Interpretation of Phase Diagrams of Ternary Reciprocal Systems by Complete Conversion Points

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A new classification of ternary reciprocal systems is proposed taking into account the number of thermal effects in the thermograms of complete conversion points. The classification is useful for general evaluation of the liquid surface of the systems.

Phase diagram construction requires much expenditure of labor, material, and time, so current research efforts are directed toward the minimization of experimental work. At present, there are two main directions of effort: thermodynamic calculations of phase diagram ([1970Kau], [1985Com], [1981Lup], [1992Pel]) and semiempirical approaches, which include analysis of the most informative points in the phase diagram. The latter allow prognosis of liquidus surface features and require limited experimental study of a few samples to confirm the prognosis results ([1984Pro], [1995Roz]).

It is most convenient to start consideration of a ternary reciprocal system in the context of the semiempirical approach, with the thermogram record of a point of complete conversion (PCC), which is the intersection point of stable and metastable diagonals in the composition square ([1964Rad], [1978Pos]). This article aims to show the information content of a PCC, which allows a theoretically substantiated prognosis of phase diagrams. For this purpose, a classification of ternary reciprocal systems based on the number of thermal effects in the thermograms of complete conversion points is developed.

It has been shown by [1984Pro] and [1978Pos] that examination of the points of complete conversion enables one to solve the following problems connected with the construction of phase diagrams of ternary reciprocal systems:

- determination of the salt pair stability,
- determination of the phase that occupies the largest field on the crystallization surface,
- determination of the primary reaction (the exchange reaction or the reaction of complex formation) in the case when a double salt appears in the system,
- determination of the maximum work of the exchange reaction [1994Gry], and
- determination of the ternary eutectic temperature.

The solution of the problems listed at the initial consideration of a ternary reciprocal system can greatly reduce expenditure of time and necessary experimental measurement. This allows a rational choice of the areas of the phase diagram for more detailed research and to reduce the requisite number of compositions to be experimentally studied.

The most complete information on the PCC can be obtained using differential thermal analysis, zone melting, high-temperature x-ray analysis, investigation of microstructure, and chemical analysis.

Depending on the chemical reciprocal interaction in the system, the PCC thermograms can show several thermal effects. One can single out the following types (Table 1).

1. Two Effects in the PCC Thermogram

1.1 Irreversible reciprocal systems (in binary restricting systems, there are neither congruently melting compounds nor unlimited solid solutions).

1.2 Reversible reciprocal systems (combination of unlimited solid solutions on the opposite sides of the composition square and simple eutectic systems on the two other sides of the square).

1.3 Reversible reciprocal systems (limited solid solutions in the binary subsystems). There are no lines of joint crystallization in their liquidus surface.

2. Three Effects in the PCC Thermogram

2.1 Irreversible reciprocal systems with one compound (double salt), exhibiting congruent fusion, on the lateral side of the composition square. The exchange reaction is primary and the reaction of compound formation is secondary.

2.2 Adiagonal systems with a stable congruently melting compound in one of the binary subsystems (on the lateral side of the composition square). The reaction of compound formation is as significant as the exchange reaction.

3. Four Effects in the PCC Thermogram

3.1 Reversible reciprocal systems with compounds appearing on the adjoining sides of the composition square.

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Table 1 Classification of ternary reciprocal salt systems

No.	System type	Examples
1.1	Irreversible reciprocal system without compounds and solid solutions	Na,K//F,Cl; Na,Ba//F,MoO_4; Na,Ba//F,WO_4
1.2	Reversible reciprocal system with unlimited solid solutions in two binary subsystems and eutectics in two other ones	Na,Ba//MoO_4,WO_4
1.3	Reversible reciprocal system with unlimited solid solutions	Na,K//Br,Cl
2.1	Irreversible reciprocal system with one congruently melting compound	Na,K//F,WO_4; Na,K//F,MoO_4; Na,Ba//F,WO_4
2.2	Adiagonal system with one stable compound of congruent fusion having large area in the liquidus surface	Na,K//Cl,WO_4
3.1	(a) Reversible reciprocal system with two compounds in the adjoining binary subsystems and without unlimited solid solutions	K,Ba//F,MoO_4; K,Ba//F,WO_4
	(b) Reversible reciprocal system with two incongruent melting compounds in binary subsystems on the opposite sides of the composition square forming unlimited solid solutions	K,Ba//MoO_4,WO_4; Na,K//MoO_4,WO_4
3.2	Reversible reciprocal system with two incongruent melting compounds and unlimited solid solutions	Na,K//MoO_4,WO_4

