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COMPLEX FORMATION IN A QUATERNARY RECIPROCAL SYSTEM OF CHLORIDES, SULFATES, AND TUNGSTATES OF LITHIUM AND POTASSIUM

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As it is known, in the case when the components of a quaternary reciprocal system crystallize out in pure state and do not form solid solutions, the volume of the prism resolves into six volumes of crystallization of the six components (cubes) of the system. The prism Na, Tl // NO_3, Cl, SO_4 studied by N. P. [illegible][1] may be cited as an example. In this case the prism can be divided by two stable ternary sections into three stable tetrahedrons in each of which there is a quaternary eutectic. In case of appearance in the system of a series of solid solutions, the number of crystallization volumes is decreased, as is the number of stable tetrahedrons. For example in the ternary reciprocal system Na, K // [illegible], Br, I, studied by N. S. Dombrovskaia[2], the number of crystallization volumes [illegible] the prism is reduced to three and the prism is cut (divided) into two [illegible].

In case of complex* formation between the individual components, the [illegible] of such a system as well as its analysis are further complicated. [illegible] stable crystallization volumes and the stable tetrahedral sections [illegible]. An illustrative example of such a system is the one studied by the [illegible] help of the visual polythermic method[3] - namely the quaternary [illegible] Li, K // [illegible], SO_4, WO_4.

[illegible] system, if depicted, as usual, as a three sided [illegible] by the presence of two double salts, the 1:1 [illegible] on the opposite sides of the prism. [illegible] by the authors during the study of the ternary [illegible] Li, K // SO_4, WO_4[3].

The tetrahedron describing the above reciprocal system, shown in [illegible] by depicting the presence of congruently melting complex compositions [illegible] on the Li_2SO_4-K_2SO_4 binary side, with a maximum at 626°C and [illegible] on the Li_2SO_4-K_2SO_4 binary side with a maximum at 736°C.

Projection of the space diagram for the reciprocal salt pair system Li, K // SO_4, WO_4 on the composition square

Fig. 1

* Of the double salt type
** The Li_2SO_4.K_2SO_4 and the Li_2SO_4.K_2SO_4 double salts are shown as [illegible] respectively in this article.

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The melting point data pertaining to the Li,K // SO_4, WO_4 system are listed in Table 1.

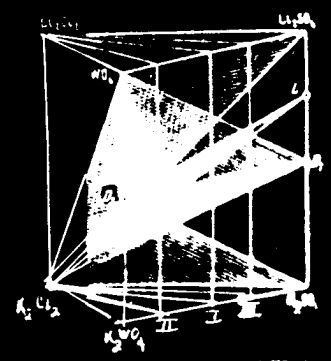
Binary Li_2WO_4-K_2WO_4				Binary Li_2SO_4-K_2SO_4		
% K_2			% K_2SO_4	t°	% K_2SO_4	t°
0				[illegible]	32	[illegible]
5				[illegible]	35	[illegible]
10			[illegible]	[illegible]	38	702
15			[illegible]	[illegible]	42	722
20			[illegible]	[illegible]	46	730
25			[illegible]	[illegible]	50	732
30			[illegible]	[illegible]	55	736
32			[illegible]	574	60	716
35		546	28	600	65	770
40		926	30	625	70	[illegible]
45				648	100	1089

The surfa liquidus system consist fields of crystallization, two of which are the crystallization fields of $Li_2WO_4.K_2WO_4$ and $Li_2SO_4.K_2SO_4$, occupying correspondingly the 10,04 and 21.8% areas, while the other four fields pertain to the pure components.

The fields of potassium sulfate, lithium sulfate and lithium tunstate are further broken up into the and modification areas. Situated on opposite sides of the composition square the two double salts (complexes) establish the principal characteristics of the system and displace the equilibrium to the side of the newly formed stable section $Li_2WO_4.K_2WO_4$-$Li_2SO_4.K_2SO_4$, which bisects the composition square into two quadrangles which triangulate in turn to two phase triangles. (See Fig. 2). In the system the complex forming reaction on the two opposite sides of the composition square is predominant to the double decomposition reaction. The system Li, K // SO_4, WO_4 is classified as reciprocal system of the belt-a-diagonal type. In order to verify the stablility of the two complexes (double salts) $Li_2WO_4.K_2WO_4$ and $Li_2SO_4.K_2SO_4$ in the quaternary reciprocal system Li, K // Cl, SO_4, WO_4 the "inside" of prism composition was studied by means of determination of its various sections, in particular the three "book"* sections (I, II, III,) and the five triangular sections, as shown in Fig. 2.

