

Miscibility Gaps in Fused Salts

Note V. Systems of Silver Halides with Alkali Chromates and Tungstates *

GIORGIO FLOR and CESARE SINISTRI

Institute of Physical Chemistry, University of Pavia, Italy

(Z. Naturforsch. **25 a**, 1484—1489 [1970]; received 19 June 1970)

The two families of systems formed by silver halides with alkali chromates and tungstates have been systematically investigated in order to bring into evidence possible demixing phenomena. It has been found that silver chloride demixes with lithium chromate and tungstate and with sodium tungstate; silver bromide demixes with lithium and sodium chromates and tungstates; silver iodide demixes with lithium, sodium and potassium chromates and tungstates. Moreover the whole composition square of the ternary reciprocal system Ag, Na/Cl, WO₄ has been investigated.

The tendency to demix in these systems has been discussed on the basis of the characteristics of the ions.

In a previous work ¹ of this series the miscibility gaps (MG) in molten mixtures formed by silver halides with alkali molybdates have been investigated. In order to obtain a more general picture, demixing phenomena have been systematically studied in the two families of molten systems formed by silver halides with alkali chromates and tungstates.

In particular the mixtures AgX + Me₂CrO₄ (Me = alkali cations; X = Cl, Br, I) and AgX + Me₂WO₄ have been analyzed. These systems are the stable diagonals of the corresponding reciprocal ternary Ag, Me/X, YO₄ (Y = Cr, W). For the AgCl + Na₂WO₄ system, research has also been extended to the whole composition square.

Notice on the presence of MG in some of these systems has been reported by BELYAEV ²; LESNYKH and BERGMAN ³ instead give extensive measurements on the reciprocal ternary systems Ag, Li/Cl, YO₄ (Y = Cr, W). This whole information has been summarized in an Atlas ⁴ that reports all the data available in literature regarding demixing phenomena in molten salts.

Apparatus and Materials

The employed apparatus and some experimental features have already been described ^{1, 5}.

Reprints request to Prof. CESARE SINISTRI, Istituto di Chimica Fisica, Università di Pavia, I-27 100 Pavia, Italien.

* Work carried out with the financial aid of the CNR (Rome).

¹ C. SINISTRI, G. FLOR, and P. FERLONI, Z. Naturforsch. **23 a**, 2073 [1968].

² I. N. BELYAEV, Zh. Neorg. Khim. **3**, 2805 [1958].

³ a) D. S. LESNYKH and A. G. BERGMAN, Zh. Fiz. Khim. **30**, 1959 [1956]; b) idem, J. Gen. Chem. USSR **26**, 1749 [1956].

The salts used were: Li₂CrO₄ and Li₂WO₄ (Alfa Inorg. Inc.); Na₂CrO₄, Na₂WO₄, K₂CrO₄ and NaCl (C. Erba RP); K₂WO₄ (BDH Analar). Rb₂WO₄ has been prepared according to SPITSYN ⁶: the measured m.p. was 952 °C identical to the value given by this author. SCHMITZ-DUMOND and WEEG ⁷ report a value of 961 °C. Finally Ag₂WO₄ has been prepared by precipitation from an aqueous solution of Na₂WO₄ with AgNO₃ in stoichiometric proportions. For comparison a second sample of this salt (Alfa Inorg. Inc.) has been utilized. In both cases the m.p. was 604 °C: literature reports the values 584 °C ^{3b} and 610 °C ⁸. A study by differential thermal analysis (DTA) has brought into evidence that both sam-

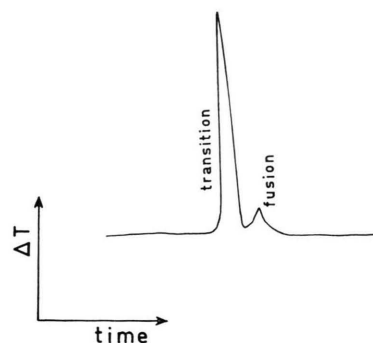


Fig. 1. DTA curve (ΔT versus time) for a sample of pure Ag₂WO₄. The transition temperature is 592 °; the fusion temperature is 604 °C.

