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Abstract**Full Text**

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Chemistry

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ON STABLE ELEMENTS OF SEPTENARY RECIPROCAL SYSTEMS

(Presented by Academician I. V. Tananaev, 13 V 1965)

Determining the type of a singular star in multicomponent reciprocal systems makes it possible to carry out a rational subdivision of the composition diagram, to determine the possible combinations of salts in eutectic equilibria (parageneses), and thereby to reduce substantially the amount of experimental work in studying chemical interactions; moreover, identifying the types of stars makes it possible to determine the direction of exchange reactions in multicomponent reciprocal systems.

The theoretical scheme of a singular star (unfortunately not available) for a septenary reciprocal system of type $16C^*$ was first derived by V. P. Radishchev⁽²⁾. Real representatives of type $16C$ are systems composed of the halides of the first group of elements of the periodic system, as well as systems involving Tl^{1+} and Ag^{1+} . For example, Li, Na, K, Rb || J, Br, Cl, F⁽³⁾; Li, Na, K, Tl || J, Br, Cl, F⁽⁴⁾.

When halides are replaced by other anions, the type of system may remain unchanged. Thus, the systems Li, Na, K, Tl || Br, Cl, SO_4 , F and Li, Na, K, Tl || J, Br, NO_3 , F belong to type $16C$. As a result of the work carried out, real salt systems were reflected in the geometric elements of the singular star, each type of system being expressed by a quite definite geometric form of the star and by a quite definite set of indices^(5,6). The scheme of the singular star of type $16C$ is given in Fig. 1a; beside it is placed the table of indices for this type.

In some cases replacement of halides by other anions causes the appearance of new types of systems. For example, replacement of iodide by sulfate ion in the system Li, Na, K, Rb || Br, Cl, SO_4 , F led to the appearance of type $2A2B12C$. The scheme of the singular star for this type is shown in Fig. 1b. It differs in that it contains not a cube, as in type $16C$, but a three-dimensional figure bounded above and below by plane five-membered cycles, while the lateral boundary consists of 5 square cycles. Adjoining this figure along its edges are three square plane cycles on the frontal side and two on the distal side. At the

center of the figure there is a tetrahedron common to ten heptatopes, reflecting the four most stable salts of the given system: $\text{LiF} - \text{Na}_2\text{SO}_4 - \text{KCl} - \text{RbBr}$. The most stable pair of salts in this system, $\text{LiF} - \text{RbBr}$ (with a maximum thermal effect of the exchange reaction = 24.6 kcal/eq), enters into the eutectic equilibria (parageneses) of any possible mixtures of the 16 salts.

The system $\text{Li, Na, Rb, Tl} \parallel \text{Br, Cl, SO}_4, \text{NO}_3$ also belongs to type $2A2B12C$, but the singular star and the table of indices differ from the preceding one. Thus, these two systems may be regarded as peculiar structural “isomers.”

Previously we assigned the system $\text{Li, Na, Rb, Tl} \parallel \text{Br, Cl, SO}_4, \text{NO}_3$ to type $16C$ (7), but a more detailed study of it leads to the form shown in Fig. 1c, in which a somewhat different arrangement of square

* The type of systems of 16 salts is determined by the types of reciprocal systems of 9 salts (1).

and five-membered cycles with respect to the cube, although the cube itself remains the same. The most stable salts in this system— $\text{Li}_2\text{SO}_4, \text{NaCl}, \text{RbNO}_3, \text{TlBr}$ —are reflected in the basic tetrahedron, which has been investigated experimentally (8,9).