3.2 Systems with two congruently melting compounds on the lateral sides and unlimited solid solutions that are stable inside the system.

The first thermal effect corresponds to precipitation of primary crystals of the phase, which crystallizes at the PCC; the second one corresponds to the crystallization of two phases being formed as a result of the exchange reaction or the reaction of complex formation (depending on the type of the ternary reciprocal system); the third effect represents the peritectic process with participation of the two previous phases and an incongruent melting compound; and, finally, the fourth one corresponds to crystallization of the ternary eutectic formed by the two products of the exchange or when the complexing reactions and the congruently melting compound are crystallized (depending on the nature of the binary subsystems). The interpretation of the first thermal effect is carried out with the help of one above-mentioned experimental methods. The other effects are interpreted on the basis of the information from the binary subsystems.

Examples of the ternary reciprocal systems that belong to the different types given in the above classification are as follows.

The Na,Ba//F,WO_4 System (Fig. 1a) [1980Pos]. The PCC thermogram reveals two effects. The first at 753 °C is connected with the appearance of the first crystals of $BaWO_4$ (this means that the PCC is situated in the field of crystallization of $BaWO_4$). The second at 740 °C accounts for joint crystallization of $BaWO_4$ and NaF, which are products of the exchange reaction:

$$BaF_2 + Na_2WO_4 = BaWO_4 + 2NaF$$

The K,Na//F,WO_4 system [1978Pos]. This system is characterized by formation of the $KF \cdot K_2WO_4$ complex. The following thermal effects can be seen in the PCC thermogram (Fig. 1b). The first, at 773 °C, corresponds to crystallization of NaF. The second, at 680 °C, describes the joint crystallization of NaF and K_2WO_4. It coincides with the temperature of the staging point on the stable diagonal NaF-K_2WO_4. The third thermal effect at 664 °C corresponds to the ternary eutectic reaction, which leads to simultaneous crystallizing of the products of the exchange reaction, NaF and K_2WO_4, and the congruently melting complex $KF \cdot K_2WO_4$ (Fig. 1b).

The thermal effects indicate that two competitive reactions occur in the system:

