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Abstract

Full Text

CHEMISTRY

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DETERMINATION OF THE DEGREES OF STABLE DIAGONALS IN A SEPTENARY RECIPROCAL SYSTEM OF TYPE 16C

(Presented by Academician I. V. Tananaev, 2 VI 1962)

The study of multicomponent reciprocal systems is considerably facilitated by a rational division of the composition diagram, which, for an n -component system, is an $(n-1)$ -dimensional polytope. The latter may be subdivided into simplexes, which are carriers of eutectic points. Division of the polytope leads to the identification of a singular star indicating the direction of exchange reactions. V. P. Radishchev ⁽¹⁾ pointed out that the degrees of diagonals in multicomponent reciprocal systems may be determined from thermochemical equations of exchange reactions of reciprocal pairs and by geometric criteria: diagonals of higher degree always connect the ends of two diagonals of lower degree. However, this method is rather complicated, laborious, and requires skill in multidimensional geometry. As has been shown in a number of earlier works, a multidimensional polytope can be represented in tabular form ⁽²⁾.

Let us consider how the degrees of stable diagonals are determined in a septenary reciprocal system of 16 salts Li, Na, K, Rb|J, Br, Cl, F. The division of the composition diagram of such systems was described earlier ⁽³⁾. The given system belongs to type 16C, since all reciprocal systems of lower dimensionality entering into it belong to type C. The six-dimensional polytope serving as the composition diagram of the given system is represented in the index table 1, which, for clarity of exposition, is repeated four times.

Table 1

A	A	A	A	A
"16" C	J	Br	Cl	F
Li	0	3	6	9
Na	3	4	5	6
K	6	5	4	3
Rb	9	6	3	0

B	B	B	B
J	Br	Cl	F
0	3	6	9
3	4	5	6
6	5	4	3
9	6	3	0

C	C	C	C
J	Br	Cl	F
0	3	6	9
3	4	5	6
6	5	4	3
9	6	3	0

D	D	D	D
J	Br	Cl	F
0	3	6	9
3	4	5	6
6	5	4	3
9	6	3	0

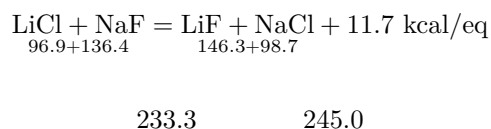
In section A of Table 1, by joining pairs of indices along diagonals, we obtain nine diagonals of the 1st degree; the thermal effects of exchange reactions corresponding to these diagonals are “independent,” as it were thermochemical components of the system. In section B of this table, by joining each pair of indices along diagonals through one cell of the vertical columns, we obtain 6 stable diagonals of the 2nd degree. In section C, we join each pair of indices along a diagonal through one cell of the horizontal rows and obtain the remaining 6 diagonals of the 2nd degree. The thermal effects of the exchange reactions corresponding to diagonals of the 2nd degree are equal to the sum of the thermal effects of the diagonal of the 1st degree with the same first index plus the diagonal of the 1st degree

Table 2

Indices	Stable diagonals	Q^*	Indices	Stable diagonals	Q^*
Diagonals of degree 1	Diagonals of degree 1	Diagonals of degree 1	Diagonals of degree 2	Diagonals of degree 2	Diagonals of degree 2
1	1	1	2	2	2

Indices	Stable diagonals	Q^*	Indices	Stable diagonals	Q^*
9 5 - -	LiF–NaCl	11.7 (Q_1)	9 4 - -	LiF–NaBr	12.9 ($Q_1 + Q_2$)
6 4 - -	LiCl– NaBr	1.2 (Q_2)	6 3 - -	LiCl–NaJ	2.6 ($Q_2 + Q_3$)
3 3 - -	LiBr–NaJ	1.4 (Q_3)	- 6 5 -	NaF–KBr	9.2 ($Q_4 + Q_5$)
- 6 4 -	NaF–KCl	7.4 (Q_4)	- 5 6 -	NaCl–KJ	3.6 ($Q_5 + Q_6$)
- 5 5 -	NaCl– KBr	1.8 (Q_5)	- - 3 6	KF–RbBr	2.5 ($Q_7 + Q_8$)
- 4 6 -	NaBr–KJ	1.8 (Q_6)	- - 4 9	KCl–RbJ	1.5 ($Q_8 + Q_9$)
- - 3 3	KF–RbCl	1.9 (Q_7)	9 - 4 -	LiF–KCl	19.1 ($Q_1 + Q_4$)
- - 4 6	KCl– RbBr	0.6 (Q_8)	6 - 5 -	LiCl–KBr	3.0 ($Q_2 + Q_5$)
- - 5 9	KBr–RbJ	0.9 (Q_9)	3 - 6 -	LiBr–KJ	3.2 ($Q_3 + Q_6$)
9	9	9	- 6 - 3	NaF– RbCl	9.3 ($Q_4 + Q_7$)
diagonals	diagonals	diagonals	- 5 - 6	NaCl– RbBr	2.4 ($Q_5 + Q_8$)
			- 4 - 9	NaBr– RbJ	2.7 ($Q_6 + Q_9$)
			12	12	12
			diagonals	diagonals	diagonals