Type 1BC

$\text{Li, Na, K, Rb} \parallel \text{J, Br, Cl, F}$

$K \setminus A$	J	Br	Cl	F
Li	0	3	6	9
Na	3	4	5	6
K	6	5	4	3
Rb	9	6	3	0

Type 2A2B12C

$\text{Li, Na, K, Rb} \parallel \text{Br, Cl, SO}_4, \text{F}$

$K \setminus A$	Br	Cl	SO_4	F
Li	0	3	6	9
Na	3	4	5	6
K	6^a	6^b	3^a	3^b
Rb	9	5	4	0

Type 2A2B12C

$\text{Li, Na, Rb, Tl} \parallel \text{Br, Cl, NO}_3, \text{SO}_4$

$K \setminus A$	Br	Cl	NO ₃	SO ₄
Li	0	3	6	9
Na	3	5	4	6
Rb	6	5	4	3
Tl	9	6	3	0

Type 3A3B10C

Li, Na, K, Rb || Br, Cl, NO₃, F

$K \setminus A$	Br	Cl	NO ₃	F
Li	0	3	6	9
Na	3 ^a	6 ^a	3 ^b	6 ^b
K	6	5	4	3
Rb	9	4	5	0

Type 7A2B7C

Mg, Ca, Sr, Ba || J, Br, Cl, F

$K \setminus A$	J	Br	Cl	F
Mg	0	3	6	9
Ca	6 ^a	2	4	6 ^b
Sr	5 ^a	5 ^b	5 ^c	3
Ba	7	8	3	0

Fig. 1. Schemes of singular stars

In the system Li, Na, K, Rb || F, Cl, Br, NO₃, the introduction of the ion NO₃⁻ in place of a halide leads to a new type, 3A3B10C (Fig. 1d).

The scheme of the singular star of this system is characterized by the presence of two five-membered planar cycles and four square cycles adjoining the cube along its edges. At the center of the cube there is shown a tetrahedron reflecting the salts that are most stable in this system: LiF – NaCl – KNO₃ – RbBr. The most stable pair of salts, LiF – RbBr, has the maximum thermal effect of the exchange reaction, 24.6 kcal/eq, and enters into the eutectic equilibria of any mixtures in this system.

The septenary reciprocal system formed by halides and the cations of group 2 of the periodic system of elements, Mg, Ca, Sr, Ba || J, Br, Cl, F, has a singular star of type 7A2B7C, shown in Fig. 1e. As in the preceding type, the scheme of the singular star has two five-membered and ten square planar cycles, six of which form a cube, at the center of which there is shown a tetrahedron reflecting the most stable salts: MgF₂ – CaJ₂ – SrCl₂ – BaBr₂.

The most stable pair of salts is $\text{MgF}_2 - \text{BaBr}_2$; it corresponds to the maximum thermal effect.

Table 1

Stable cells (heptatopes)

Type 16C Li, Na, K, Rb || J, Br, Cl, F* || **Type 3A3B10C** Li, Na, K, Rb || Br, Cl, NO_3 , F

Nos.	Li	Na	K	Rb	Nos.	Li	Na	K	Rb
1	0369	3	6	9	1	9	6 ^b	3	9450
2	369	34	6	9	2	9	6 ^b	53	945
3	69	345	6	9	3	9	6 ^b	543	95
4	9	3456	6	9	4	9	6 ^b	6543	9
5	369	4	65	9	5	9	6 ^a 6 ^b	5	945
6	69	45	65	9	6	9	6 ^a 6 ^b	54	95
7	9	456	65	9	7	9	6 ^a 6 ^b	654	9
8	369	4	5	96	8	69	6 ^a	5	945
9	69	45	5	96	9	69	6 ^a	54	95
10	9	456	5	96	10	69	6 ^a	654	9
11	69	5	654	9	11	369	6 ^a	5	94
12	9	56	654	9	12	369	6 ^a	65	9
13	9	6	6543	9	13	9	6 ^a 3 ^b 6 ^b	4	95
14	69	5	54	96	14	9	6 ^a 3 ^b 6 ^b	64	9
15	9	56	54	96	15	69	6 ^a 3 ^b	4	95
16	9	6	543	96	16	69	6 ^a 3 ^b	64	9
17	69	5	4	963	17	9	3 ^a 6 ^a 3 ^b 6 ^b	6	9
18	9	56	4	963	18	69	3 ^a 6 ^a 3 ^b	6	9
19	9	6	43	963	19	369	3 ^a 6 ^a	6	9
20	9	6	3	9630	20	0369	3 ^a	6	9