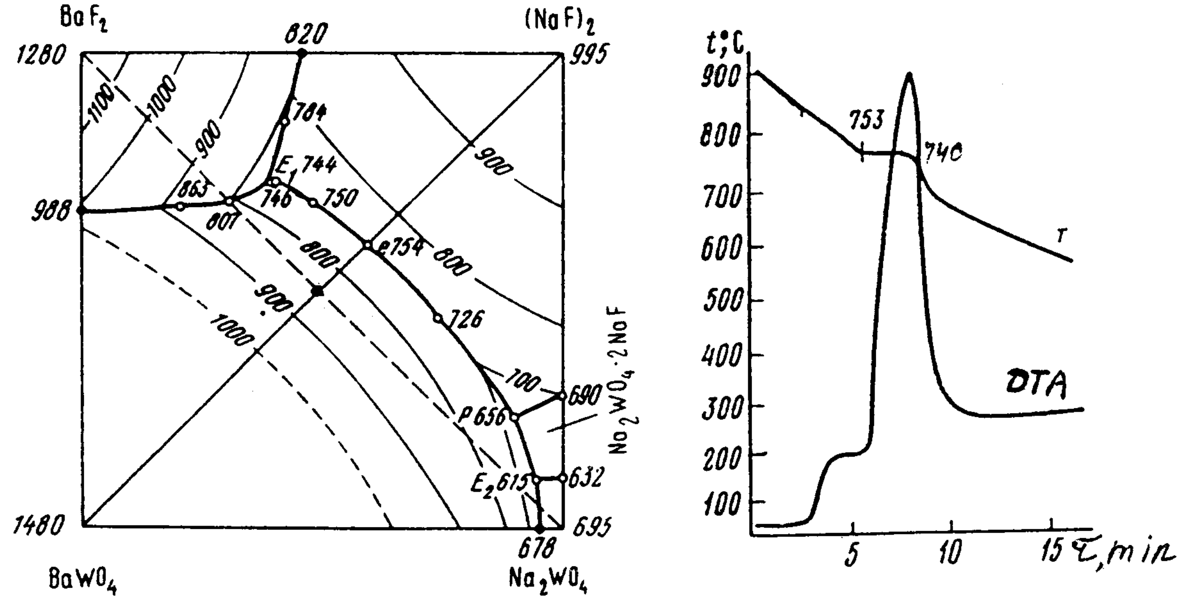
$$2KF + Na_2WO_4 = 2NaF + K_2WO_4$$

$$3KF + Na_2WO_4 = 2NaF + KF \cdot K_2WO_4$$

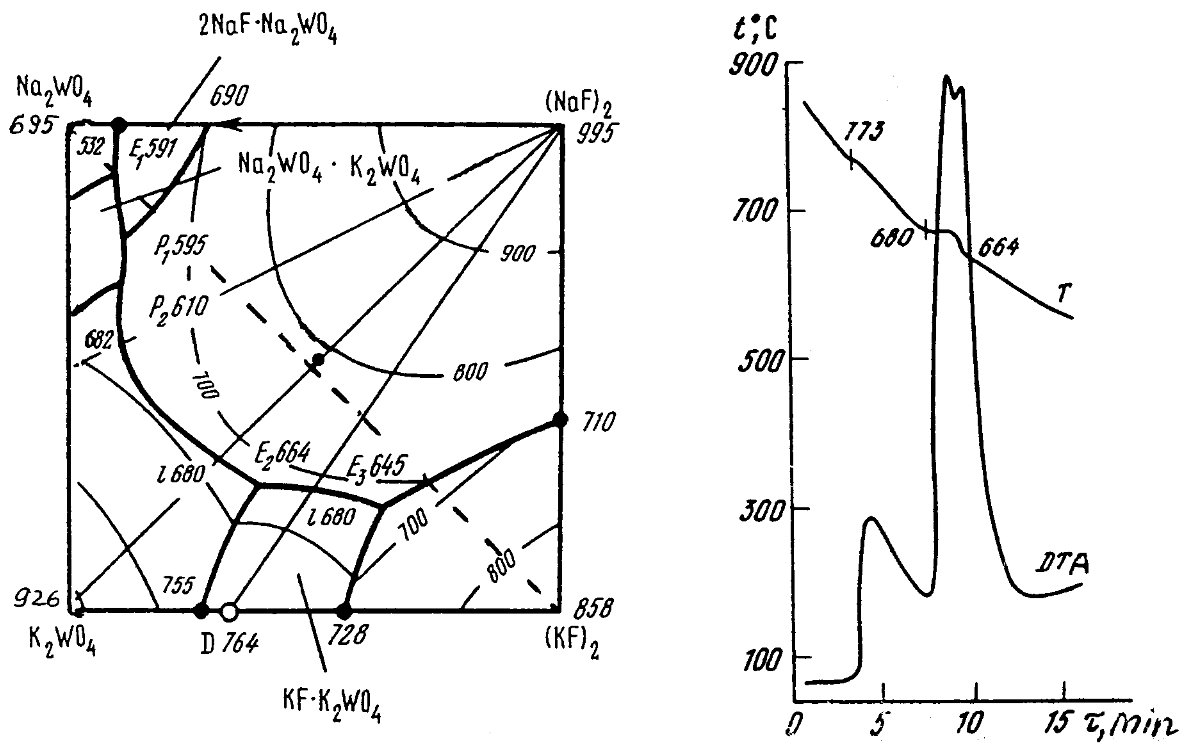
This brings up the question, which of these two reactions is primary? According to [1976Pos], the exchange reaction is primary, while the complexing reaction is secondary and does not take place at the stoichiometric ratio of the metastable salt pair. Thus, the system under consideration is an irreversible reciprocal system.

