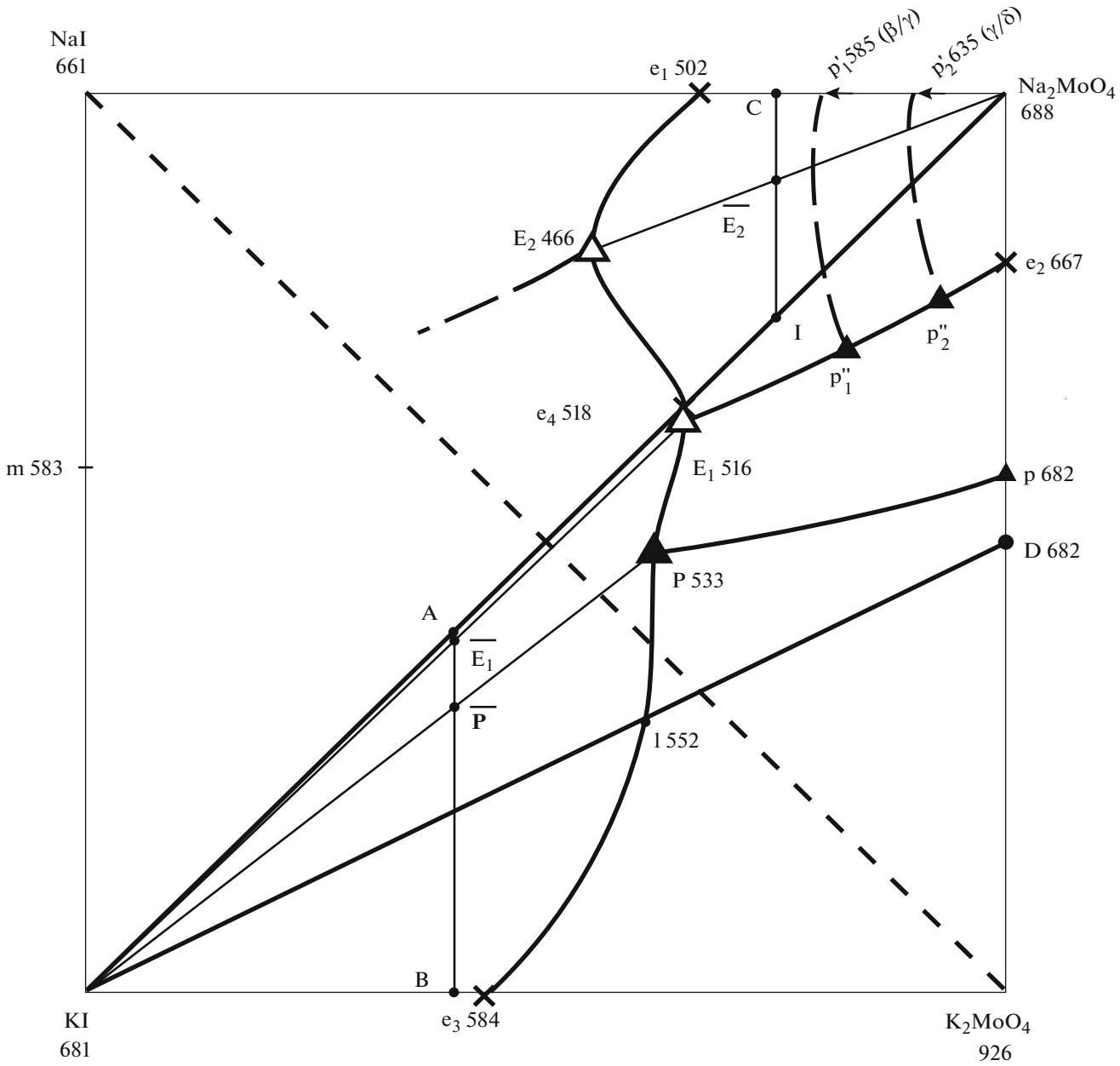

Fig. 1. Three-component reciprocal system Na,K‖I,MoO_4.