* The thermal effect of the exchange reaction was calculated on the basis of the heats of formation of the salts from the elements. For example:



with the same second index. Finally, in section D of Table 1 we connect the indices pairwise through two cells and through two rows: in this way the diagonals of degree 3 are revealed. It is interesting to note that the thermal effect of a diagonal of degree 3 can be considered as the sum of the thermal effects of diagonals

Table 3

Indices	Stable diagonals	Q	Indices	Stable diagonals	Q
Diagonals of degree 3	Diagonals of degree 3	Diagonals of degree 3	Diagonals of degree 4	Diagonals of degree 4	Diagonals of degree 4
9 3 - -	LiF-NaJ	14.3 ($Q_1 + Q_2 + Q_3$)	9 - 5 -	LiF-KBr	22.1 ($Q_1 + Q_2 + Q_4 + Q_5$)
9 - - 3	LiF-RbCl	21.0 ($Q_1 + Q_4 + Q_7$)	6 - 6 -	LiCl-KJ	6.2 ($Q_2 + Q_3 + Q_5 + Q_6$)
6 - - 6	LiCl-RbBr	3.6 ($Q_2 + Q_5 + Q_8$)	- 6 - 6	NaF-RbBr	11.7 ($Q_4 + Q_5 + Q_7 + Q_8$)
3 - - 9	LiBr-RbJ	4.1 ($Q_3 + Q_6 + Q_9$)	- 5 - 9	NaCl-RbJ	5.1 ($Q_5 + Q_6 + Q_8 + Q_9$)
- 6 6 -	NaF-KJ	11.0 ($Q_4 + Q_5 + Q_6$)	4 diagonals	4 diagonals	4 diagonals
- - 3 9	KF-RbJ	3.4 ($Q_7 + Q_8 + Q_9$)			
6 diagonals	6 diagonals	6 diagonals			

of degree 2 with the same first index and diagonals of degree 1 with the same second index. In a similar way the total thermal effect is found for diagonals of degree 4 and the other higher degrees.

Table 4

Indices	Stable diagonals	Q	Components of the thermal effects
Diagonals of degree 6	Diagonals of degree 6	Diagonals of degree 6	Diagonals of degree 6
9 - 6 -	LiF-KJ	23.3	$Q_1 + Q_2 + Q_3 + Q_4 + Q_5 + Q_6$
- 6 - 9	NaF-RbJ	14.4	$Q_4 + Q_5 + Q_6 + Q_7 + Q_8 + Q_9$
6 - - 9	LiCl-RbJ	7.7	$Q_2 + Q_3 + Q_5 + Q_6 + Q_7 + Q_8$
9 - - 6	LiF-RbBr	24.6	$Q_1 + Q_2 + Q_4 + Q_5 + Q_8 + Q_9$
4 diagonals	4 diagonals	4 diagonals	4 diagonals

Indices	Stable diagonals	Q	Components of the thermal effects
Diagonals of degree 9 9 - - 9	Diagonals of degree 9 LiF–RbJ	Diagonals of degree 9 28.7	Diagonals of degree 9 $Q_1 + Q_2 + Q_3 + Q_4 + Q_5 + Q_6 + Q_7 + Q_8 + Q_9$
1 diagonal	1 diagonal	1 diagonal	1 diagonal

degrees. For the first time, such a rule for stable diagonals in prisms of the first kind was derived by V. I. Posypaiko ⁴.

It remains to mention the last, most stable diagonal, with indices 9—9. The heat effect of the exchange reaction corresponding to it is equal to the sum of all nine heat effects of the diagonals of the 1st degree.

Thus, among the 36 stable diagonals of a septenary reciprocal system of type 16 C, we have 9 diagonals of the 1st degree, 12 diagonals of the 2nd degree, 6 diagonals of the 3rd degree, 4 diagonals of the 4th degree, 4 diagonals of the 6th degree, and 1 diagonal of the 9th degree. Diagonals of the 5th, 7th, and 8th degrees are absent.

The arrangement of diagonals of different degrees in the scheme of a singular star requires special consideration.

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CITED LITERATURE

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- ³ E. A. Alekseeva, N. S. Dombrovskaya, *ZhNKh*, **6**, No. 9 (1961).
- ⁴ V. I. Posypaiko, *ZhFKh*, **36**, No. 11 (1962).

Note: Figure translations are in progress. See original paper for figures.

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