Azeotropic Phase Equilibrium Diagrams: A Survey

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An analysis of the structural properties of vapor-liquid equilibrium (VLE) diagrams provides a fundamental understanding of the thermodynamic behavior of azeotropic mixtures upon distillation.

In addition to a review of well-known fundamental work on the analysis of VLE diagrams, this survey comprises less known published results, especially from the Russian literature. Some new results are also presented for the first time.

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1 Introduction

Distillation, where a liquid mixture is separated by successive evaporation and condensation, is the most important separation process in the chemical industry. The basis for the separation is that the vapor phase is richer in the more volatile components than the liquid. This enrichment is determined by the vapor-liquid phase equilibrium. As a result, feasible separations in distillation columns and the operating parameters required for these separations depend on the vapor-liquid equilibrium of the mixture to be separated.

For ideal and nearly ideal mixtures the components can be ranked in order of their volatility, or, equivalently, in order of the pure components boiling points, and one can easily list all feasible separation sequences. In practice, we often have to deal with nonideal mixtures where the composition space is split into regions with different volatility order of the components, and the identification of feasible sequences is much more difficult. Furthermore, azeotropic behavior is often encountered where at some point(s) in the composition space the equilibrium vapor and liquid mixture compositions are equal for a given pressure and temperature. These points are called azeotropes and mixtures with this phenomena are called azeotropic mixtures. The highly nonlinear vapor-liquid equilibrium behavior of azeotropic mixtures complicates the prediction of feasible separation sequences further.

An azeotrope itself cannot be separated by ordinary distillation since no enrichment of the vapor phase occurs at this point. Usually, special methods are required.

Azeotropic distillation is defined as distillation that involves components that form azeotropes. Generally, there are two cases of azeotropic distillation: 1) where the original mixture to be separated is an azeotropic mixture, and, 2)where an azeotropic mixture is formed deliberately by adding one or more azeotrope-forming components to the original mixture. In the first case we have to find a way to separate the azeotropic mixture and obtain the desired product specifications and recovery. In the second case, in addition, we have to select an azeotrope-forming component (called entrainer) that is effective for the desired separation and easily recovered afterwards. In either case we should establish the options before analyzing them in detail. For this purpose we need a tool to qualitatively predict the feasible separations of multicomponent azeotropic mixtures. The tool is known as *thermodynamic topological analysis of distillation* (in Russian literature) or *residue curve (or distillation line) map analysis*. It provides an efficient way for preliminary analysis of nonideal distillation problems and presynthesis of separation sequences.

Thermodynamic Topological Analysis

The thermodynamic topological analysis is based on the classical works of Schreinemakers (1901*b*; 1901*c*; 1902) and Ostwald (1902), where the relationship between the vapor-liquid equilibrium of a mixture and the behavior of open evaporation *residue curves* for ternary mixtures was established. Although open evaporation (a single vaporization step with no reflux) itself is not of much industrial interest in the 21st century, it nevertheless forms an important basis for the understanding of distillation (a sequence of partial vaporization steps with reflux). The findings by Schreinemakers did not receive recognition until the 1940s when Reinders and de Minjer (1940) and Ewell and Welch (1945) showed the possibility to use this approach to predict the behavior of batch distillation. These achievements stimulated subsequent investigations by Haase and Lang (1949; 1950*a*; 1950*b*; 1951) and Bushmakin *et.al.* (1957; 1957) on the structure of phase equilibrium diagrams and its connection with batch distillation behavior. In 1958, Gurikov (1958) formulated the *Rule of azeotropy* and proposed a classification of ternary mixtures based on their thermodynamic topological structures (that is, *residue curve map analysis*).

In the late 1960s, Zharov (1967; 1968*c*) gave a more rigorous mathematical foundation of the residue curve map analysis and expanded it to multicomponent mixtures. During the same period, Serafimov

(1968*a*; 1968*d*) proposed to use structural information of VLE diagrams to predict feasible separations in continuous distillation. The results of Zharov and Serafimov initiated a large effort in Russia (USSR) on the development and application of qualitative analysis of multicomponent nonideal and azeotropic distillation. One reason for this large interest in this "pen-and-paper" approach in Russia in the 1960s and 70s was the fact that during these years the Russian chemical industry expanded whereas there was a shortage of computers and limited possibilities for numerical computation.

The contribution of Doherty and Perkins and co-workers (1978*a*; 1978*b*; 1979*a*; 1979*b*; 1985*a*; 1985*b*; 1985; 1985) formed the basis for a renewed interest in this subject also in the West. The reason for this renewed interest was the realization that, in spite of (or maybe because of) the great advances in vapor-liquid equilibrium calculations and simulations, there was a need for simpler tools to understand the fundamental limitations and possibilities in distillation of azeotropic mixtures. These tools are today well-established, and residue curve map analysis is included in the main recent encyclopedia in chemical engineering (Perry, 1997; Stichlmair, 1988; Doherty and Knapp, 1993). Four review papers have been published during the last few years (Pöllmann and Blass, 1994; Fien and Liu, 1994; Widagdo and Seider, 1996; Westerberg and Wahnschafft, 1996). Furthermore, the topic is treated in recent textbooks (Biegler *et al.*, 1997; Seader and Henley, 1998; Stichlmair and Fair, 1998; Doherty and Malone, 2001) as a fundamental part of chemical engineering.

Nevertheless, the field is still rather bewildering and we believe that many of the recent results have not been put into proper perspective and compared to earlier work, especially to work in the Russian literature. The main objective of this paper is therefore to present a broad survey of the field, which includes references also to papers that are less recognized in the English-language literature.

The theory of thermodynamic topological analysis (TTA) of distillation can be divided into two parts.

1. The first considers in detail the feasible structures of VLE diagrams (including their classification). The main concept is that there is a unique and relatively simple correspondence between the vapor-liquid equilibrium characteristics of a given mixture and the path of equilibrium phase transformations such as residue curves and distillation lines.

2. The second part of the TTA is directed to the prediction of feasible separations in distillation, for which the main concepts are:

    - There is a unique correspondence between the state of a distillation column at extreme operating conditions (infinite flows or infinite stages) and the composition trajectories of simple phase transformations like residue curves. Consequently, these column states can be determined from specific VLE characteristics of the mixture to be separated depending on the feed composition of the mixture.
    - The state of a distillation column at real operating conditions can be qualitatively determined from the column states at extreme operating conditions, that is, from the composition trajectories of the simple equilibrium phase transformations such as residue curve maps.
    - As a result, the product composition areas for all combinations of the operating parameters can be predicted qualitatively based on information about the simple phase transformation map (distillation line or residue curve map) and, thus, the feasible separations and separation sequences can be determined.