We studied non-quasi-binary section KI–D. From its *T*–*x* diagram, we found the parameters of the intersection point with a monovariant line: 552°C, 39.0% KI, 30.5% Na_2MoO_4, 30.5% K_2MoO_4. These sections are triangulating, and the composition square is partitioned into three phase triangles, namely, KI–NaI–Na_2MoO_4, KI–Na_2MoO_4–D, and KI–D–K_2MoO_4.

For constructing the liquidus of the system, we experimentally studied *T*–*x* diagrams of vertical sections AB, where A = [60% KI + 40% Na_2MoO_4] and B = [60% KI + 40% K_2MoO_4] (Fig. 3), and CI, where C = [75% Na_2MoO_4 + 25% NaI] and I = [75% Na_2MoO_4 + 25% KI] (Fig. 4), lying in different simplexes of the system.

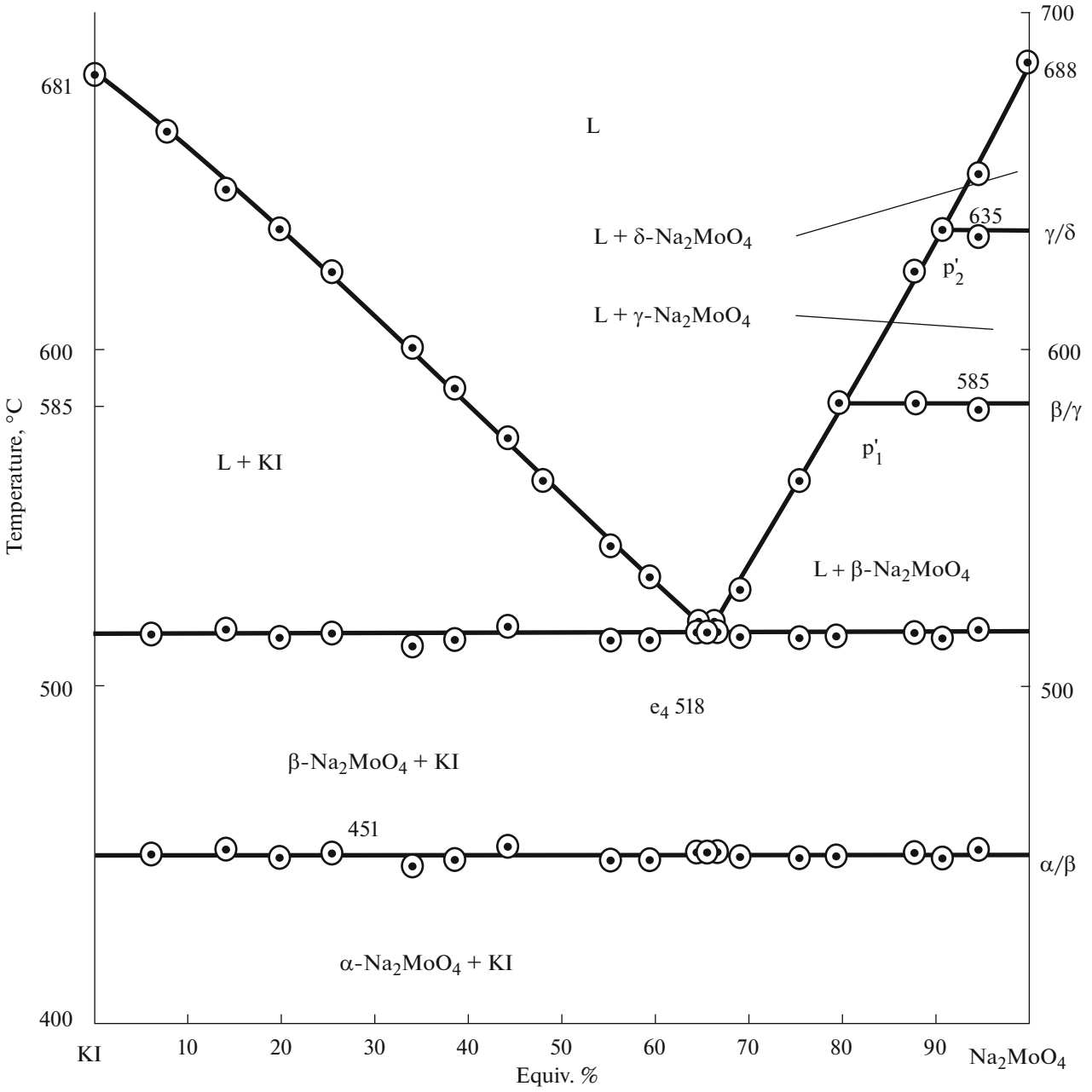

Fig. 2. *T*–*x* diagram of diagonal section KI–Na_2MoO_4 of system Na,K‖I,MoO_4.

Section AB lies in the potassium iodide field, so its onset crystallization curve corresponds to the liquidus line. The KI + Na_2MoO_4 and KI + K_2MoO_4 secondary crystallization lines meet the eutectic line at point $\overline{E}_1$ and meet the peritectic line at point P, these points being central projections on ternary eutectic E_1 516 and ternary peritectic P 533, respectively, from the potassium iodide crystallization pole. Studying vertical sections KI → $\overline{E}_1 \rightarrow E_1$ and KI → P → P (Figs. 5, 6), we determined the characteristics of the alloys corresponding to the ternary eutectic and ternary peritectic: E_1 516 with component concentrations of 35% KI, 64% Na_2MoO_4, 1%