⁴ C. SINISTRI, P. FRANZOSINI, and M. ROLLA, An Atlas of Miscibility Gaps in Molten Salt Systems, Ed. Institute of Phys. Chem., University of Pavia 1968.

⁵ C. SINISTRI, P. FRANZOSINI, A. TIMIDEI, and M. ROLLA, Z. Naturforsch. **20 a**, 561 [1965].

⁶ I. SPITSYN, J. Gen. Chem. USSR **17**, 11 [1947].

⁷ O. SCHMITZ-DUMOND and A. WEEG, Z. Anorg. Allgem. Chem. **265**, 139 [1951].

⁸ I. N. BELYAEV and R. G. KAZANBEKOV, Russ. J. Inorg. Chem. **12**, 1683 [1967].



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

ples of this salt present a large peak at a temperature (592°C) just above the melting point. This peak could be assigned to a phase transition: Fig. 1 reports a typical DTA curve of this salt.

Results

A) Mixtures $(\text{AgX})_2 + \text{Me}_2\text{CrO}_4$

Figure 2 shows solid-liquid (SL) and liquid-liquid (LL) equilibria in the mixtures $(\text{AgX})_2$

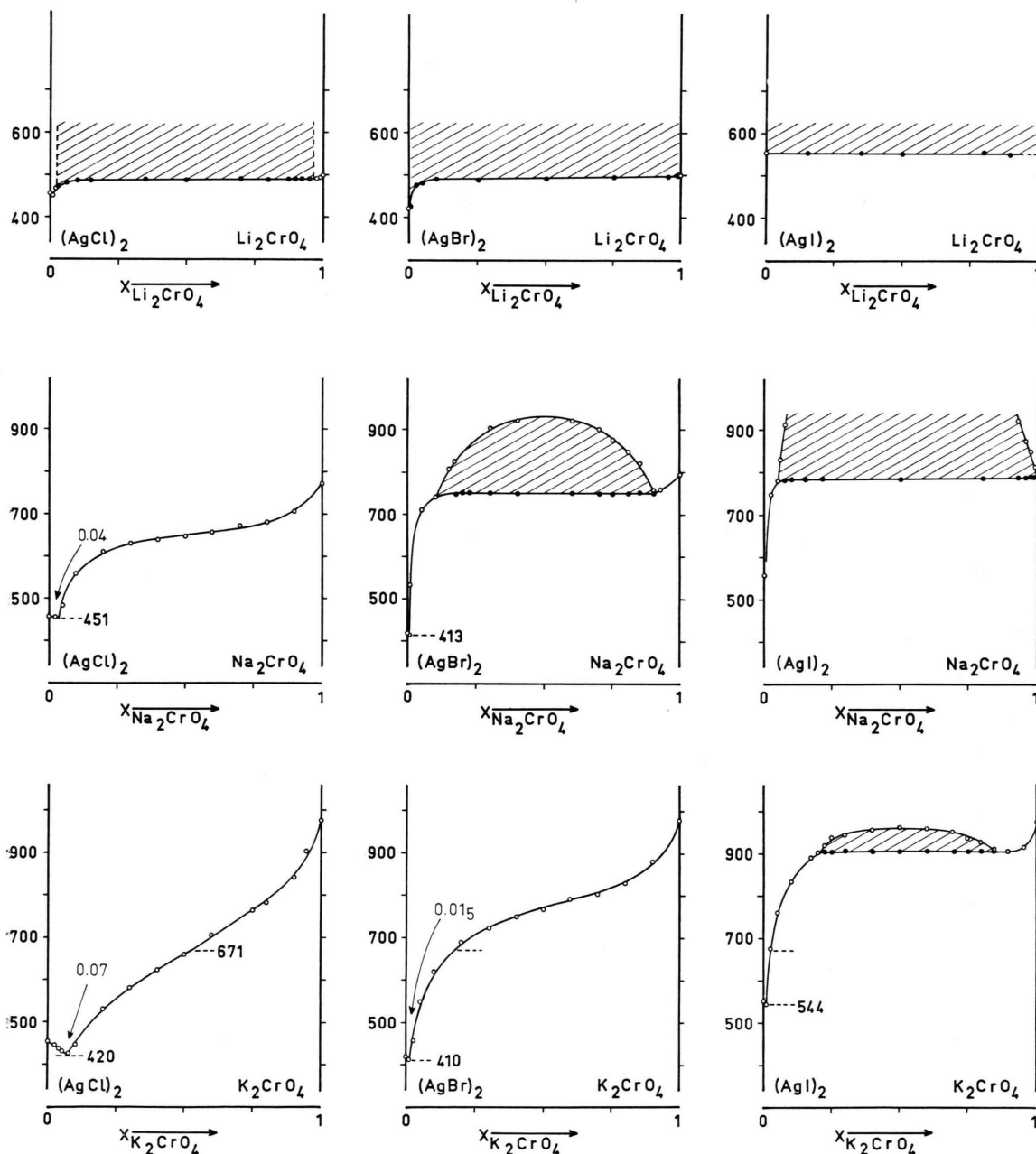


Fig. 2. SL and LL equilibria in the mixtures $(\text{AgX})_2 + \text{Me}_2\text{CrO}_4$ ($\text{Me} = \text{Li, Na, K}$). Demixing areas are shaded.

Mixtures with of	AgCl m.p. 456°	AgBr m.p. 421°	AgI m.p. 553°
Li ₂ CrO ₄ m.p. 500°	MG between: .03 (476°) — .96 (491°)	MG almost from pure to pure salt	MG almost from pure to pure salt
Li ₂ MoO ₄ m.p. 700°	MG between: .01 ₅ (674°) — .96 ₅ (678°)	MG almost from pure to pure salt	MG almost from pure to pure salt