Scheme of Sections through a prism of composition for the system Li, K // Cl, SO_4, WO_4

Fig. 2



* The "book" sections the authors conditionally define as eciprocal systems and thus treat them as such in their investigations.

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In the article the authors describe only the sections of the system that pertain directly to the above mentioned double salts D_1 and D_2 and which define the boundaries of their crystallization volumes.

It is first necessary to define and elaborate on the three "Rook" sections.

I "Rook" Section -

(50% Li_2MO_4 + 50% Li_2SO_4) - (50% K_2MO_4 + 50% K_2SO_4) - Li_2Cl_2 - [illegible]

II "Rook" Section -

(80% Li_2MO_4 + 20% Li_2SO_4) - (80% K_2MO_4 + 20% K_2SO_4) - Li_2Cl_2 - [illegible]

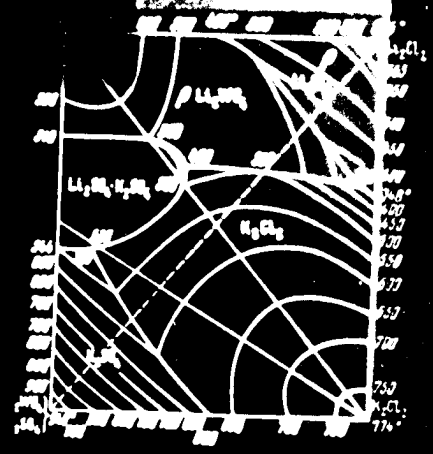
III "Rook" Section -

(30% Li_2MO_4 + 70% Li_2SO_4) - (30% K_2MO_4 + 70% K_2SO_4) - Li_2Cl_2 - [illegible]

[illegible] representing the I "Rook Section", as shown in Fig. [illegible] (Fig. 3) [illegible] binary system Li_2Cl_2-K_2Cl_2 with a [illegible] [illegible] three quadrilaterals, of which one is made through the [illegible] (50% Li_2MO_4 + 50% Li_2SO_4) - (50% K_2MO_4 + 50% K_2SO_4) and its [illegible] [illegible] a congruently melting double salt Li_2SO_4-K_2SO_4 [illegible] [illegible] through ternary systems describing the [illegible] [illegible] in the 70% Li_2SO_4 + 30% Li_2MO_4) - Li_2Cl_2 [illegible] [illegible] (70% Li_2SO_4 + 30% Li_2MO_4) and the [illegible] [illegible] 30% K_2SO_4. [illegible] I "Rook Section" is [illegible] [illegible] of the double salt Li_2SO_4-K_2SO_4 [illegible] [illegible] fields of the pure component salts.

Scheme of I "Rook Secti[illegible]

Fig. 3



*In using the prism to describe the quaternary reciprocal system, the [illegible] reciprocal systems therein would naturally be represented as rectangl[illegible]

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The field of crystallization [illegible] $Li_2SO_4.K_2SO_4$ is flat in appearance, characterized by almost [illegible] isotherms, as this double salt melts without decomposition [illegible] ity and displaces the crystallization fields of pure [illegible] potassium chloride exhibits isotherms that curve upward. The pure [illegible] shows a steep slope, as seen from the closely situated isotherms [illegible] chloride field exhibits the α and β homeomorphic forms. The lithium [illegible] field is characterized by its [illegible] form and the upwardly curving [illegible] In this section the complex forming reaction is predominant.

Thus the I "Book Section" establishes that the double salt $Li_2SO_4.K_2SO_4$ is congruently melting, stable and is found to occupy 10.68% of the total surface of the "Book Section." It is further characterized by the flatness of the [illegible] field with an almost complete absence of isotherms.

The rectangle representing the II "Book Section", shown in Fig. 4, [illegible]

1) A binary system Li_2Cl_2-K_2Cl_2 with a eutectic at 346°C and [illegible]
2) A section through a reciprocal system (80% Li_2WO_4 + 20% [illegible] + 20% K_2WO_4) characterized by the presence of [illegible] $Li_2WO_4.K_2WO_4$.
3) A section through the top of the prism (80% Li_2WO_4 + 20% Li_2SO_4) [illegible] a monovariant point at 475°C and 46.5% (80% Li_2WO_4 + 20% Li_2SO_4) [illegible]
4) A section through the bottom of the prism (80% K_2WO_4 + 20% [illegible]) [illegible] a monovariant point at 600°C and 45% K_2Cl_2.

