The mutually attainable spaces of concentration polyhedra of multicomponent condensed systems*

[a]M. MALINOVSKÝ and [b]S. SVOBODOVÁ-KAŠÍKOVÁ

[a]*Department of Inorganic Technology, Slovak Technical University, 880 37 Bratislava*

[b]*Department of Ferrous Metallurgy and Coke Production, Technical University of Mining and Metallurgy, 701 00 Ostrava*

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The paper discusses the possibility of the determination of parts of the concentration polyhedra of reciprocal systems corresponding to mixtures that may be synthesized if not all the fundamental constituents of the considered systems are at disposal.

A general solution of the problem is presented and the practically important problem of synthesizing the quaternary reciprocal systems formed by fluorides and chlorides of sodium, magnesium, and aluminium has been solved for the case, when one or two fundamental constituents of the system are not available.

1. Introduction

In the experimental investigation of multicomponent systems it may occur that one or even more of the fundamental constituents** of the given k-component system are not easily attainable or they have some properties complicating work with them (*e.g.* hygroscopy).

When considering an ordinary system, it is evident that under these circumstances its investigation becomes difficult or sometimes even impossible. Another problem arises, however, when a reciprocal system is under consideration. In this case it is possible to "synthesize" certain parts of the concentration polyhedron of the given reciprocal system even though some of the fundamental constituents are not at our disposal.

Since most of the problems of the applied character and many theoretical questions do not require an investigation of the concentration polyhedron as a whole, but only of some of its parts, the discussed problems are without doubt very topical.

The analysis shows that in the given case there may arise two different problems:

A. The problem of preparing a system that should have a required phase composition in the solid state. In this case it is not indifferent how the individual substances or their

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** A fundamental constituent is the chemical substance, the figurative point of which is situated on some of the vertices of the concentration polyhedron of the given system. In the case of reciprocal systems the number of fundamental constituents is always greater than that of the components.

subelements (*e.g.* ions) react together in the process of solidification. The solution of this problem requires also the knowledge of the nature of the given system (whether it is a reversibly or irreversibly reciprocal system, *etc.*).

B. The problem of preparing a system with a required chemical composition in the liquid state. This case is important in the experimental investigation of all the parameters in the liquid phase (density, electrical conductivity, viscosity, *etc.*) as well as in studying the diagram of the liquidus of systems of the given chemical composition. In all these cases the phase composition of the system after its solidification is not substantial and the knowledge of the character of interactions between the constituents of the system is not necessary.

We will direct our attention to the problem *ad B* and analyze a system that is closed with respect to its mass.

2. General part

2.1. Ternary reciprocal systems

The concentration polygon is a square, the vertices of which correspond to the figurative points of four fundamental constituents (Fig. 1). Thus, if no reduction of the system order should take place, only one of these constituents, *e.g.* MA, might be inaccessible.

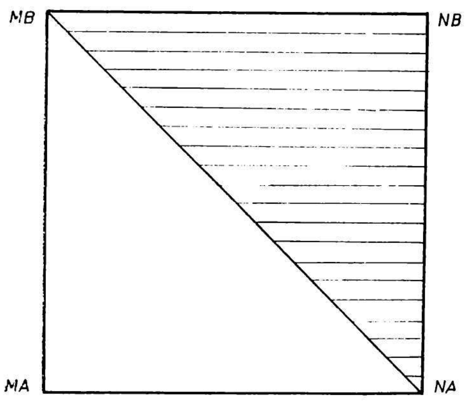

Fig. 1. Concentration square of the ternary reciprocal system M,N || A,B. The mutually attainable triangle MB—NA—NB is marked by hatching.

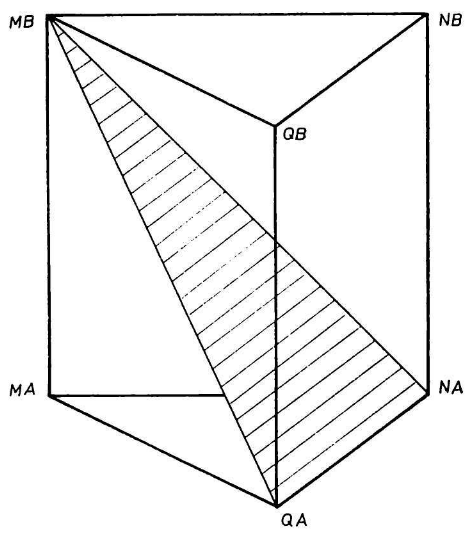

Fig. 2. The concentration triangular prism of the quaternary reciprocal system M,N,Q || A,B. The planar (triangular) concentration diagonal MB—NA—QA, separating the mutually attainable formations from the unattainable ones is marked by hatching.