Li ₂ WO ₄ m.p. 739°	MG between: ≅ 0 (≅ 500°) — .96 ₅ (703°)	MG almost from pure to pure salt	MG almost from pure to pure salt
Na ₂ CrO ₄ m.p. 796°	No MG "S" shaped SL curve	MG between: .10 ₅ (740°) — .91 (750°)	MG between: .05 (784°) — .99 (788°)
Na ₂ MoO ₄ m.p. 693°	No MG "S" shaped SL curve	MG between: .05 (662°) — .93 (670°)	MG almost from pure to pure salt
Na ₂ WO ₄ m.p. 698°	MG between: .18 ₅ (596°) — .62 (607°)	MG between: .01 ₅ (600°) — .95 ₅ (674°)	MG almost from pure to pure salt
K ₂ CrO ₄ m.p. 979°	No MG	No MG "S" shaped SL curve	MG between: .20 (903°) — .85 (907°)
K ₂ MoO ₄ m.p. 926°	No MG	No MG "S" shaped SL curve	MG between: .01 (630°) — .90 ₅ (856°)
K ₂ WO ₄ m.p. 923°	No MG	No MG "S" shaped SL curve	MG between: .01 (620°) — .91 (870°)
Rb ₂ MoO ₄ m.p. 955°	—	—	No MG "S" shaped SL curve
Rb ₂ WO ₄ m.p. 952°	—	—	No MG "S" shaped SL curve

Table 1. Data for the extension of the miscibility gaps (MG) in the systems (AgX)₂ + Me₂YO₄ (Me = alkali cations; Y = Cr, Mo, W; X = Cl, Br, I). The solubility limits are given in equivalent fractions of Me₂YO₄; the temperatures in °C. The values for the molybdate systems have been previously reported¹.

+ Me₂CrO₄ (Me = Li, Na, K): demixing areas have been shaded. In the same figure the coordinates of the eutectic points are indicated. The limits of the MG and the primary crystallization temperatures (PCT) are briefly summarized in Table 1 which will be discussed later.

