General topological analysis of reciprocal chemical systems. I.
Simple eutectic systems and systems with compounds

M. MALINOVSKÝ

Department of Inorganic Technology, Slovak Technical University, 880 37 Bratislava

Received 29 July 1976

Accepted for publication 19 November 1976

Dedicated to Professor RNDr PhMr S. Škramovský, DrSc, on his 75th birthday

The topological analysis of phase diagrams for reciprocal chemical systems has been carried out. The number of structure components and the number of elementary crystallization spaces for irreversible reciprocal simple eutectic systems as well as for systems containing congruently melting compounds were determined.

A topological analogy has been found to exist between irreversible reciprocal systems and additive systems containing congruently melting compounds.

Работа занимается общим топологическим анализом диаграмм состояния взаимных химических систем. Было определено число структурных составляющих и число элементарных пространств кристаллизации как для необратимых взаимных простых эвтектических систем, так и для систем с химическими соединениями, плавящимися конгруэнтно.

Было найдено, что существует топологическая аналогия между необратимыми взаимными системами с простой эвтектикой и аддитивными системами, которые содержат химические соединения, плавящиеся конгруэнтно.

In previous papers [1—5] additive chemical systems have been subjected to general topological analysis. The present paper deals with some categories of irreversible reciprocal systems without any solubility in the solid state.

Irreversible reciprocal systems of the simple eutectic type

Determination of the number of structure components

The ternary system of this type is schematically shown in Fig. 1. The concentration connection line MA—NB has the character of a stable diagonal (of a quasi-binary system). The point R is the van Rijn point [6]; the points E_1 and E_2

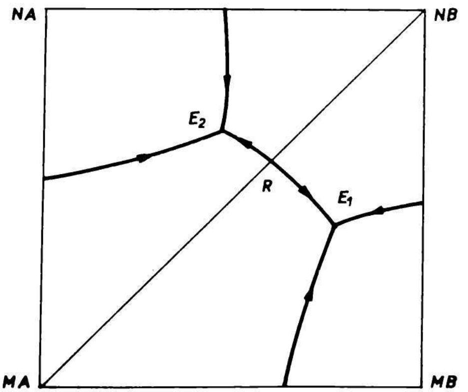

Fig. 1. Projection of the isobaric phase diagram of the ternary reciprocal irreversible system M, N || A, B in the direction of the temperature axis on the concentration square of the system.

are ternary non-variant eutectic points. The presence of the stable diagonal MA—NB means that the equilibrium

$$\mathrm{MA} + \mathrm{NB} \rightleftarrows \mathrm{MB} + \mathrm{NA}$$

is entirely shifted in favour of the formation of the substances MA and NB.

In the triangle MA—MB—NB (see Fig. 1) there exist the following structure components of the first order: the phases MA, MB, NB. If their number is $(Z_k^i)_1$ (i being the order, k the number of components of the system), then it holds

$$(Z_3^1)_1 = C_3^1 = 3 .$$

(The symbol C_3^1 represents the number of combinations of the structure components of the first order.)

The structure components of the second order are: MA + MB, MA + NB, and MB + NB; thus

$$(Z_3^2)_1 = C_3^2 = 3 .$$

Finally, there exists a single structure component of the third order, *viz.*, the ternary eutecticum MA + MB + NB

$$(Z_3^3)_1 = C_3^3 = 1 .$$

In the triangle MA—NA—NB several new structure components appear, *viz.*, the phase NA, the binary eutectica MA + NA and NA + NB, and the ternary eutecticum MA + NA + NB.

Consequently

$$(Z_3^1)_2 = C_{3-1}^{1-1} = C_2^0 = 1 ,$$

$$(Z_3^2)_2 = C_{3-1}^{2-1} = C_2^1 = 2 ,$$

$$(Z_3^3)_2 = C_{3-1}^{3-1} = C_2^2 = 1 \, .$$

After summation we obtain

$$Z_3^1 = (Z_3^1)_1 + (Z_3^1)_2 = C_3^1 + C_2^0 = 4 \, ,$$

$$Z_3^2 = (Z_3^2)_1 + (Z_3^2)_2 = C_3^2 + C_2^1 = 5 \, ,$$

$$Z_3^3 = (Z_3^3)_1 + (Z_3^3)_2 = C_3^3 + C_2^2 = 2 \, .$$

The quaternary system of this type is shown in Fig. 2.

A quaternary system of this type is obtained by adding another component C to the former system, forming with all basic components of the former system simple eutectic systems. Analogically, as in the foregoing case, we find that

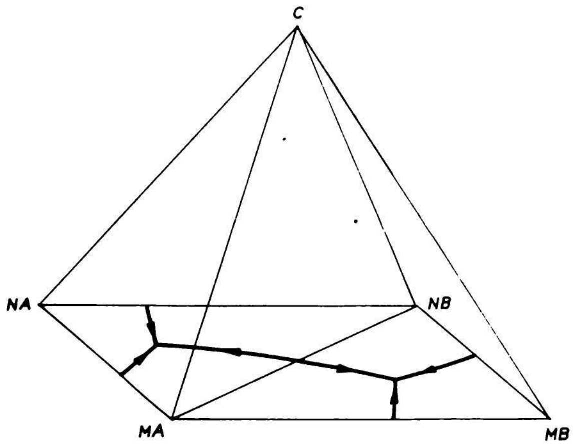

Fig. 2. Tetrahedral concentration pyramid of the irreversible quaternary reciprocal system MA, MB, NA, NB, C.

$$Z_4^1 = C_4^1 + C_3^0 = 4 + 1 = 5 \, ,$$

$$Z_4^2 = C_4^2 + C_3^1 = 6 + 3 = 9 \, ,$$

$$Z_4^3 = C_4^3 + C_3^2 = 4 + 3 = 7 \, ,$$

$$Z_4^4 = C_4^4 + C_3^3 = 1 + 1 = 2 \, .$$

This procedure may be generalized.