Then the mutually accessible polygon is the concentration triangle MB—NA—NB with all its subsystems. The remaining parts of the concentration square M,N || A,B are mutually inaccessible in the given case.

2.2. Quaternary reciprocal systems

Let us consider the system M,N,Q || A,B (M,N,Q are cations, A, B anions). This system has $3 \cdot 2 = 6$ fundamental constituents, the figurative points of which are situated on the vertices of the triangular concentration prism (Fig. 2).

2.2.1. One of the fundamental constituents is inaccessible — MA

The mutually attainable space formation, the melts of which may be prepared from the remaining five constituents, is the concentration pentahedron MB—NB—QB—NA—QA (Fig. 2) and all its subsystems of lower order. The concentration tetrahedron MA—MB—NA—QA is evidently a mutually inaccessible formation.

If we choose equal lengths for all the edges of the concentration prism and denote them a, then the volume of this prism is equal to $a^3 \sqrt{3}/4$, while the volume of the mutually attainable concentration pentahedron is $a^3 \sqrt{3}/6$. The volume of the pentahedron takes two thirds of the total volume. The ratio between these two volumes is proportional to the probability of the possibility of preparing any melt belonging to the given system using the five remaining fundamental constituents.

2.2.2. Two of the fundamental constituents are inaccessible

2.2.2.1. Both inaccessible constituents have a common subelement

a) Both inaccessible constituents belong to the true ternary system as well as to one of the ternary reciprocal systems (*e.g.* MA and NA, with a common subelement A) (Fig. 3).

If only one fundamental constituent, MA, would be inaccessible, the mutually unattainable formation would be the tetrahedron MA—MB—NA—QA. If the inaccessible constituent would be NA, the unattainable formation would be the tetrahedron MA—NA—NB—QA. If both constituents, *viz.* MA and NA are inaccessible at the same time, the principle of superposition is not applicable since the total area of the reciprocal ternary system M,N || A,B is unattainable. Therefore only the regular tetrahedron MB—NB—QB—QA is a mutually attainable formation, the volume of which equals 1/3 of the volume of the concentration prism.

b) Both inaccessible constituents belong to one of the ternary reciprocal systems which form one of the faces of the discussed polyhedron (*e.g.* MA and MB with a common subelement M) (Fig. 3). In this case the subelement M is completely missing in the resulting system. Therefore the remaining system degenerates to a system lower by one order than that of the original system, *i.e.* in the given case to the ternary reciprocal system N,Q || A,B.

2.2.2.2. The two inaccessible fundamental constituents have no common subelement (*e.g.* MA and NB) (Fig. 4)

In this case all the original subelements remain in the system. The mutually unattainable formations are the tetrahedra MA—MB—NA—QA and MB—NB—NA—QB. Without using the constituents MA and NB only the tetrahedron MB—NA—QA—QB is attainable and its volume is equal to 1/3 of that of the original concentration prism.

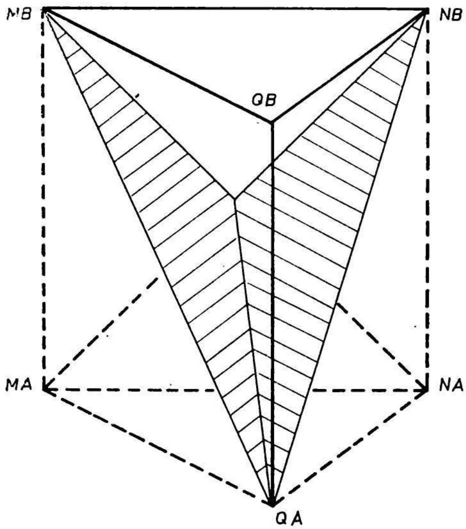

Fig. 3. The concentration triangular prism of the quaternary reciprocal system M,N,Q || A,B, with the marked planar concentration diagonals MA—NB—QA and MB—NA—QA.