As regards the systems containing AgCl, demixing occurs only in the mixture (AgCl)₂ + Li₂CrO₄. The data reported by Russian AA.^{3a} for this system give a constant PCT at 472 °C and a MG extending at this temperature from 10 to 80 equiv. % of Li₂CrO₄. These values are quite different from those found in the present work (see Table 1). For the system (AgCl)₂ + Na₂CrO₄ no demixing was observed but only a liquidus curve clearly "S" shaped. BELYAEV² instead reports for this system a MG extending, at constant temperature 618 °C, from 18 to 55 moles % of Na₂CrO₄. Discrepancies of this type with Belyaev's data have been pointed out also in other cases (see e. g. Ref. 1).

As regards systems with AgBr, demixing phenomena have been observed with Li₂CrO₄ and Na₂CrO₄. Only for the system (AgBr)₂ + Na₂CrO₄ the complete area of the MG could be measured. The coordinates of the point of maximum (PM)

are: $x_{\text{Na}_2\text{CrO}_4} = .47$; $t = 930$ °C. Unlike the preceding cases the system containing K₂CrO₄ shows a liquidus curve "S" shaped.

Finally the systems containing AgI demix with the three chromates of Li, Na and K. Only for the system (AgI)₂ + K₂CrO₄ the complete area of the MG, extending vertically about 50–60 degrees, could be measured. The coordinates of the PM are: $x_{\text{K}_2\text{CrO}_4} = .50$; $t = 960$ °C.

B) Mixtures (AgX)₂ + Me₂WO₄

Figure 3 shows the SL and LL equilibria in the system (AgX)₂ + Me₂WO₄ (Me = Li, Na, K) and (AgI)₂ + Rb₂WO₄.

As regards the systems containing AgCl, demixing occurs in the mixtures with Li₂WO₄ and Na₂WO₄. For the system (AgCl)₂ + Li₂WO₄ Russian AA.^{3b} reported the following data: PCT constant at 702 °C; MG extending from about pure AgCl to 94 equiv. % of Li₂WO₄. These values are in fairly good agreement with the ones found in the present work (see Table 1). The system (AgCl)₂ + Na₂WO₄ will be discussed later.

As regards the systems containing AgBr, again demixing occurs with the Li and Na tungstates.