Scheme of II "Book Section"

Fig. 4

The surface of the rectangular II "Book Section" shows five distinct [illegible] (volumes) of crystallization of which four are the fields of pure [illegible] while the fifth depicts the field of a double salt $Li_2WO_4.K_2WO_4$. The field of crystallization of the double salt has a flat appearance, characterized by the absence of isotherms. It being congruently melting, the stability is preserved and even spread quite deeply into the inside volumes of the whole system. The field of lithium tungstate has an elongated appearance with isotherms curving upward and presence of the α and β crystalline areas. The field of potassium chloride also shows isotherms curved upward, the curvature somewhat diminishing with decrease in temperature.

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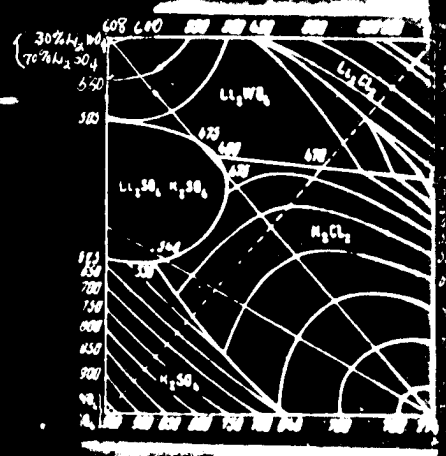
The field of potassium tungstate is distinguished by the steepness of [illegible] as shown by the closely spaced isotherms. In this section the complex [illegible] reaction is predominant. Thus the results of the analysis of II "Book [illegible] establishes the presence inside the section of a double salt field [illegible] occupying 9.9% of the total rectangular section. The field of this [illegible] has a flat appearance and is characterized by the absence of isotherms. [illegible] from the field of the complex D_1, the presence of the following fields is [illegible] Li_2Cl_2 (α and β), K_2Cl_2, K_2WO_4 and Li_2WO_4 (α and β).

The rectangle representing the III "Book Section", as shown in Fig. 5, is [illegible] by the following sections:

1) (30% Li_2WO_4 + 70% Li_2SO_4) - (30% K_2WO_4 + 70% K_2SO_4), characterized by the presence of a congruent double salt $Li_2SO_4.K_2SO_4$.
2) (30% Li_2WO_4 + 70% Li_2SO_4) - Li_2Cl_2 with a monovariant point at [illegible] (30% Li_2WO_4 + 70% Li_2SO_4).
3) (30% K_2WO_4 + 70% K_2SO_4) - K_2Cl_2 with a monovariant point at [illegible] (30% K_2WO_4 + 70% K_2SO_4)
4) A binary system Li_2Cl_2 - K_2Cl_2 with an eutectic at [illegible]

Volume of III "Book [illegible]

Fig. 5



The crystallization surface of the [illegible] is composed of five [illegible] (Li_2WO_4), the $Li_2SO_4.K_2SO_4$ double [illegible], K_2SO_4 and Li_2Cl_2. Of [illegible] the field of the double salt, the others are those of pure components. [illegible] character of isotherms is the same as in the previously described [illegible] (I and II). Again, as in the other two "Book Sections" the equilibrium [illegible] in the system is displaced toward complex formation.

Therefore, the III "Book Section" confirms that the double salt $Li_2SO_4.K_2SO_4$, being congruently melting, is stable and occupies a relatively large [illegible] portion of the total volume of the prism of the overall system.

The data pertaining to the analyses of the two component sides of the three "Book" sections, on which the double salt compositions and characteristics are based, are listed in Table 2.