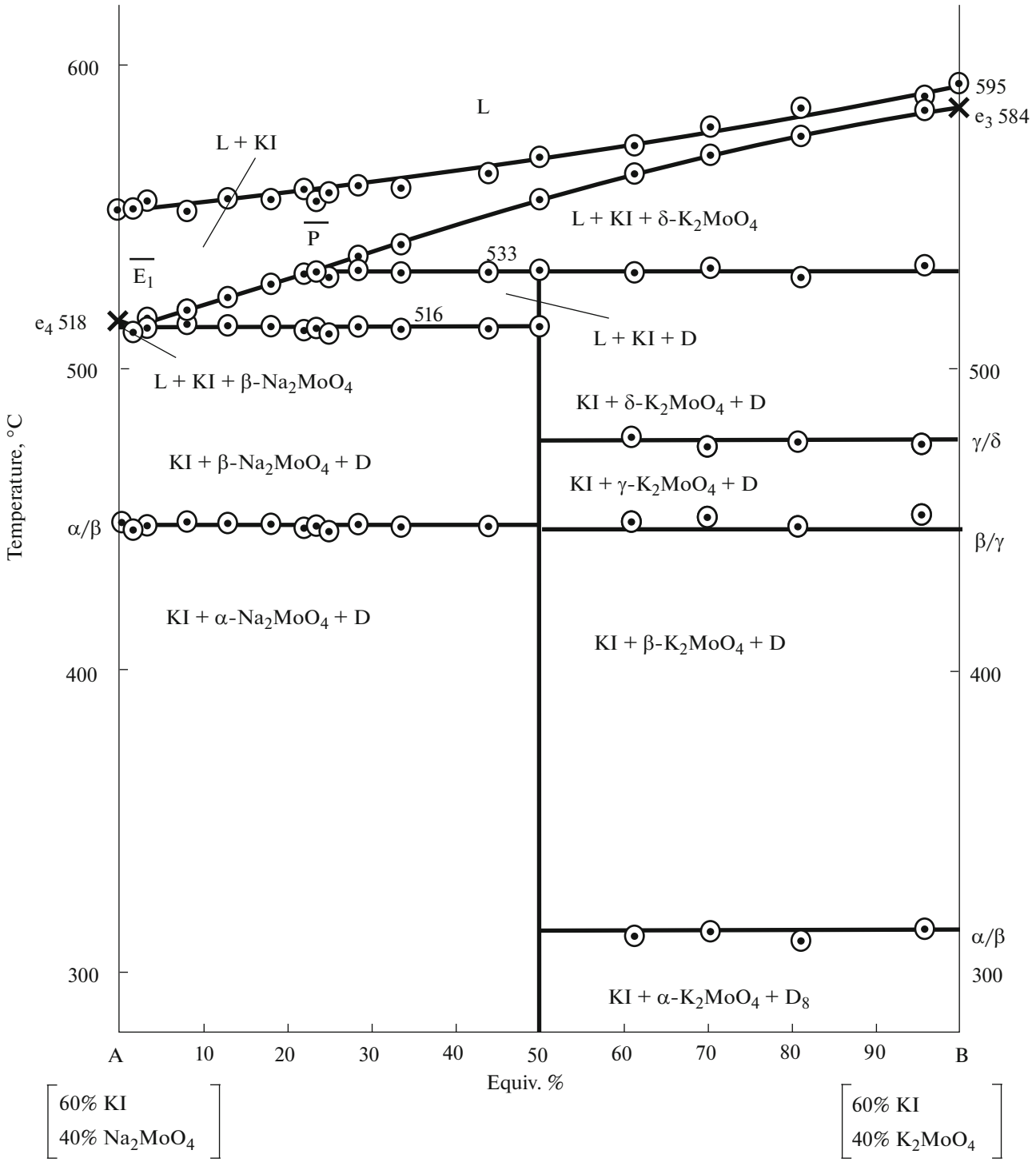

Fig. 3. *T*–*x* diagram of section *AB* of system Na,K‖I,MoO_4.

K_2MoO_4; and P 533 with component concentrations of 37% KI, 48% Na_2MoO_4, 15% K_2MoO_4.

In the same manner, we studied section CI in the sodium molybdate field to determine the melting temperature and direction to three-component eutectic $\overline{E}_2$ 466. The eutectic composition was elucidated from the study of section KI → $\overline{E}_2$ → E_2 (Fig. 7) to be 28% NaI, 17% KI, 55% Na_2MoO_4.