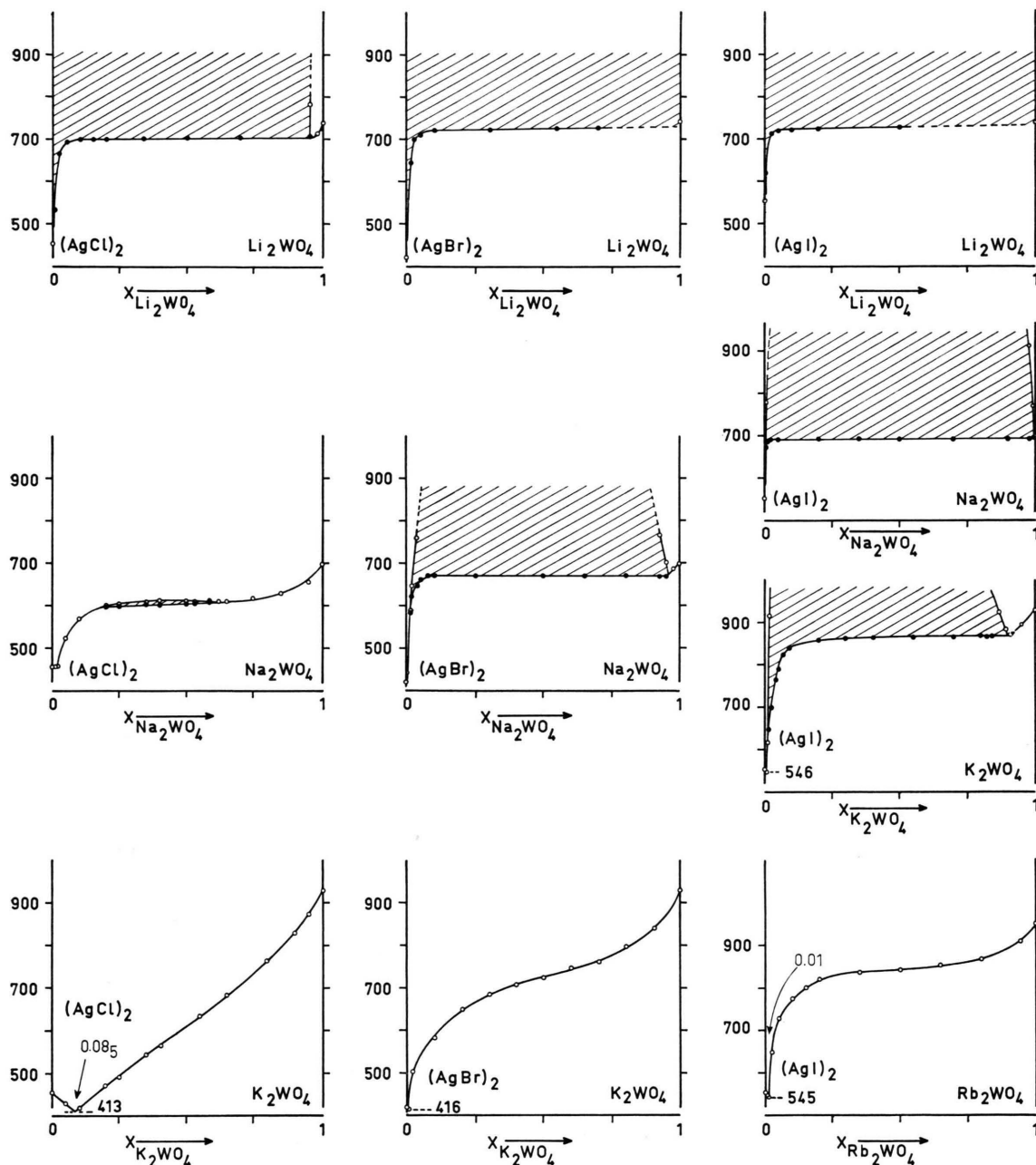


Fig. 3. SL and LL equilibria in the mixtures $(\text{AgX})_2 + \text{Me}_2\text{WO}_4$ ($\text{Me} = \text{Li, Na, K}$) and $(\text{AgI})_2 + \text{Rb}_2\text{WO}_4$. Demixing areas are shaded.

Finally for the systems containing AgI there is splitting into two phases with the Li , Na and K tungstates, whilst with Rb_2WO_4 a liquidus curve "S" shaped and no demixing phenomenon were observed.

C) The system Ag, Na/Cl, WO_4

Figure 4 shows SL equilibria relative to the four binary systems which are the sides of the composition square. In the same figure the coordinates of the eutectic points are reported.

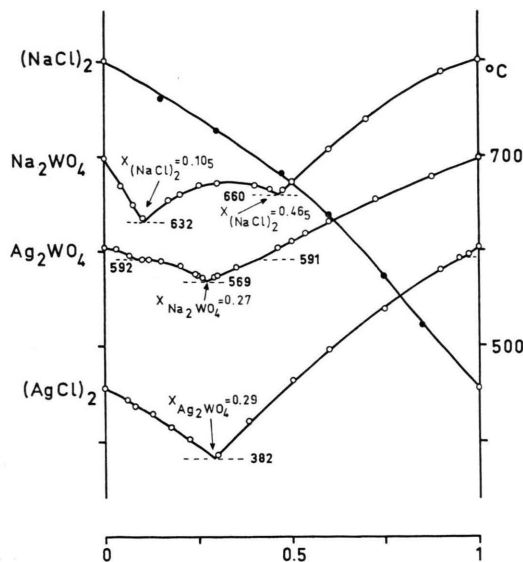


Fig. 4. SL equilibria for the four binary systems which are the sides of the composition square of the reciprocal ternary Ag, Na/Cl, WO_4 .