The K,Ba//MoO_4,WO_4 System [1975Pos]. Two binary constituent subsystems situated on the opposite sides of the composition square of this ternary reciprocal system are characterized by formation of limited solid solutions. Two thermal effects are observed in the thermogram of the PCC. The first, at 1140 °C, corresponds to the crystallization of the solid solutions $BaMoO_4$-$BaWO_4$ (Fig. 1c, phase b). The second, at 1067 °C, describes crystallization of two solid solutions: $BaMoO_4$-$BaWO_4$ and $K_2MoO_4 \cdot BaMoO_4$-$K_2WO_4 \cdot BaWO_4$ (phase n) The latter is a point on the multivariant curve that separates the b and n phases. Thus, the system K,Ba//MoO_4,WO_4 belongs to the ternary reciprocal systems with stable limited solid solutions in the binary subsystems and characterized by the occurrence of two thermal effects in the PCC thermogram, which corresponds to the crystallization of solid solutions only (Fig. 1c).

The Ba,K//F,WO_4 system (Fig. 1d) [1981Pos]. Four thermal effects are registered in the thermogram of the complete conversion point. The order of crystallization of the phases is as follows. (1) BaF_2 precipitates at 839 °C (this conclusion can be drawn from comparison of the temperature of the thermal effect with data for the liquidus of the diagonal BaF_2-K_2WO_4 and of binary restricting subsystems). (2) Joint crystallization of BaF_2 and highly stable incongruent melting compound $K_2WO_4 \cdot BaWO_4$ at 790 °C, the latter appearing through peritectic reaction. (3) Crystallization of three phases: BaF_2, K_2WO_4, and $K_2WO_4 \cdot BaWO_4$ at 724 °C. (4)



(a)



(b)

Fig. 1 Phase diagrams and thermograms of the points of complete conversion of ternary reciprocal systems: (**a**) Na,Ba//F,WO_4, (**b**) Na,K//F,WO_4, (**c**) K,Ba//MoO_4,WO_4; and (**d**) K,Ba//F,WO_4 (continued on next page)

Eutectic decomposition of the liquid to three phases: BaF_2, $KF \cdot K_2WO_4$, and K_2WO_4 at 701 °C.