Type 2A2B12C- α Li, Na, K, Rb || Br, Cl, SO_4 , F || **Type 7A2B7C**
Mg, Ca, Sr, Ba || J, Br, Cl

Nos.	Li	Na	K	Rb	Nos.	Mg	Ca	Sr	Ba
1	0369	3	6 ^a	9	1	0369	6 ^a	5 ^a	7
2	369	34	6 ^a	9	2	369	6 ^a	5 ^a	78
3	369	4	6 ^a 6 ^b	9	3	369	6 ^a	5 ^a 5 ^b	8
4	369	4	6 ^b	95	4	369	6 ^a 2	5 ^b	8
5	69	345	6 ^a	9	5	69	6 ^a 2 ₄	5 ^b	8
6	69	45	6 ^a 6 ^b	9	6	69	6 ₄ ^a	5 ^b 5 ^c	8
7	69	45	6 ^b	95	7	69	6 ^a	5 ^a 5 ^b 5 ^c	8
8	9	3456	6 ^a	9	8	69	6 ^a	5 ^a 5 ^c	78
9	9	456	6 ^a 6 ^b	9	9	69	6 ₄ ^a	5 ^c	78

Nos.	Li	Na	K	Rb	Nos.	Mg	Ca	Sr	Ba
10	9	456	6 ^b	95	10	69	4	5 ^c	783
11	69	5	6 ^a 6 ^b 3 ^a	9	11	9	6 ^a 2 ₄ 6 ^b	5 ^b	8
12	69	5	6 ^b 3 ^a	94	12	9	6 ₄ 6 ^b	5 ^b 5 ^c	8
13	69	5	6 ^b	954	13	9	6 ^a 6 ^b	5 ^a 5 ^b 5 ^c	8
14	9	56	6 ^a 6 ^b 3 ^a	9	14	9	6 ^b	5 ^a 5 ^b 5 ^c 3	8
15	9	56	6 ^b 3 ^a	94	15	9	6 ^b	5 ^a 5 ^c 3	78
16	9	56	6 ^b	954	16	9	6 ^a 6 ^b	5 ^a 5 ^c	78
17	9	6	6 ^a 6 ^b 3 ^a 3 ^b	9	17	9	6 ₄ 6 ^b	5 ^c	78
18	9	6	6 ^a 3 ^a 3 ^b	94	18	9	46 ^b	5 ^c	783
19	9	6	6 ^b 3 ^b	954	19	9	6 ^b	5 ^c 3	783
20	9	6	3 ^b	9540	20	9	6 ^b	3	7830

Type 2A2B12C-β Li, Na, Rb, Tl || Br, Cl, NO₃, SO₄

Nos.	Li	Na	Rb	Tl	Nos.	Li	Na	Rb	Tl
1	0369	3	6	9	11	9	3546	6	9
2	369	35	6	9	12	9	546	65	9
3	369	5	64	9	13	9	546	5	96
4	369	5	4	96	14	9	46	5	963
5	69	354	6	9	15	9	56	645	9
6	69	54	65	9	16	9	56	45	96
7	69	5	645	9	17	9	6	6453	9
8	69	5	45	96	18	9	6	453	96
9	69	54	5	96	19	9	6	53	963
10	69	4	5	963	20	9	6	3	9630

* Anions associated with the given cations correspond to the vertex indices in the tables of Fig. 1.

In all the enumerated types we find 12 flat cycles and two “offshoots.” In each type we find a tetrahedron reflecting the four most stable salts, including all the cations and anions of the system, and in each case we have the most stable pair of salts with the greatest thermal effect of the exchange reaction.

Table 1 gives a list of stable cells, whose numbers correspond to Fig. 1.

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