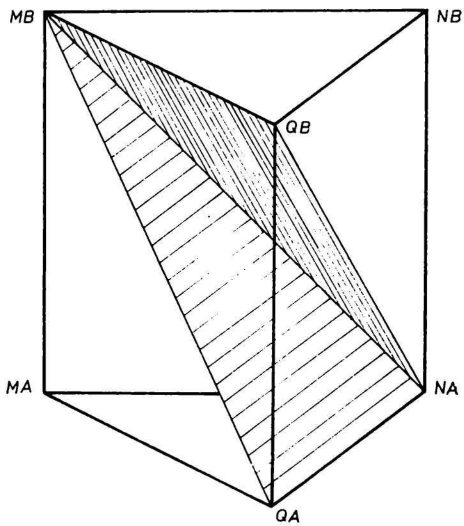

Fig. 4. The concentration triangular prism of the quaternary reciprocal system M,N,Q || A,B. Hatching marks the two tetrahedra MA—MB—NA—QA and MB—NB—NA—QB that are mutually unattainable if the fundamental constituents MA and NB are not available.

The case, when three fundamental constituents are inaccessible, results in a degeneration of the original system to one of lower order; therefore this case is of no interest for the given investigation.

3. Application

It is known that the so-called "classical" electrolyte for aluminium production consists of an active component — aluminium oxide — and of a molten medium represented by cryolite with additions of aluminium and calcium fluorides. In order to improve the properties of the aluminium electrolyte different additives were tested. As most promising there have been found the additives containing Mg^{2+}, Li^{+}, and Cl^{-} ions [1, 2].

Let us consider the addition of the ions Mg^{2+} and Cl^{-} to the "classical" electrolyte. The resulting melt apparently belongs to the quaternary reciprocal system Na,Mg,Al || || F,Cl (Fig. 5). The problem is to determine the limiting composition of molten mixtures that can be synthesized when one or two constituents of this system are not accessible.

3.1. One of the fundamental constituents is inaccessible

Let us suggest first that $MgCl_2$ is the inaccessible substance. The question is, to what concentration of this substance the melts belonging to the binary system Na_3AlF_6—$MgCl_2$ and to the system Na_3AlF_6—AlF_3—$MgCl_2$ may be prepared, the latter being interesting with respect to industrial application.

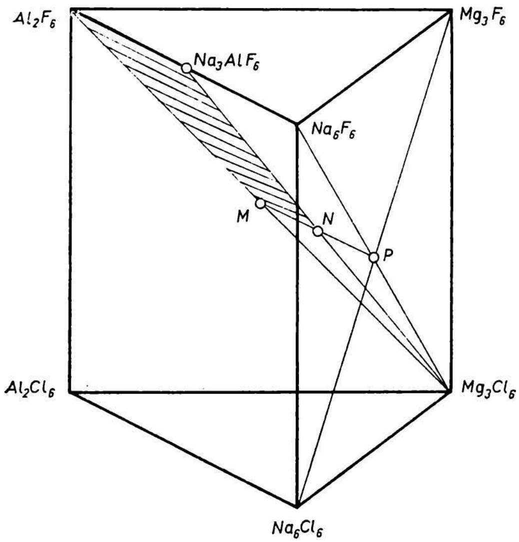

Fig. 5. The concentration triangular prism of the quaternary reciprocal system Na,Mg,Al || F,Cl. The connection line of Na_3AlF_6—Mg_3Cl_6 and the mutually attainable part of the inner concentration triangle Al_2F_6—Na_3AlF_6—Mg_3Cl_6 are marked for the case that the fundamental constituent $MgCl_2$ is not available.

The mutually unattainable formation is a tetrahedron, *viz.* Mg_3Cl_6—Na_6Cl_6—Al_2Cl_6—Mg_3F_6. The concentration triangle of the system Na_3AlF_6—AlF_3—$MgCl_2$ penetrates into this formation with its part M—N—$MgCl_2$. Therefore it appears necessary to determine the position of the points M and N in the concentration prism of the original system.

The point M is identical with the point of intersection of the diagonals Mg_3F_6—Al_2Cl_6 and Al_2F_6—$MgCl_6$. Thus the melt, the figurative point of which corresponds to the point M, contains 40 mole % AlF_3 and 60 mole % $MgCl_2$.