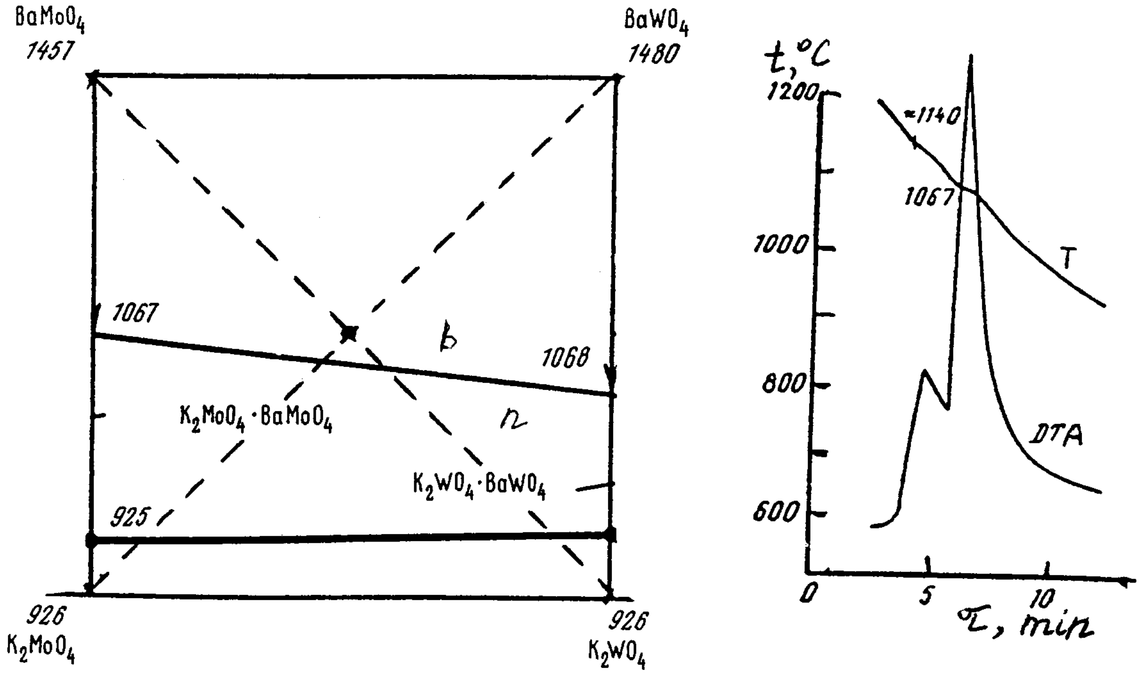
Therefore, the system under consideration is a reversible reciprocal system with a complex on the two adjoining sides. Three reactions take place in this type of ternary reciprocal system: one is the mutual exchange, and the two others lead to formation of complexes:

$$2KF + BaWO_4 = BaF_2 + K_2WO_4$$

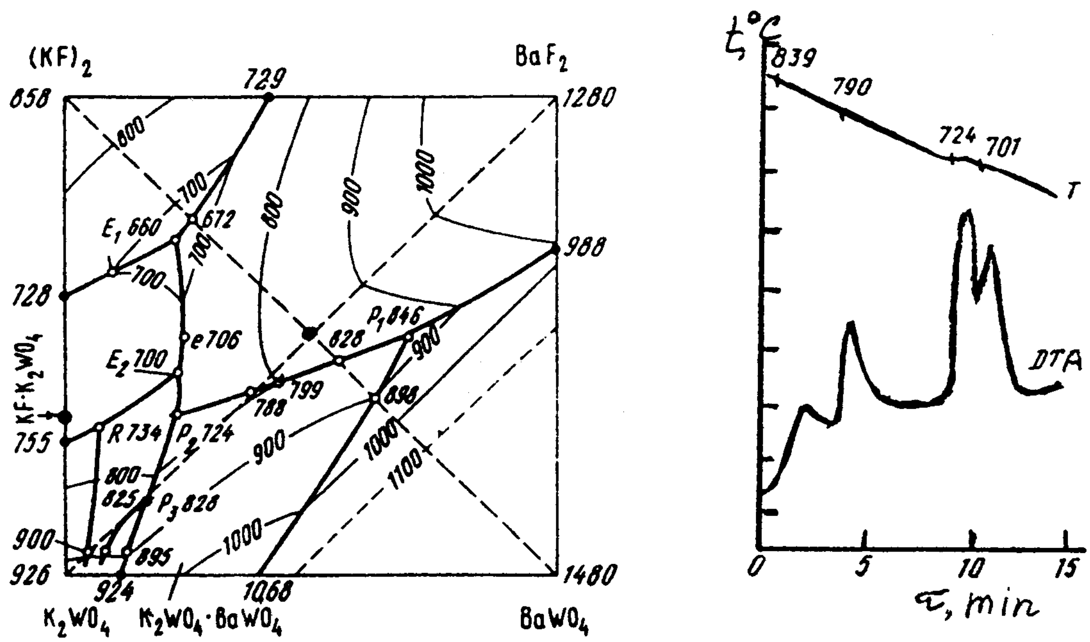
$$3(KF)_2 + 2BaWO_4 = 2BaF_2 + 2(KF \cdot K_2WO_4)$$

$$2KF + 2BaWO_4 = BaF_2 + (K_2WO_4 \cdot BaWO_4)$$

It has been established that there are other systems of the



(c)