Therefore, analysis of VLE diagrams is the starting point for the prediction of feasible separations by distillation. It allows us to determine the thermodynamic possibilities and limitations of the separation caused by the nature of the mixture. After determining the feasible separations, we can synthesize the alternative separation sequences that should be subject to further investigation and comparison in order to choose the appropriate one. Such an approach is called analysis-driven distillation synthesis (Westerberg and Wahnschafft, 1996). As a result of the analysis it may turn out that the mixture cannot be separated by conventional distillation. Then, special distillation methods may be employed. TTA (or residue curve map analysis) also provides a tool for the evaluation of these separation techniques. In particular, TTA is very useful for the screening of entrainers for heteroazeotropic and extractive distillation (see, for example, Hilmen (2000)).

Comment on terminology

There are many alternative and even conflicting terms in the distillation literature. Table 1 gives the correspondence between four central terms in the English-language, Russian and German literature. Note in particular that in many Russian publications "distillation lines" means residue curves, "c-lines" means distillation lines and "node" means vector. One reason for this incompatible terminology is due to the historical fact that the term distillation was originally used to denote simple distillation (open evaporation or Rayleigh distillation). Schreinemakers (1901*b*) and succeeding researchers used the term "distillation lines" as a short term for distillation line of the residue, which was later termed *residue curves* by Doherty and Perkins (1978*a*). Today, the term distillation has in English become synonymous with fractional distillation with reflux. Stichlmair (1988) uses the term *distillation line* to denote the total reflux composition profile in an equilibrium staged distillation column. The term "node" is just a result of poor translation from Russian to English. In the present text we use the terms that are broadly accepted in English-language publications. See also list Definitions of Terms given in the back of this paper for more detail.

Table 1: *Correspondence between English, Russian and German terms in the distillation literature*

Current terms commonly found in English-language literature (and in this paper)	Equivalent terms mainly found in Russian- and German-language literature	Example of reference where this term is used
equilibrium vector	tie-line	Zharov and Serafimov (1975)
	node line	Serafimov (1996)
	mapping vector	Widagdo and Seider (1996)
distillation line (continuous and discrete)	connecting line (c-line)	Zharov (1968*c*)
	chain of conjugated tie-lines	Zharov (1968*c*)
	tie-line curve	Westerberg (1997)
	equilibrium rectification line	Pelkonen *et al.* (1997)
residue curve	distillation line of the residue	Schreinemakers (1901*c*)
	residue curve	Ostwald (1902)
	distillation line	Serafimov (1968*b*)
distillate curve	distillation line of the vapor	Schreinemakers (1901*b*)
	vapor line	Bushmakin and Kish (1957)
	boil-off curve	Fidkowski *et al.* (1993)

Structure of the survey

This survey is devoted to the first part of thermodynamic topological analysis, that is, to the characteristics of vapor-liquid equilibrium diagrams. The thermodynamic basis of vapor-liquid equilibrium and ways to graphically represent the VLE of a mixture are briefly given in Section 2. The various representations of the VLE for ternary mixtures in particular are considered in detail in the subsequent sections: isotherm maps (Section 3); residue curve maps and open evaporation distillate curve maps (Section 4); open condensation curve maps and distillation line maps (Section 5). These sections also include the structures of these maps and the relationship between the different representations. Some peculiarities of the simple equilibrium phase transformation maps for heterogeneous mixtures are considered in Section 6.

Section 7 is devoted to the classification of VLE diagrams for ternary mixtures and related issues such as completeness of classification, occurrence of the various structure classes in nature, and more. Determination of the VLE diagram structures based on incomplete information is discussed. Section 8 covers unidistribution and univolatility line diagrams and their role in the determination of the geometry (pathway) of the residue curve and distillation line maps. Finally, overall conclusions made from this paper are summarized in Section 9.

Contributions

Fundamental theory on structural properties of VLE diagrams for azeotropic mixtures are reviewed. In addition, some new results and concepts are presented for the first time. In particular:

- A simple *rule on residue curve regions* is formulated: The composition space splits into the same number of residue curve regions as there are repeated nodes in the system. For example, if the residue curve system has two stable nodes and one unstable node, the number of nodes of the same type is two, and the residue curve map is split into two regions.
- The *relative location of the region boundaries* (separatrices) of residue curves, distillate curves and distillation lines in the composition space are presented.
- The thermodynamical meaning of *distillation lines* is emphasized and explained.
- Peculiarities of residue curves for heterogeneous mixtures are examined. Although the topology of the residue curve maps generally do not differ from homogeneous mixtures, and can be determined in a similar way from the shape of the boiling temperature surface, there are some peculiarities of the inner topology of heterogeneous mixtures.
- A table of *correspondence between the different classifications* of ternary VLE diagrams is given. The classifications by Gurikov (1958), Serafimov (1970*b*), Zharov and Serafimov (1975) and Matsuyama and Nishimura (1977) are included.
- The question of the *existence* of all the classified structures is evaluated. Although a structure may be thermodynamically and topologically feasible, its occurrence is determined by the probability of certain combinations of molecular interactions. We present data on the reported *occurrence* of real ternary mixtures, and reveal factors that limit the natural occurrence of mixtures with certain VLE diagram structures.
- The problem of *indeterminacy* in predicting ternary VLE diagram structures based on incomplete information (binary or experimental data only) is critically considered.
- Feasible patterns of the VLE functions for binary mixtures represented by the equilibrium line, distribution coefficients and relative volatility depending on the molecular interactions are presented.
- The structures of *unidistribution and univolatility line diagrams* for ternary mixtures of different classes and types, and the relation to the *shape* of simple equilibrium phase transformation trajectories such as residue curves and distillation lines, are considered in detail. We show that a combined diagram of these unitylines can successfully be used as a characteristic of the VLE. These maps are easy to generate and a lot of information can be retrieved from them.
- Rules on the *location of the inflection point curves* in the composition space are given.