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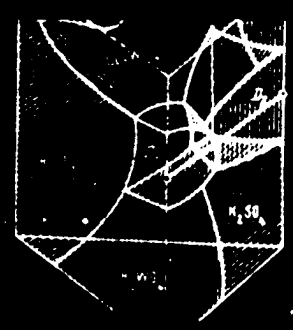
Binary System		Binary System		Binary System	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	t°
[illegible]	[illegible]	[illegible]	702	0	606
[illegible]	[illegible]	[illegible]	678	2	600
10	[illegible]	[illegible]	660	5	580
[illegible]	[illegible]	[illegible]	606	10	552
20	[illegible]	[illegible]	570	15	530
[illegible]	[illegible]	[illegible]	546	20	512
27,5	[illegible]	[illegible]	546	22,5	512
[illegible]	[illegible]	[illegible]	552	25	526
[illegible]	[illegible]	[illegible]	566	30	566
[illegible]	[illegible]	[illegible]	558	35	585
40	[illegible]	[illegible]	580	40	610
[illegible]	[illegible]	[illegible]	565	45	620
[illegible]	[illegible]	[illegible]	562	50	625
57,5	[illegible]	57,5	558	55	625
60	[illegible]	[illegible]	544	57,5	627
[illegible]	[illegible]	[illegible]	564	60	635
70	[illegible]	70	645	70	722
80	[illegible]	80	735	80	810
90	[illegible]	90	836	90	900
100	[illegible]	100	920	100	[illegible]

Analysis of the data allows the following observations and conclusions to be made: the three "book" sections confirm the presence of 8 different volumes of crystallization in the prism of Li, K // Cl, SO_4, WO_4 - two double salt volumes and six single component volumes, as shown in Fig. 6. The $Li_2SO_4.K_2SO_4$ double salt is also confirmed inside the prism by the study of "book" sections I and III. The double salt (complex) forming reaction in all three "book" sections is predominant over the equilibrium exchange reaction. In this manner, the $Li_2SO_4.K_2SO_4$ double salt, being congruently melting, maintains its stability even inside the prism. The $Li_2SO_4.K_2SO_4$ double salt crystallization volume is found to be a relatively large portion of the total prism volume and even somewhat displaces the crystallization volume of the other double salt, namely the $Li_2WO_4.K_2WO_4$, which is situated on the opposite side of the prism.

Inner crystallization volumes in a prism of composition for the system Li, K // Cl, SO_4, WO_4.

Fig. 6



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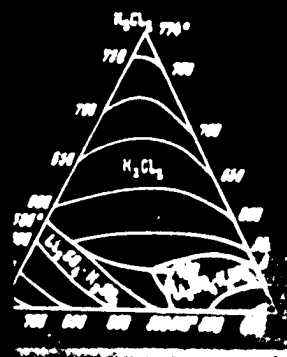
The second double salt, $Li_2WO_4.K_2SO_4$, is confirmed in the "book" section II. The double salt (complex) forming reaction in the "book" section II is also [illegible] but to a much lesser extent than in the other two "book" sections. This is [illegible] firmed by the smaller volume of the tungstate double salt $Li_2WO_4.K_2WO_4$ as compared to the sulfate double salt $Li_2SO_4.K_2SO_4$. Moreover the formation of the above [illegible] tioned double salts and their stability is further confirmed in one of the [illegible] interesting inner triangular sections: (50% Li_2WO_4 + 50% K_2WO_4) - (50% [illegible] + 50% K_2SO_4) - K_2Cl_2, as shown in Fig. 7. This section is obtained by a [illegible] cut through the prism side which depicts the Li, K // SO_4, WO_4 reciprocal [illegible] system. In the quaternary reciprocal system Li, K // Cl, SO_4, WO_4 this [illegible] represents a simple ternary eutectic system with an invariant point at [illegible] 13% K_2Cl_2, 59% D_1 and 38% D_2 and represents a stable diagonal section of the [illegible] depicting the composition of the given system.

Inner Triangular Section

Fig. 7



This section, inside the prism, cuts through only three of the total of [illegible] volumes of crystallization, namely, K_2Cl_2, D_1 and D_2.

In the ternary reciprocal system Li, K // SO_4, WO_4, represented as a [illegible] prism, we have a "belt-a-diagonal" system, the general characteristics of [illegible] cipal determines the character of our quaternary reciprocal system, [illegible] the simple eutectic characteristics of the inner triangular section [illegible] Fig. 8 represents the scheme of unfolded sides of the prism of composition [illegible] system Li, K // Cl, SO_4, WO_4. With the increase of the number of [illegible] volumes by the presence of the two double salts, the number of stable [illegible] is also increased.