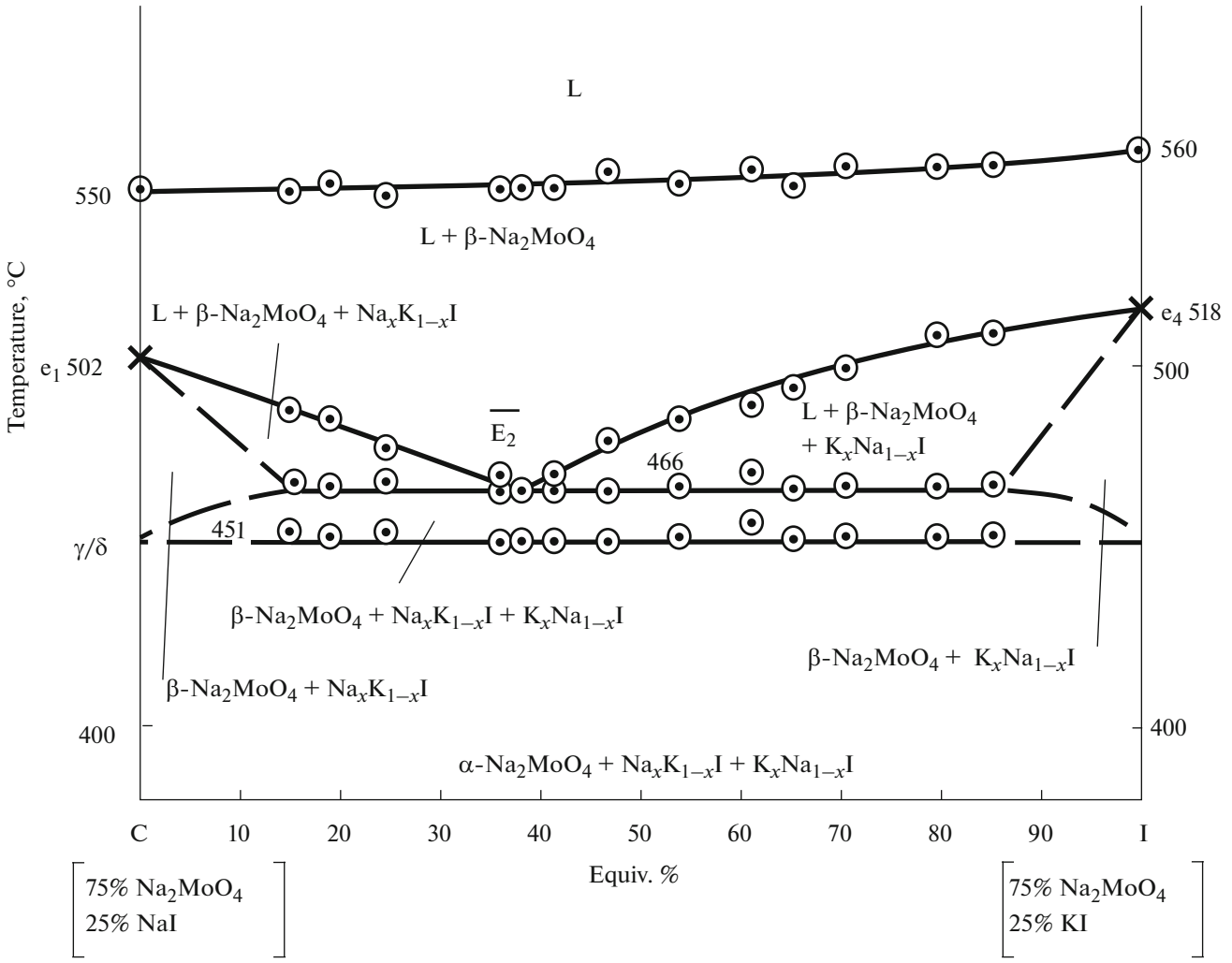

Fig. 4. *T–x* diagram of section CI of system Na,K‖I, MoO_4.

In summary, the liquidus projection of system Na,K‖I,MoO_4 is represented by six crystallization fields, which belong to potassium molybdate; solid solutions based on sodium and potassium iodides, which decompose to yield a three-component eutectic; compound D; and α-, β-, and γ-sodium molybdate phases (Table 1). Monovariant lines meet two ternary eutectics, one ternary peritectic, and two peritectics that correspond to the polymorphic transitions in sodium molybdate.

Table 1. Phase equilibria in system Na,K‖I,MoO_4

Element of diagram	Phase equilibrium	Equilibrium
Eutectic E_1	$L \rightleftarrows \gamma\text{-}Na_2MoO_4 + KI + D$	Invariant
Peritectic P	$L + \alpha\text{-}K_2MoO_4 \rightleftarrows KI + D$	Invariant
Eutectic E_2	$L \rightleftarrows \gamma\text{-}Na_2MoO_4 + Na_xK_{1-x}I + K_xNa_{1-x}I$	Invariant

ACKNOWLEDGMENTS

This study was performed in the frame of the basic part of State task to Samara State Technical University (project no. 4.5534.2017/8.9).