2 Thermodynamic Basis

The fundamental laws of thermodynamics and phase equilibrium are all that is needed to derive the results presented in this paper, and in this section we briefly review the thermodynamic basis. From thermodynamics, the compositions of liquid and vapor in phase equilibrium are determined by the vapor-liquid equilibrium condition which may be expressed as:

$$\boldsymbol{y} \;=\; f(P, T, \boldsymbol{x}) \tag{1}$$

where $\boldsymbol{x}$ and $\boldsymbol{y}$ are the liquid and vapor composition vectors, and P and T are the system pressure and temperature, respectively. P, T and $\boldsymbol{x}$ are not independent at the equilibrium state since:

$$\sum_{i=1}^{n} y_i \;=\; 1 \tag{2}$$

For example, $[T, \boldsymbol{y}]$ may be determined as a function of $[P, \boldsymbol{x}]$. Thus, at *isobaric* conditions we may use only the liquid composition $\boldsymbol{x}$ as the independent variable, and we may write:

$$\boldsymbol{y} = E(\boldsymbol{x}), \qquad T = T_{bp}(\boldsymbol{x}) = T_{dp}(\boldsymbol{y}) \tag{3}$$

where E is the equilibrium mapping function, E-mapping, that assigns a composition in the liquid phase to the corresponding equilibrium vapor phase composition, and T_{bp} and T_{dp} are the mixture boiling temperature (bubble-point) and condensation temperature (dew-point), respectively. Equivalently, we may write:

$$\boldsymbol{x} = C(\boldsymbol{y}), \qquad T = T_{dp}(\boldsymbol{y}) = T_{bp}(\boldsymbol{x}) \tag{4}$$

where $C = E^{-1}$ is the inverse equilibrium mapping function, C-mapping, that assigns a composition in the vapor phase to the corresponding equilibrium liquid phase composition.

For any liquid composition $\boldsymbol{x}$, there is a point $[T, \boldsymbol{x}]$ on the boiling temperature surface $T_{bp}(\boldsymbol{x})$ and a corresponding point $[T, \boldsymbol{y}]$ on the condensation (dewpoint) temperature surface $T_{dp}(\boldsymbol{y})$ that are connected by an equilibrium vector, also called a vapor-liquid tie-line. The projection of this equilibrium vector onto the composition space represents the *equilibrium mapping vector* $\overrightarrow{\boldsymbol{xy}}$, that is, the graph of the function $E : \boldsymbol{x} \rightarrow \boldsymbol{y}$. In this sense, the condensation temperature surface $T_{dp}(\boldsymbol{y})$ is simply an equilibrium E-mapping of the boiling temperature surface $T_{bp}(\boldsymbol{x})$. The two temperature surfaces merge at the points of pure components where $x_i = y_i = 1$ for component i and $x_j = y_j = 0$ for all other components $j \neq i$. According to Gibbs-Konovalov Law formulated in the 1880s (Prigogine and Defay, 1954; Tester and Modell, 1997) the existence of a singular point of the boiling temperature function $T_{bp}(\boldsymbol{x})$ leads to a singular point of the condensation temperature function $T_{dp}(\boldsymbol{y})$. At the singular points, the liquid and its equilibrium vapor compositions are equal and the temperature surfaces are in contact. The existence of such singular points not connected to pure components is called *azeotropy*, and the corresponding compositions where $\boldsymbol{y}$ = $\boldsymbol{x}$ are called *azeotropes*. Mixtures that form azeotropes are called *azeotropic*, and mixtures that do not form azeotropes are called *zeotropic*.

The existence of azeotropes complicates the shape of the boiling and condensation temperature surfaces and the structure of the *vapor-liquid envelope* between them, and the equilibrium mapping functions. The envelope of the equilibrium temperature surfaces defines the operating region in $T - \boldsymbol{x}, \boldsymbol{y}$ space in which any real distillation process must operate. This motivates a more careful analysis of the VLE behavior. For the prediction of feasible separations upon distillation of azeotropic mixtures we need a qualitative characterization of the VLE, preferable a graphical representation.

Graphical VLE representation

The possibility to graphically represent the VLE depends on the number of components in the mixture. In a mixture of n components, the composition space is (n-1)-dimensional because the sum of molefractions must be equal to unity. For binary mixtures the composition space is one-dimensional. Graphical representations of the VLE for the most common types of binary mixtures are presented in Figure 1. The left part of Figure 1 shows a combined graph of the boiling and condensation temperatures and the vapor-liquid equilibrium phase mapping, which gives a complete representation of the VLE. In addition, the right part gives the equilibrium phase mapping alone. Each of these diagrams uniquely characterizes the type of the mixture (zeotropic or azeotropic, minimum- or maximum-boiling etc.), and, what is more important, we do not need the exact trajectories of the functions to make this characterization. It is sufficient to know the boiling points of the pure components and azeotropes, if any, to determine the type of the mixture and to qualitatively predict the distillation behavior for various feed compositions of the mixture.