In the systems containing Ag_2WO_4 it is interesting to observe the slope variations of the liquidus curves at the transition temperature of this salt (592°C). An analogous variation is presented by the system containing Na_2WO_4 , due to the phase transition of this salt⁹ (591°C). BELYAEV and KAZANBEKOV⁸ report the liquidus curve for the binary $\text{Ag}_2\text{WO}_4 + \text{Na}_2\text{WO}_4$ without noticing the slope variation relative to the phase transition of Ag_2WO_4 .

Along the stable diagonal of this reciprocal ternary system [$(\text{AgCl})_2 + \text{Na}_2\text{WO}_4$, see Fig. 3] PCT increases regularly from 596°C to 607°C while $x_{\text{Na}_2\text{WO}_4}$ increases from .185 to .62. The coordinates of the PM are: $x_{\text{Na}_2\text{WO}_4} = .47$; $t = 612^\circ\text{C}$.

Along the unstable diagonal PCT increases from 602° ($x_{\text{Ag}_2\text{WO}_4} = .52$) to 609°C ($x_{\text{Ag}_2\text{WO}_4} = .45$) and it passes through the eutectic point at 600°C . The coordinates of the PM are: $x_{\text{Ag}_2\text{WO}_4} = .475$; $t = 614^\circ\text{C}$. It has been found that this point corresponds to the upper critical point of the reciprocal ternary system.

Figure 5 shows the projections of the 13 examined cuts and the temperatures corresponding to significant points of various type. The stratification lens (dotted) impinges on two crystallization fields and occupies 5.7% of the area of the composition square. The main axis of the lens (also dotted) is neatly

⁹ R. RICCARDI and C. SINISTRI, Ric. Sci. **35**, 1026 [1965].

displaced from the stable diagonal toward the NaCl corner. Along this axis the PCT is constant at $602 \pm 1^\circ\text{C}$.

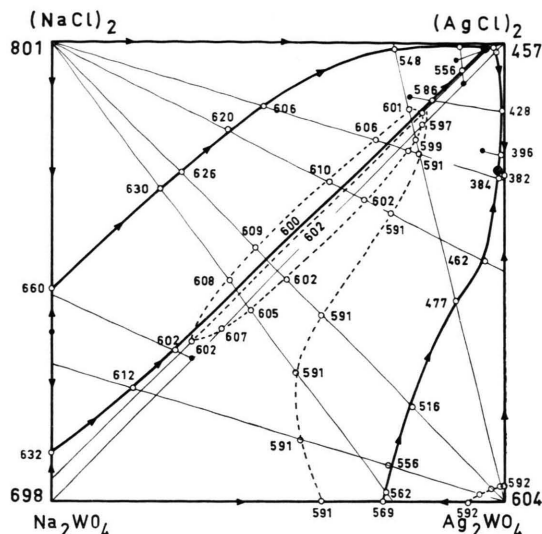


Fig. 5. Diagonal and offdiagonal cuts studied in the reciprocal ternary Ag, Na/Cl, WO_4 with some significant temperatures. Dotted lines indicate the stratification lens and the transition points of the two tungstates.

In Fig. 5 the behaviour of the transitions of the two silver and sodium tungstates is also indicated with dotted lines. Finally Fig. 6 reports some SL isotherms and also indicates the position of the ternary eutectic E ($x_{\text{Na}_2\text{WO}_4} = .01$; $x_{(\text{AgCl})_2} = .71$; $x_{\text{Ag}_2\text{WO}_4} = .28$; $t = 380^\circ\text{C}$) and of the peritectic P ($x_{\text{Na}_2\text{WO}_4} = .01$; $x_{(\text{AgCl})_2} = .955$; $x_{(\text{NaCl})_2} = .035$; $t = 464^\circ\text{C}$). The general topology of this system agrees with the triangulation rules.