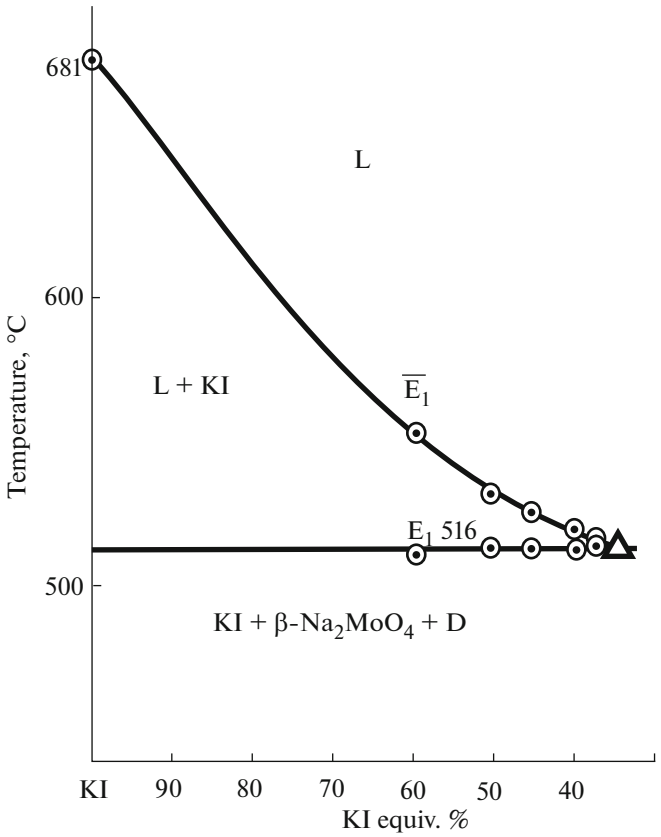

Fig. 5. *T*–*x* diagram of section KI → $\overline{E}_1$ → E_1 of system Na,K‖I,MoO_4.

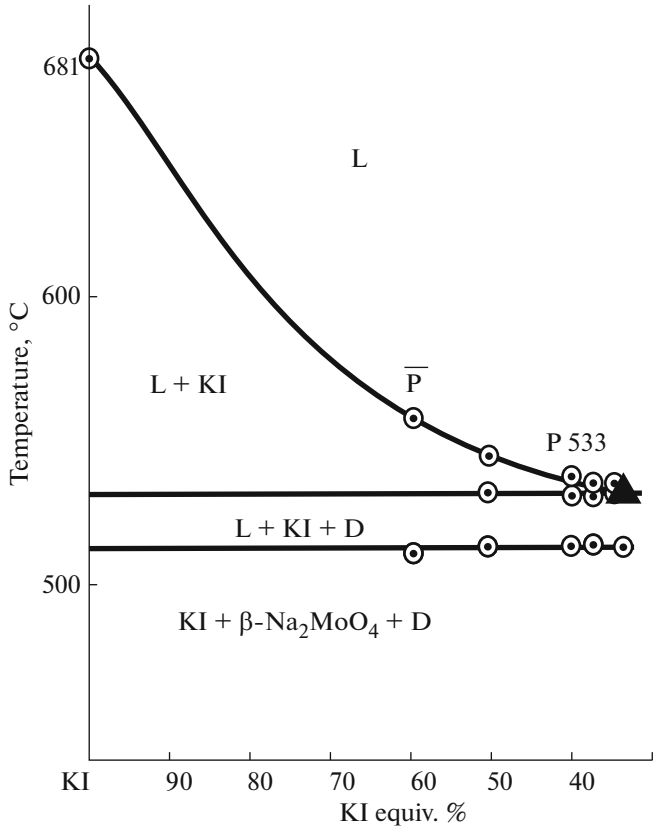

Fig. 6. *T*–*x* diagram of section KI → $\overline{P}$ → P of system Na,K‖I,MoO_4.