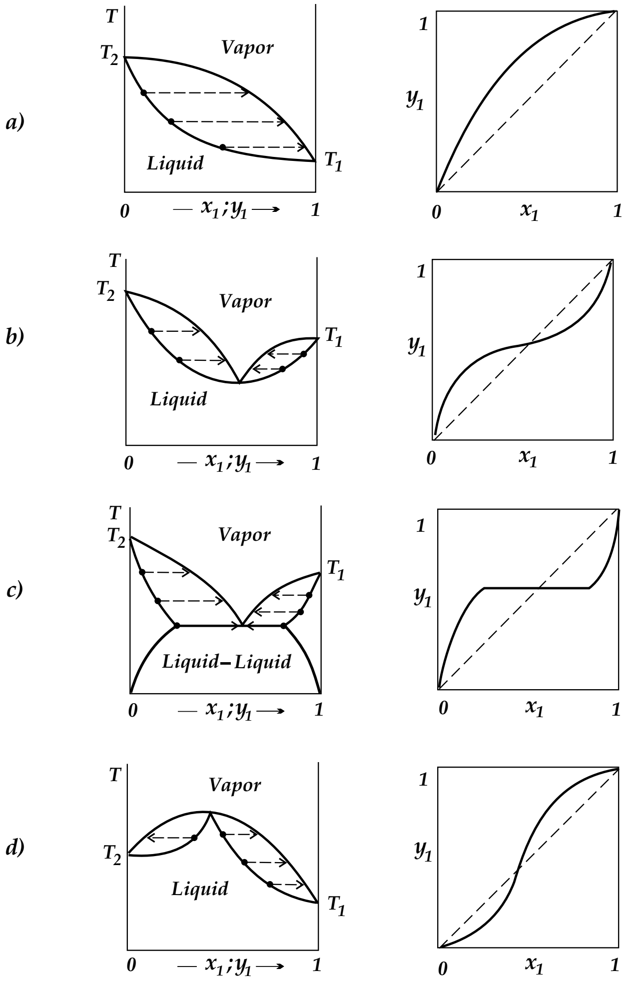

Figure 1: *Graphical representations of the VLE for the most common types of binary mixtures at constant pressure: a) zeotropic; b) minimum-boiling homoazeotrope; c) minimum-boiling heteroazeotrope; d) maximum-boiling azeotrope. Left: boiling temperature* T_{bp} *and condensation temperature* T_{dp} *and the equilibrium mapping vectors in* $T - \boldsymbol{x}, \boldsymbol{y}$ *space. Right:* $\boldsymbol{x} - \boldsymbol{y}$ *relationship (equilibrium line).*

For ternary mixtures the composition space is a two-dimensional normalized space and its graphical representation is an equilateral or rectangular triangle. The VLE functions are surfaces in a three-dimensional prism. The complete representation of the VLE is the vapor-liquid envelope of the boiling and condensation temperature surfaces, and the set of equilibrium vectors between them, as illustrated in Figure 2a. The equilibrium mapping function itself can be represented by pair of the surfaces $y_i(\boldsymbol{x})$ and $y_j(\boldsymbol{x})$ in the prism $Y-X$, as illustrated in Figure 2b. It is difficult to interpret three-dimensional surfaces in a two-dimensional representation, thus other representations are preferred for ternary mixtures. The most straightforward approach is to use contour plots of the surfaces similar to topographic maps with isolines of constant values of the functions to be represented. Such isoline maps, specially isotherm map of the boiling temperature, play an important role in the qualitative analysis of VLE diagrams. Isotherm maps are considered in Section 3.

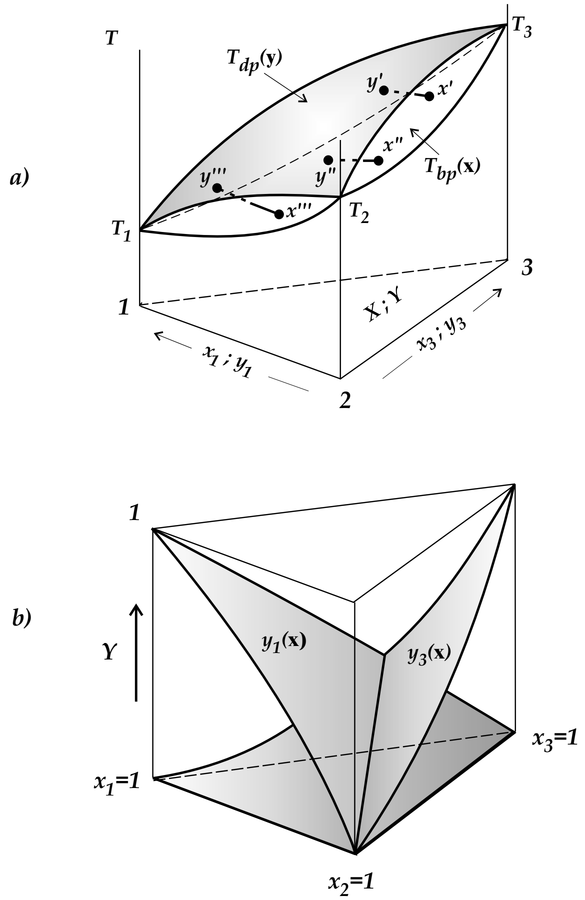

Figure 2: *Graphical representation of the VLE for a ternary zeotropic mixture: a) boiling and condensation temperature surfaces and the connecting equilibrium vectors; b) equilibrium vector surfaces.*

The dependence of the equilibrium vapor composition on the liquid composition given by the equilibrium E-mapping function can be graphically represented by a field of equilibrium vectors in the composition plane. Such vector fields usually appear rather chaotic (see, for example, the equilibrium vector fields for ternary mixtures in Gmehling's ”Vapor-Liquid Equilibrium Data Collection”). They do not give a clear graphical representation of the VLE. In addition, this representation has the disadvantage of being discrete and requires a great number of (experimental) data to draw it.

An alternative method to graphically represent the VLE for a given mixture is by using *simple equilibrium phase transformations* such as open evaporation, open condensation and repeated equilibrium phase mapping. The liquid and vapor composition changes during these transformations can be represented by trajectories in the composition space. The pathway of these trajectories depends on the vapor-liquid equilibrium only, and in turn characterizes the VLE. This is the topic of Sections 4 and 5.

For multicomponent mixtures ($n \geq 4$) the composition space is (n-1)-dimensional and its graphical image is a polyhedron (tetrahedron for $n = 4$, pentahedron for $n = 5$ and so on). In the case of quaternary mixtures it is possible to graphically represent the VLE functions in a composition tetrahedron, but it may be complicated to interpret. If the number of components is more than four, graphical representation is difficult. However, a multicomponent mixture may be divided into ternary (or even binary) subsystems of components and pseudo-components, and the ternary VLE sub-diagrams evaluated as a whole. Alternatively, a multicomponent mixture may be represented by a pseudo-ternary or quaternary system of three or four of its key components. Obviously, VLE information may be used without graphical representation too.

In conclusion, most of the studies on the qualitative analysis of VLE are focused on ternary mixtures where graphical representations are readily visible and can be used for the prediction of distillation behavior.