(d)

Fig. 1 Continued. Phase diagrams and thermograms of the points of complete conversion of ternary reciprocal systems: (**c**) K,Ba//MoO_4,WO_4; and (**d**) K,Ba//F,WO_4

M_1,M_2//MoO_4,WO_4 (M = Na, K, Ba) type where binary continuous solid solutions are stable inside the ternary reciprocal systems and no ternary invariant points exist. If, as in the case discussed here, continuous solid solubility occur in two opposite binary constituents while the other two are simple eutectic systems, two thermal effects should be observed on PCC thermograms. They correspond to the number of phases crystallizing on the liquidus surface of the system. Additional thermoeffects can appear only if several solid solutions form in the system.

If, instead of simple eutectics, incongruent melting compounds form, the number of thermal effects should be one less than the number of phases crystallizing, that is, three.

In conclusion, we should emphasize that the classification described above, with the help of x-ray analysis when it is necessary, enables one to interpret thermal effects found in the PCC thermogram. It allows determination of the order of crystallization at the conversion points. It also helps in consideration of the nature of the chemical interaction and in prediction of the liquidus surface.

References

1970Kau: L. Kaufman and H. Bernstein: *Computer Calculation of Phase Diagram*, Academic Press, New York, NY, 1970.

1985Com: *Proc. Symp. Sponsored by the Alloy Phase Diagram Data Committee of the Materials Science Division of the American Society for Metals,* Fall Meeting of TMS, Toronto, Canada, Oct. 13–17, 1985.

1981Lup: T.G. Lupeiko: *Analiz Solevykh Sistem* (Salt System Analysis), Rostov-Don, Rostov Gos. University, 1981 (in Russian).

1992Pel: A.D. Pelton, P.K. Talley, and R.A. Sharma: *J. Phase Equilibrium,* 1992, vol. 13 (4), pp. 384-96.

1984Pro: *Prognozirovanie Khimicheskogo Vzaimodejstviya v Sistemakh iz Mnogikh Komponentov* (Prediction of Chemical Interaction in Multicomponent Systems), Nauka, Moscow, 1984 (in Russian).

1995Roz: A.E. Rozhanskaya: Ph.D. Thesis, Samara, 1995.

1964Rad: V.P. Radishchev: *Mnogokomponentnye Sistemy* (Multicomponent Systems), Moscow, Izd. AN SSSR, 1964 (in Russian).

1978Pos: V.I. Posypaiko, N.A. Vasina, E.S. Gryzlova, A.S. Trunin, and G.E. Shter: *Dokl. Akad. Nauk SSSR*, 1978, vol. 241, pp. 650-3 (*Dokl. Chem. Technol.*, English translation).

1994Gry: E.S.Gryzlova, N.A. Kozyreva and B.F. Myasoedov: *Mendeleev Comm.*, 1994, Nov., No. 6, pp. 228-30.

1980Pos: V.I. Posypaiko, G.E. Shter, A.S. Trunin, N.A. Vasina, and E.S. Gryzlova: *Fizikokhimia Ionnykh Rasplavov i Tverdykh Electrolitov (Physical Chemistry of Ionic Melts and Solid Electrolytes),* Naukova Dumka, Kiev, 1980, pp. 72-82 (in Russian).

1976Pos: V.I. Posypaiko, N.A. Vasina, and I.G. Popova: *Dokl. Akad. Nauk SSSR*, 1976, vol. 226, pp. 102-04 (*Dokl. Chem. Technol.*, English translation).

1981Pos: V.I. Posypaiko, G.E. Shter, A.S. Trunin, E.S. Gryzlova, and N.A. Vasina: *Ukr. Khim. Zh.,* 1981, vol. 47, pp. 46-50 (in Russian).

1975Pos: V.I. Posypaiko, A.S. Trunin, and G.E. Shter: *Zh. Neorg. Khim.*, 1975, vol. 27, pp. 1664-66 (*J. Inorg. Chem. USSR*, English translation).