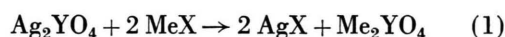
Discussion

Table 1 schematically summarizes the presence and the extension of MG for the systems $(\text{AgX})_2 + \text{Me}_2\text{YO}_4$ ($\text{X} = \text{Cl, Br, I}$; $\text{Me} = \text{alkali cations}$; $\text{Y} = \text{Cr, Mo, W}$). The corresponding SL and LL equilibria are graphically shown in Figs. 2, 3 of the present work and in Fig. 1 of Note IV of this series¹. Provided some reserves due to the fact that a comparison is made among salts with different thermodynamic characteristics, Table 1 suggests that in these families the tendency to demix increase, other factors being constant, when:

- as silver halide one takes chloride, bromide and iodide successively;

- b) as oxygenated anion one takes chromates, molybdates and tungstates successively;
 c) as alkali cation one takes rubidium, potassium, sodium and lithium successively.

Some of these regularities had already been encountered in other families of molten salts, systematically analyzed in previous works⁴. They must be related to the characteristics of the ions in the system. These characteristics affect the free energy of the metathetic reaction:



which permits to individualize the "stable pair" of the system and to express in quantitative terms the concept of "tendency to demix". Unfortunately a calculation of the ΔG values for reaction (1) at de-

mixing temperatures is not possible owing to lack of data. For the examined systems instead, it is often possible to calculate the ΔH_{298}^0 values of reaction (1).

Russian A.A.¹⁰ suggested to assume these quantities as an indication of the corresponding ΔG . Sometimes the available enthalpy of formation (standard at 25 °C) of the salts in reaction (1) can in fact give an idea of the tendency to demix. For instance, they give a fairly good account of the empirical condition a) above reported. Generally though the ΔH_{298}^0 values are quantities too rough to allow a deeper discussion.

The problem to know a priori whether a certain system demixes or not, involves the possibility to draw the SL and LL equilibrium surfaces. But this can be done only on the basis of the knowledge of the excess thermodynamic quantities (excess potentials of single ions and their temperature dependence) and of the stability fields of the solid phases. Attempts in this sense have been carried out by BLANDER and TOPOL¹¹ but there are, generally, too many parameters that must be evaluated in order to obtain sufficiently precise calculations.

From a formal view-point the tendency to demix in these systems can be correlated with some physical properties. Among these, two in particular seem to be the most important: the ionic radii or the polarizing powers and the ionic polarizabilities.

On the basis of these properties¹², it is possible to observe that, other factors being constant, the tendency to demix in a reciprocal ternary system containing a silver halide, increases as the radius (or polarizability) of the alkali cation decreases, and increases as the radius (or polarizability) of the anion increases.

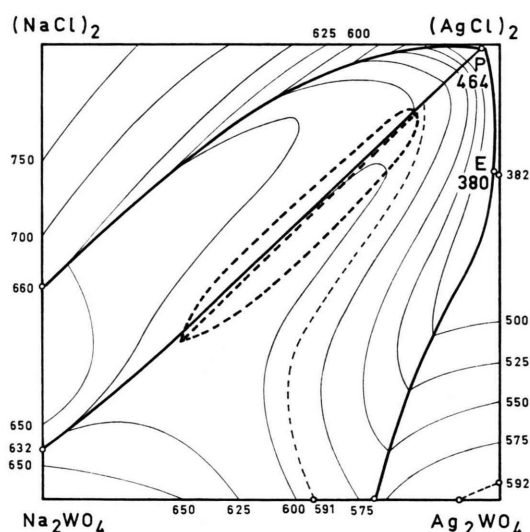


Fig. 6. Projections of the melting diagram of the reciprocal ternary system Ag, Na/Cl, WO_4 with some SL isotherms.

¹⁰ For a general review of this subject see: M. ROLLA, P. FRANZOSINI, and C. SINISTRI, *Atti Soc. Peloritana*, XI Suppl., 47 [1965].

¹¹ M. BLANDER and L. E. TOPOL, *Inorg. Chem.* **5**, 1641 [1966].

¹² For the numerical values of radii and polarizabilities see: L. PAULING, *The Nature of the Chemical Bond*, Cornell Univ. Press 1960, p. 514; J. R. TESSMAN, A. H. KAHN, and W. SCHOCKLEY, *Phys. Rev.* **92**, 890 [1953].