3 Isotherm Maps of Ternary Mixtures

Throughout this paper we consider systems of constant pressure. Isotherms are contour lines of constant temperature (also called isotherm-isobars). Isotherm maps as a way to represent the system of VLE functions given by Equations (3) and (4) were first used by Schreinemakers (1901*b*). Isotherms of the boiling temperature surface $T_{bp}(\boldsymbol{x})$ and the isotherms of the condensation temperature surface $T_{dp}(\mathbf{y})$ were later called *liquid isotherms* and *vapor isotherms*, respectively, by Reinders and de Minjer (1940). The liquid compositions of a liquid isotherm are connected with the vapor compositions of the corresponding vapor isotherm (at the same temperature) by the equilibrium vectors in the composition space $\overrightarrow{\boldsymbol{xy}}$ illustrated in Figure 3. Such a diagram is a complete graphical representation of the VLE system Equation (4). Schreinemakers (1901*c*) studied complete graphical representations of the VLE system Equation (3) for various combinations of a given binary azeotropic mixture with a third component that forms additional binary and ternary azeotropes. He also showed the analogy between an isobar map at constant temperature and the isotherm maps at constant pressure. Isotherm maps are presented in Figure 4 as they are given in the original publication by Schreinemakers (1901*b*). From this study, Schreinemakers established that:

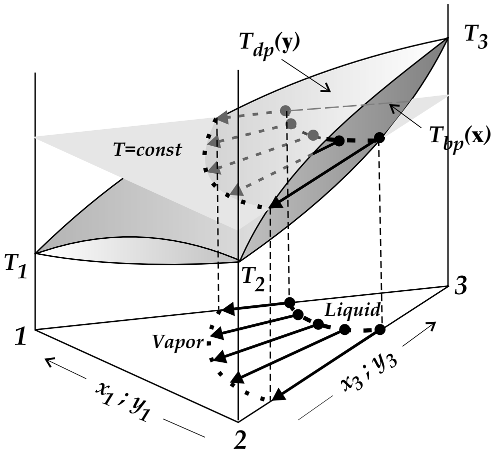

Figure 3: *Liquid and vapor isotherms and the equilibrium vectors that connects them for a ternary zeotropic mixture with pure component boiling points T_1, T_2 and T_3 at constant pressure (Schreinemakers, 1901*b*).*

1. Ternary mixtures may exhibit distinctly different isotherm maps depending on the existence of azeotropes,

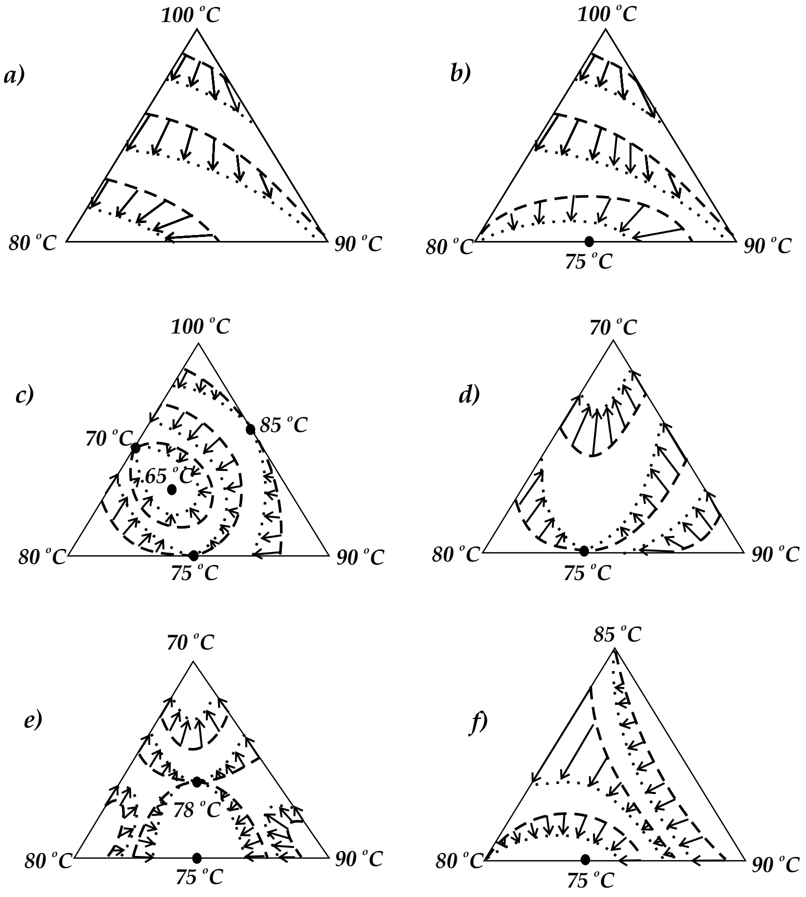

Figure 4: *Liquid and vapor isotherms and equilibrium vectors in the composition space at constant system pressure: a,b,c,d: examples from Schreinemakers (1901*b*); e,f: additional examples.*

their type (binary or ternary, minimum-, maximum- or intermediate-boiling), their location, and the relative order of the boiling points of the pure components and azeotropes.

2. A binary azeotrope that is an extremal point of the binary mixture temperature functions, is not necessary a global temperature extreme for the ternary mixture as a whole, thus being a saddle point.

3. In the same way, a ternary azeotrope is not necessary a global temperature extreme for the ternary mixture, thus being a saddle point (min-max) of the temperature surface.

The examples of isotherm maps given in Figure 4 are only for purposes of illustration. In practice, it is difficult to draw such combined diagrams of liquid and vapor isotherms (at constant pressure) because an isotherm of one phase may be (and usually is) intersected by isotherms of the other phase at other temperatures. Equilibrium vector field diagrams are also confusing since the equilibrium vector projections in the composition space intersect each other. The more detailed diagram we want to draw, the less understandable it becomes. Isotherm maps, for example as a representation of the boiling temperature function, are more readable. But, with the exception of binary mixtures, it is difficult to immediately understand the distillation behavior of ternary mixtures from the liquid isotherm map without special knowledge. Schreinemakers demonstrated the severity of the problem, and it has taken the efforts of many investigators to find a proper way of characterizing vapor-liquid equilibrium diagrams.

The key to a qualitative characterization of the VLE lies with the analysis of *simple equilibrium phase transformation processes,* and above all that of open evaporation which is the topic of the next section.