Scheme of unfolded sides of the prism of composition

Fig. 8

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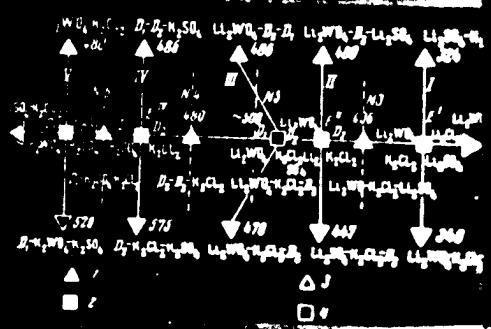
TABLE 3

Tetra-hedron	Point	Character	Composition, Volume %	Equilibrium Solid Phases
I	E^{I}	Quaternary Eutectic	64 36 78 18 4	Li_2WO_4, Li_2Cl_2, K_2Cl_2, Li_2SO_4
II	E^{II}	Quaternary Eutectic	80 20 20 64 16	Li_2WO_4, D_2, Li_2SO_4, K_2Cl_2
III	P	Quaternary Transition	73 27 18 43 39	Li_2WO_4, D_2, D_1, K_2Cl_2
IV	E^{IV}	Quaternary Eutectic	42 58 10 32 58	D_1, D_2, K_2SO_4, K_2Cl_2
V	E^{V}	Quaternary Eutectic	27 73 16 12 62	D_1, K_2Cl_2, K_2WO_4, K_2SO_4

Scheme of Crystallisation "tree" for the system Li, K // Cl, SO_4, WO_4

Fig. 9



1. Ternary eutectics. 2. Quaternary eutectics. 3. Ternary transition points. 4. Quaternary transition points.

This is also verified by the study of the Li, K // Cl, SO_4, WO_4 system, offered by the authors as an example. By means of a number of inner sections, shown earlier in Fig. 2, it is shown that the above system can be divided by 4 such inner sections into five tetrahedrons each of which has a quaternary eutectic point, while the fifth tetrahedron has a quaternary transition point. Their compositions are listed in Table 3.

The visual confirmation of these data are shown schematically in Fig. 9.

CONCLUSION

1. The study of complex formation of the quaternary reciprocal system Li, K // Cl, SO_4, WO_4 is reported in this article.

2. Formation of two double salts Li_2WO_4, K_2WO_4 and $Li_2SO_4.K_2SO_4$ in the ternary reciprocal system Li, K // SO_4, WO_4, which forms a vertical side of the prism for the quaternary system Li, K // Cl, SO_4, WO_4, is shown.

3. The three book section:

I. (50% Li_2WO_4 + 50% Li_2SO_4) - (50% K_2WO_4 + 50% K_2SO_4) - Li_2Cl_2 - K_2Cl_2
II. (80% Li_2WO_4 + 20% Li_2SO_4) - (80% K_2WO_4 + 20% K_2SO_4) - Li_2Cl_2 - K_2Cl_2
III. (30% Li_2WO_4 + 70% Li_2SO_4) - (30% K_2WO_4 + 70% K_2SO_4) - Li_2Cl_2 - K_2Cl_2

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and one inner section (50% Li_2WO_4 + 50% K_2WO_4) - (50% Li_2SO_4 + 50% K_2SO_4) - K_2Cl_2 show the stability of $Li_2WO_4.K_2WO_4$ and $Li_2SO_4.K_2SO_4$ double salts. The inner boundaries of their crystallization volumes have been described.

4. The inner structure of the prism Li, K, // Cl, SO_4, WO_4 has been studied and found to have 8 volumes of crystallization - two of the above mentioned double salts and six of the single components.

5. The overall character of the ternary reciprocal system Li, K // Cl, SO_4, WO_4 is discussed in detail.

Literature

1. Loujnaya, N. P., Reports of Govt. Institute of Applied Chemistry [illegible], [illegible], ([illegible])
   (T2. 60s In-ta prikl. chim.)
2. Dombrovskaya, N. S., Izv C.F.KL. A 20, 124 (1950)
3. Bergman, A. C., Izv. C.F.KL. A 19, 113, (1949)
4. Janecke, E., Zs. anorg.chem. 53, 319 (1907)
   Zs. phys. chem. 82, 1 (1913)
5. Bergman, A. C., Kislova, A. I., Posipaiko, V. I., D.A.N. [illegible], 5, 815 ([illegible])

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