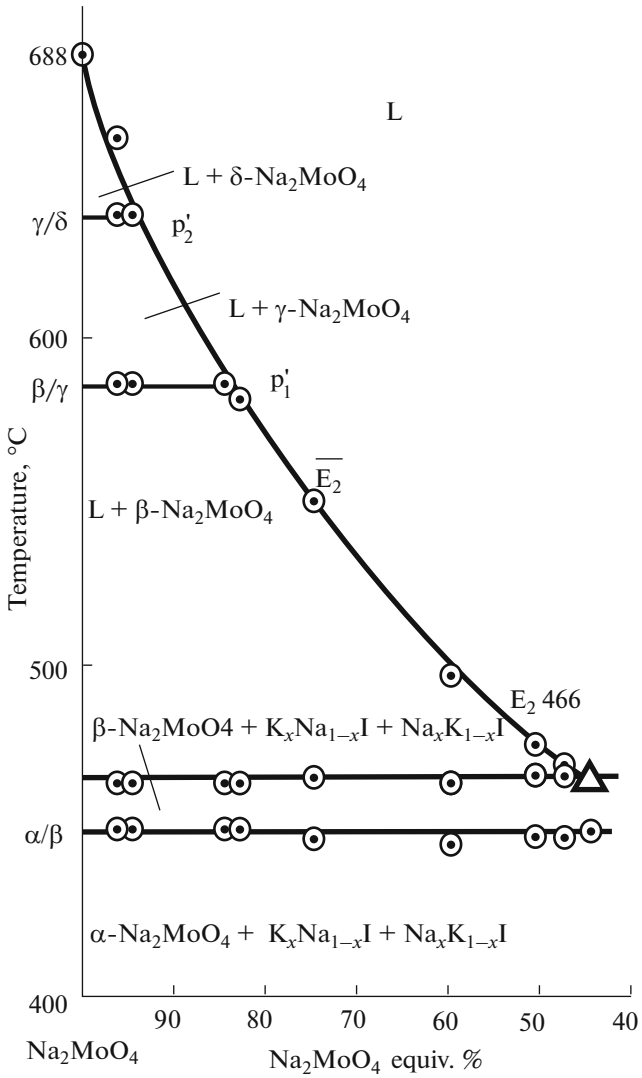

Fig. 7. T–x diagram of section KI → $\overline{E}_2$ → E_2 of system Na,K‖I,MoO_4.

REFERENCES

1. I. K. Garkushin, T. V. Gubanova, E. I. Frolov, et al., Russ. J. Inorg. Chem. **60**, 324 (2015).
2. I. K. Garkushin, G. E. Egortsev, and M. A. Istomova, Elektrokhim. En. **9**, 95 (2009).
3. I. K. Garkushin, E. O. Ignat'eva, and E. M. Dvoryanova, RF Patent No. 2011141995, Byull. Izobret., No. 9 (2013).
4. I. K. Garkushin, E. O. Ignat'eva, and E. M. Dvoryanova, RF Patent No. 2011143547, Byull. Izobret., No. 29 (2013).
5. G. Wallez, Ph. Raison, A. Smith, et al., J. Solid State Chem., No. 215, 225 (2014).
6. Y. Ding, N. Hou, N. Chen, et al., Rare Metals **25**, 316 (2006).
7. W. Wendlandt, *Thermal Methods of Analysis* (Wiley, New York, 1974; Mir, Moscow, 1978).
8. L. G. Breg, *Introduction to Thermal Analysis*, 2nd ed. (Nauka, Moscow, 1969) [in Russian].
9. V. P. Egunov, *Introduction to Thermal Analysis* (Samara, 1996) [in Russian].
10. *Thermal Constants of Materials. Handbook*, Ed. by V. P. Glushko (VINITI, Moscow, 1981), Iss. X, Pt 1 [in Russian].
11. *Thermal Constants of Materials. Handbook*, Ed. by V. P. Glushko (VINITI, Moscow, 1981), Iss. X, Pt. 2 [in Russian].
12. V. I. Posypaiko, *Melting Diagrams of Salt Systems*, Part III: *Binary Systems with a Common Cation* (Metallurgiya, Moscow, 1979) [in Russian].
13. V. I. Posypaiko and E. A. Alekseeva, *Melting Diagrams of Salt Systems*, Part II: *Binary Systems with a Common Anion* (Metallurgiya, Moscow, 1977) [in Russian].
14. E. O. Ignat'eva, E. M. Dvoryanova, I. K. Garkushin, and I. M. Kondratyuk, Vestn. Gos. Tekhn. Univ. **57** (10), 153 (2011).
15. E. O. Ignat'eva, E. M. Dvoryanova, and I. K. Garkushin, Vektor Nauki Tol'yattinsk. Gos. Univ., No. 2 (16), 28 (2011).

Translated by O. Fedorova