4 Open Evaporation

4.1 Residue curves

Open evaporation, also known as simple distillation or Rayleigh distillation, is batch distillation with one equilibrium stage where the vapor formed is continuously removed so that the vapor at any instant is in equilibrium with the still-pot liquid (residue). Schreinemakers (1901*c*) considered the instantaneous mass balance equation of this process:

$$d(Lx_i) = -y_i dV \quad \Rightarrow \quad L dx_i = -dV(y_i - x_i) \tag{5}$$

where L [mol] is the amount of the residue liquid in the still-pot, dV [mol] is the amount vapor evaporated, x_i and y_i are the mole fractions of the component i in the still-pot liquid and in the vapor, respectively. Schreinemakers called the liquid composition trajectory of simple distillation a *distillation line of the residue*. The present term used in English-language literature is *residue curve* (Doherty and Perkins, 1978*a*). Schreinemakers proposed for ternary mixtures (*i=1,2,3*) to consider the ratio of still-pot liquid components:

$$\frac{dx_i}{dx_j} = \frac{(y_i - x_i)}{(y_j - x_j)} \tag{6}$$

Integrating Equation (6) from any initial composition $\boldsymbol{x}_0$ will generate a residue curve. It is evident from Equation (6) that the residue curve paths are governed by the VLE solely, that is, by the set of functions in Equation system (3), and, in turn, can characterize the VLE of any given mixture. We also see from Equation (6) that the equilibrium vector in the composition space $\overrightarrow{\boldsymbol{xy}}$ is tangent to the line of still-pot residue liquid composition change at any point $\boldsymbol{x}$.

Schreinemakers established that the interior of the composition space is filled in with residue curves. The points of components and azeotropes are isolated residue curves, and the edges of the composition space between the singular points are also residue curves. He analyzed the relation between the position of the equilibrium vectors at the liquid isotherms and the path of the residue curves. This connection is presented in Figure 5. Based on this, he derived what in the Russian literature is referred to as the *Schreinemakers' Rules*:

1. A residue curve always moves along the boiling temperature surface in the direction of increasing temperature and cannot intersect twice with the same liquid isotherm;
2. Residue curves cannot intersect each other.

The path of the residue curves can be determined from the isotherm map, but the intersection angle between the liquid isotherm and the residue curve does not depend on the shape of the isotherm but rather on the direction of the equilibrium vector at this point. Hence, the path of residue curves can only be *qualitatively* determined from the isotherm map. A residue curve map is a more legible representation of the VLE than isotherms because from this diagram we can immediately see the behavior of the given mixture during the simple distillation process (open evaporation). Further, we can determine the change of the relative volatility order of the components in the mixture from the change of the tangent slope along the residue curves.

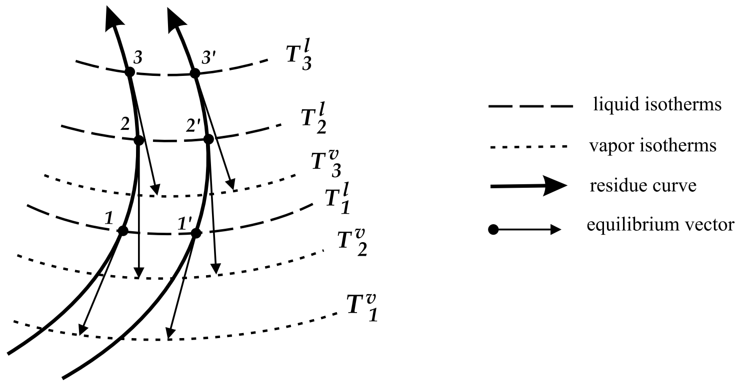

Figure 5: *Relationship between the path of residue curves and the isotherms and equilibrium vectors in the composition space (Schreinemakers, 1901*c*).*

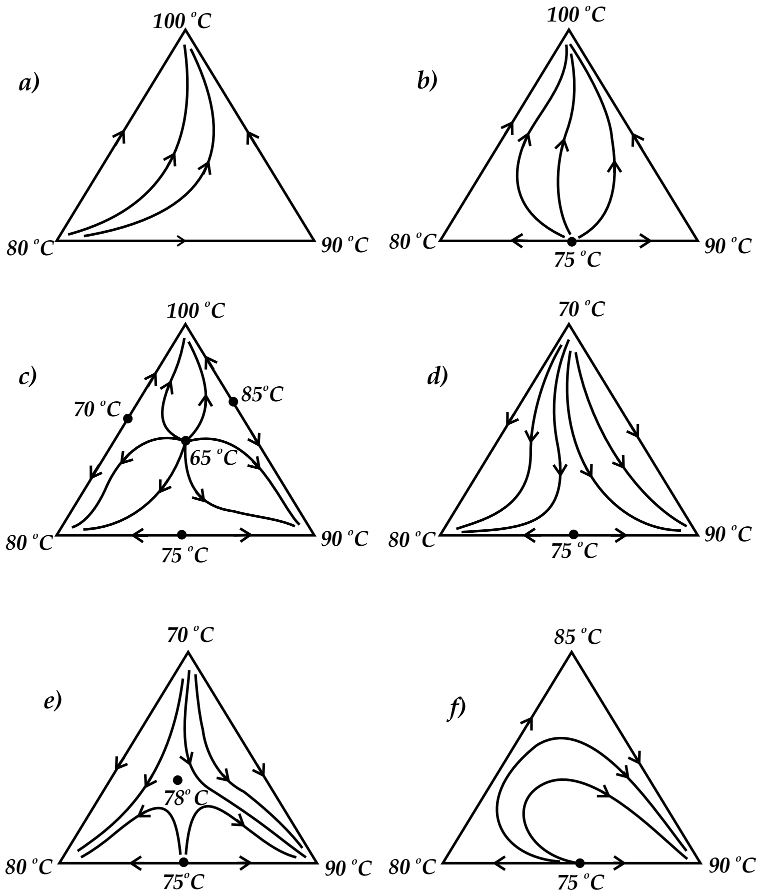

Figure 6: *Residue curve maps for the mixtures whose isotherm maps are presented in Figure 4: a,b,c,d) examples from Schreinemakers (1901*b*); e,f) additional examples.*

Residue curve maps that corresponds to the mixtures presented in Figure 4 (isotherm maps) are given in Figure 6. A point with minimum boiling temperature is an initial point of the residue curves. A point with maximum-boiling temperature is a terminal point of the residue curves. For zeotropic mixtures, Figure 6a, the residue curves have a hyperbolic path in the vicinity of singular points with intermediate boiling temperature. For azeotropic mixtures, the residue curves sometimes have a hyperbolic path in the vicinity of intermediate singular boiling points (Figure 6 b,f), and, in other cases, a singular point with intermediate boiling temperature is an initial or final point of the residue curves (Figure 6 c,d,e). Schreinemakers established that in some cases the residue curves are split into *residue curve regions* where the residue curves of each region have the same initial and final points (Figure 6 c,d,e). Schreinemakers established the existence of singular residue curves as boundaries of these regions. It has been shown (Schreinemakers, 1902) that, in general, against the opinion by Ostwald, the residue curve boundaries are curved.