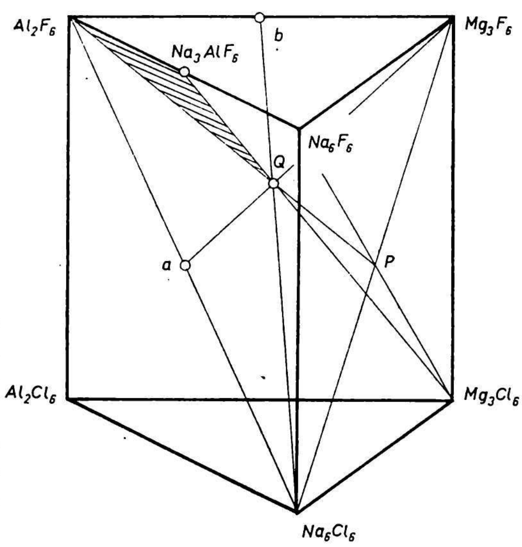

Fig. 6. The concentration triangular prism of the quaternary reciprocal system Na,Mg,Al || F,Cl. The marked inner concentration triangle Al_2F_6—Na_3AlF_6—Q corresponds to the mixtures which can be prepared in case the two fundamental constituents, $MgCl_2$ and $AlCl_3$, are not available.

The position of the point N may be found by geometrical or analytical methods. In the geometrical construction the fact may be used that the mutually unattainable triangle is a part of the triangle $Al_2F_6-Na_6F_6-Mg_3Cl_6$ intersecting the concentration triangle $Mg_3F_6-Al_2Cl_6-Na_6Cl_6$ on the straight line segment MP (Fig. 5). Therefore the point N is identical with the point of intersection of the segment MP and the straight line joining the figurative points of Na_3AlF_6 and $MgCl_2$.

In the analytical determination the circumstance may be applied that the point N is situated in the area of the triangle $Mg_3F_6-Al_2Cl_6-Na_6Cl_6$ and at the same time on the line joining Na_3AlF_6 and $MgCl_2$. The melt corresponding to the composition of the point N may be prepared in the following way:

$$x\mathrm{Mg_3F_6} + y\mathrm{Al_2Cl_6} + z\mathrm{Na_6Cl_6} = a\mathrm{Na_3AlF_6} + b\mathrm{MgCl_2}.$$

We can easily find that $x = 2$, $y = z = 1$, $a = 2$, $b = 6$. Thus the melts of the system $Na_3AlF_6-MgCl_2$ can be realized up to the concentration of 75 mole % $MgCl_2$, without requiring this chloride to be the starting substance, provided the remaining five substances are available.

3.2. Two of the fundamental constituents are inaccessible

Let us suggest that these two substances are $AlCl_3$ and $MgCl_2$ so that we have only the substances AlF_3, MgF_2, NaF, and NaCl at our disposal. It is evident that this case is very important not only from the aspect of laboratory work, but also from the point of view of industrial utilization.

Our interest is directed again to the point on the connection line of $Na_3AlF_6-MgCl_2$ with the maximum possible content of $MgCl_2$. This point, let us denote it Q, is the point of intersection of the connection line $Na_3AlF_6-MgCl_2$ and the plane determined by the figurative points Al_2F_6, Mg_3F_6, and Na_6Cl_6 (Fig. 6).

The point Q can be synthesized from equal amounts of Al_2F_6, Na_6Cl_6, and Mg_3F_6. Thus it is situated in the point of intersection of the connection lines a — Mg_3F_6 and b — Na_6Cl_6, where point a divides the concentration line segment $Al_2F_6-Na_6Cl_6$ into two equal parts and the point b lies in the half of the concentration segment $Al_2F_6-Mg_3F_6$. The point Q lies, however, also on the connection line of $Na_3AlF_6-Mg_3Cl_6$, which is divided by it in the ratio of 1 : 2 as the equation shows

$$\mathrm{Al_2F_6} + \mathrm{Mg_3F_6} + \mathrm{Na_6Cl_6} = 2\mathrm{Na_3AlF_6} + \mathrm{Mg_3Cl_6} = 2\mathrm{Na_3AlF_6} + 3\mathrm{MgCl_2}.$$

Consequently the melts of the system $Na_3AlF_6-MgCl_2$ may be realized up to the concentration of 60 mole % $MgCl_2$ using only the substances AlF_3, MgF_2, and NaCl.

References

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