From the numbers representing the number of structure components, we obtain with respect to their order and the number of the components of the system, a characteristic triangle (Table 1). For the number of structure components of the i-th order of a k-component system the relation holds

Table 1
Characteristic triangle for reciprocal systems of the simple eutectic type

	Order of structure components					
k	*1*	*2*	*3*	*4*	*5*	*6*
3	4	5	2	—	—	—
4	5	9	7	2	—	—
5	6	14	16	9	2	—
6	7	20	30	25	11	2

$$Z_k^i = C_k^i + C_{k-1}^{i-1} \qquad (1)$$

and for their sum

$$\sum_1^k Z_k^i = 2^k - 1 + 2^{k-1} = 3 \cdot 2^{k-1} - 1\ . \qquad (2)$$

Determination of the number of elementary crystallization spaces

This number apparently equals the number of permutations of the really coexisting solid phases. Thus

$$\Sigma E = Z_k^k \cdot (k)! = 2 \cdot (k)! \qquad (3)$$

We easily will find that the results are the same as obtained in the case of systems with one congruently melting compound (see [2]). Thus we come to the interesting conclusion: *Reciprocal irreversible systems of simple eutectic type without compounds are topological analogues of additive systems with one compound with a congruent melting point.*

Irreversible reciprocal systems without solid solutions containing binary compounds with a congruent melting point

Determination of the number of structure components

The simplest system of this type, containing two compounds with a congruent melting point is shown in Fig. 3.

Analogically as in the foregoing paragraph, we will find the following relations

$$Z_3^1 = 6\,; \quad Z_3^2 = 9\,; \quad Z_3^3 = 4\ .$$

If the system of the considered type contains b compounds, it holds

$$Z_3^1 = 4 + b\,; \quad Z_3^2 = 5 + 2b\,; \quad Z_3^3 = 2 + b\ .$$

These results may be arranged in the following way

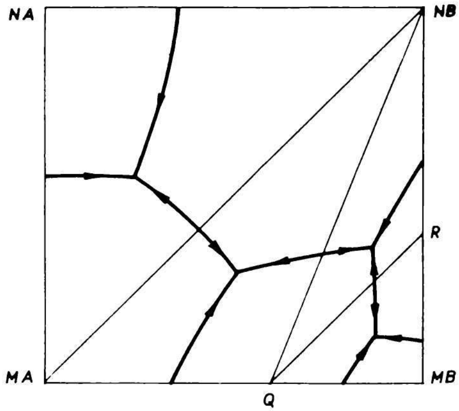

Fig. 3. Projection of the isobaric phase diagram of the ternary reciprocal irreversible system M, N || A, B in the direction of the temperature axis on the concentration tetrahedron of the system. The system contains the congruently melting binary compounds Q and R.

$$Z_3^1 = 3 + (b+1); \quad Z_3^2 = 3 + 2(b+1); \quad Z_3^3 = 1 + (b+1).$$

By substitution of $(b+1) = a$, we obtain

$$Z_3^1 = 3 + a; \quad Z_3^2 = 3 + 2a; \quad Z_3^3 = 1 + a.$$

These numbers correspond to the row for $k = 3$ of the characteristic triangle for the determination of the number of structure components of the systems with a congruently melting compounds (Table 2). For details see paper [3]. Thus it holds

$$Z_k^i = C_k^i + (b+1) \cdot C_{k-1}^{i-1}, \tag{4}$$

$$\Sigma Z_k^i = (b+3) \cdot 2^{k-1} + 1. \tag{5}$$

Consequently we again find that reciprocal irreversible systems with b binary compounds are topological analogues of additive systems with a number of $(b+1)$ binary compounds (the compounds considered are always congruently melting compounds).

Table 2

Characteristic triangle for simple eutectic additive systems with a congruently melting binary compounds

k	Order of structure components					
	1	*2*	*3*	*4*	*5*	*6*
2	$2 + a$	$1 + a$	—	—	—	—
3	$3 + a$	$3 + 2a$	$1 + a$	—	—	—
4	$4 + a$	$6 + 3a$	$4 + 3a$	$1 + a$	—	—
5	$5 + a$	$10 + 4a$	$10 + 6a$	$5 + 4a$	$1 + a$	—
6	$6 + a$	$15 + 5a$	$20 + 10a$	$15 + 10a$	$6 + 5a$	$1 + a$

Determination of the number of elementary crystallization spaces

On the basis of the above presented law of topological analogy it holds

$$\Sigma E = (b + 2) \cdot (k)! \qquad (6)$$

Conclusion

The existence of a relationship and a similarity between irreversible reciprocal systems on the one hand and additive systems containing congruently melting compounds, on the other, has been demonstrated. It will be the object of further studies to search for still other examples of topological analogy.

References

1. Malinovský, M., *Chem. Zvesti* ***12,*** 3 (1958).
2. Malinovský, M., *Chem. Zvesti* ***12,*** 83 (1958).
3. Malinovský, M., *Chem. Zvesti* ***23,*** 401 (1969).
4. Malinovský, M., *Chem. Zvesti* ***23,*** 409 (1969).
5. Malinovský, M., *Chem. Zvesti* ***28,*** 478 (1974).
6. Anosov, Yu. V. and Pogodin, S. A., *Osnovnye nachala fiziko-khimicheskogo analiza.* (Fundamentals of Physicochemical Analysis.) P. 572. Publishing House of the Academy of Sciences USSR, Moscow—Leningrad, 1947.

Translated by T. Guttmannová