Haase (1949) proved the validity of the Schreinemakers' Rules for ternary mixtures analytically by solving both the residue curve equation and the phase equilibrium condition. The assumptions by Schreinemakers were confirmed experimentally by Reinders and De Minjer (1940*a*; 1940*b*; 1947*a*; 1947*b*; 1947*c*), Ewell and Welch (1945) and Bushmakin and Kish (1957). In particular, Ewell and Welch was the first to report a ternary saddle azeotrope, the existence of which was predicted theoretically about 1900 by Ostwald and Schreinemakers.

In conclusion, Schreinemakers not only introduced the concept of residue curves, but revealed their main properties as well.

4.2 Properties of residue curves' singular points

Haase (1949) studied the behavior of the residue curves near the vertices of the composition triangle and the azeotropic points (i.e., near the residue curves' singular points). In particular, he found that a pure component vertex is an initial or a final point (node) of the residue curves if the liquid boiling temperature increases or decreases (near it) by the movement from the vertex along both adjoining edges. At other singular points (saddles), the residue curves have a hyperbolic shape in the vicinity of the vertex if the liquid boiling point temperature increases at the movement from the vertex along one of the edges and decreases at the movement along another edge. This observations are known in Russian literature as *Haase's Rule*. In summary, the residue curves originate and ends at nodes of the boiling temperature surface and have a hyperbolic path in the vicinity of their saddles.

Considering the feasible paths of isotherms and residue curves in the vicinity of nodes and saddles for homogeneous mixtures, Bushmakin and Kish (1957) and Bushmakin and Molodenko (1957) established the correspondence between their trajectories. It was found that residue curves begin or end at a (node) singular point that is an isotherm point itself (named *dot isotherm*), Figures 7a, b, c. Residue curves have a hyperbolic shape near the singular point if a *finite length isotherm* passes through this (saddle) singular point, Figure 7d, e, f. If all the residue curves terminates in a singular point, then the point is a stable node. If all the residue curves extend from a singular point, then the point is an unstable node. If the residue curves both approach and depart a singular point, then the point is a saddle.

Gurikov (1958) proposed to use the qualitative theory of ordinary differential equations to analyze the behavior of residue curves, and in this context, a singular point that is an initial or a final point of the residue curves is a *node*, and a singular point in which the residue curves have a hyperbolic shape near it is a *saddle*. Analyzing the combined solution of Equation (6) and the thermodynamic stability criteria, Gurikov showed that the residue curve system for ternary mixtures does not have singular points of the type *focus* or *isola*. However, the singular points can be nonelementary (i.e., armchair saddles) (see Section 7.2).

Zharov (1967; 1968*b*; 1968*a*; 1969), Serafimov (1968*a*; 1968*d*; 1968*b*; 1968*c*; 1969*a*; 1969*b*; 1969*c*) and later Doherty and Perkins (1978*a*; 1978*b*) considered open evaporation residue curves for the general case of multicomponent mixtures given by the following set of autonomous differential equations:

$$\frac{dx_i}{d\tau} = -(y_i - x_i) \qquad i = 1, 2, ..., n-1 \tag{7}$$

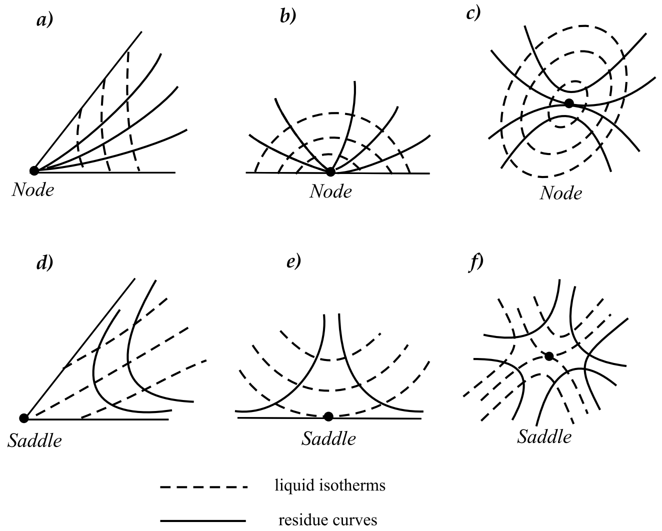

Figure 7: *Patterns of isotherms and residue curves near singular points at constant pressure (Bushmakin and Molodenko 1957).*

Here τ is a dimensionless time describing the relative loss of the liquid in the still-pot; $d\tau = dV/L$. Note that Zharov and Serafimov use opposite sign of the Equation (7) according to their definition of τ, and thus the sign of the eigenvalues are opposite in their thermodynamic topological analyses. Fortunately, the results on the properties of the residue curves' singular points are independent of this choice of preserving the minus sign in Equation (7) or not. By solving Equation (7) together with the Van der Waals-Storonkin condition of the coexistence of phases [1], Zharov proved that the Schreinemakers' rules are valid also for multicomponent mixtures. The right-hand side of Equation (7) is equal to zero at the points of pure components and azeotropes, and the system has no other singular points. From the theory of differential equations it is known that the type of a singular point depends on the signs of the eigenvalues of Equation (7) in the vicinity of the singular point. From this, Zharov showed that the singular point of Equation (7) can only be a generalized node or a generalized saddle. The signs of the eigenvalues of Equation (7) can also be determined from the signs of the derivatives $\delta T/\delta x_i$ in the vicinity of the singular point. The eigenvalue is negative (positive) if the liquid boiling point temperature decreases (increases) as we move from the singular point in the direction of the eigenvalue:

- If the temperature decreases in all directions (all eigenvalues are negative), the singular point is a stable node (SN).
- If the temperature increases in all directions (all eigenvalues are positive), the singular point is an unstable node (UN).
- If the temperature decreases in some directions and increases in other directions (eigenvalues of different signs), the singular point is a saddle (S).

Thus, the character of the behavior of the residue curves in the vicinity of a singular point uniquely depends on the shape of the boiling temperature surface near this point.

The ten possible types of singular points for *ternary mixtures* given by Zharov and Serafimov (1975) are presented in Figure 8. The arrows point in direction of increasing temperature, or equivalently, in the

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[1] That is, a generalization of Van der Waals' equation of two-component two-phase system and Clausius' equation for one-component system for the general case of multicomponent multiphase system

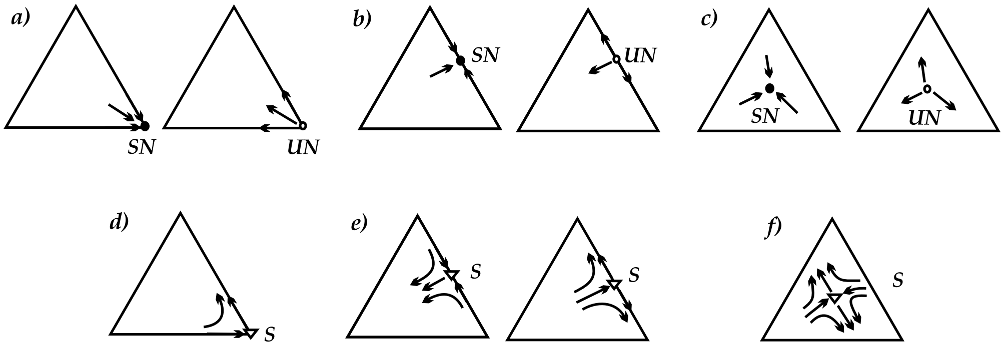


Figure 8: *Types of singular points for ternary mixtures indicated by ● stable node (SN), ○ unstable node (UN), and ▽ saddle (S) (Zharov and Serafimov, 1975). Arrows point in the direction of increasing boiling temperature, and the letters (a, b, c, d, e, f) show the correspondence to Figure 7.*

direction of increasing τ. Similar diagrams are also presented by Matsuyama and Nishimura (1977) and by Doherty and Caldarola (1985). Whereas Figure 7 is determined from the direction of increasing temperature moving along the boiling temperature surface $T_{bp}(\boldsymbol{x})$, Figure 8 is determined based on stability properties of the singular points. For ternary mixtures, the type of singular points of the residue curves of any dimension (one-component, binary or ternary) is characterized by two eigenvalues. The singular point is a stable node (SN) if both eigenvalues are negative (Figure 8a, b, c left triangles). The singular point is an unstable node (UN) if both eigenvalues are positive (Figure 8a, b, c right triangles). If one of the eigenvalues is negative and the other is positive, the singular point is a saddle (Figure 8d, e, f).

The twenty types of singular points for *quaternary mixtures* that are given in Zharov and Serafimov (1975) are presented in Figure 9. The sign of the topological indices are valid according to the sign of Equation (7). For quaternary mixtures, the type of the residue curves' singular points of any dimension (one-component, binary, ternary or quaternary) is characterized by three eigenvalues. The singular point is a stable node if all the three eigenvalues are negative (Figure 9a, e, k, q). The singular point is an unstable node if all three eigenvalues are positive (Figure 9b, f, l, r). The singular point is a saddle if one eigenvalue is positive and the other eigenvalues are negative (Figure 9c, g, i, m, o, s), or, if one eigenvalue is negative and the other eigenvalues are positive (Figure 9d, h, j, n, p, t). Only elementary singular points are presented in Figure 8 and 9.

In summary, the type of singular points (nodes and saddles) of the residue curves can be determined from the direction of increasing boiling temperature in the vicinity of these point.

4.3 Rule of azeotropy

The boiling temperature surface, in which simple distillation residue curves belong, is a continuous surface. It follows from topological theory that a combination of singular points of such surfaces corresponds to certain topological restrictions. Using Poincare's theory of topological properties of continuous surfaces, Gurikov (1958) showed that for ternary simple distillation the combination of the singular points of different type always satisfies the rule:

$$2N_3 + N_2 + N_1 = 2S_3 + S_2 + 2 \tag{8}$$

where $N_3(S_3)$ is the number of ternary nodes (saddles), $N_2(S_2)$ is the number of binary nodes (saddles), and N_1 is the number of pure component nodes. All thermodynamically and topologically feasible combinations

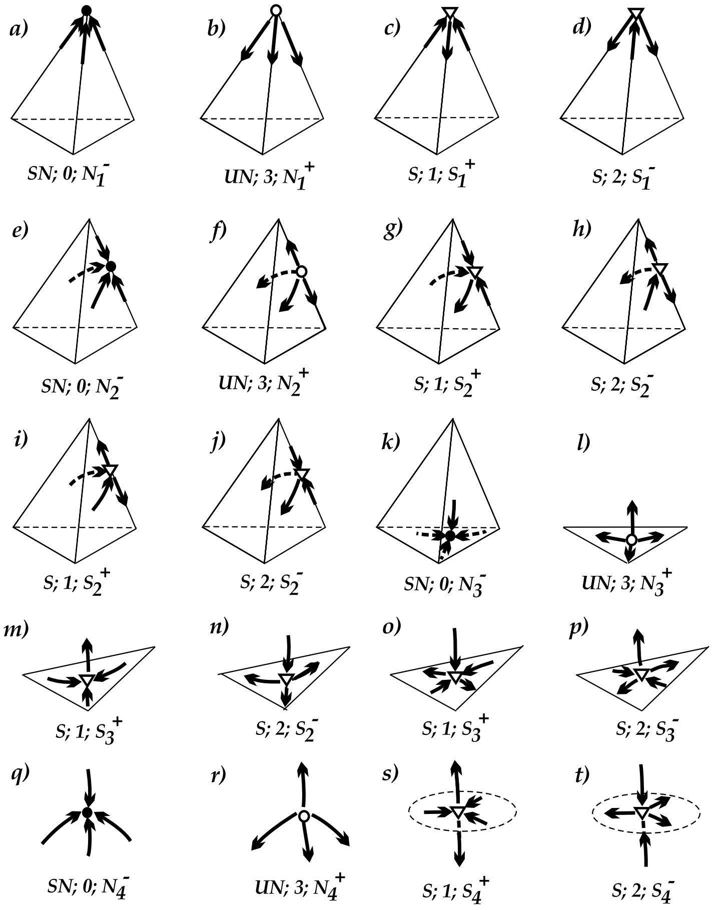


Figure 9: *Types of singular points for quaternary mixtures indicated by* ● *stable node SN,* ○ *unstable node UN, and* ▽ *saddle S, and their corresponding topological indices (Zharov and Serafimov 1975). Arrows point in the direction of increasing boiling temperature.*

of the singular points of ternary residue curve maps must obey this "Rule of azeotropy". Zharov (1969*a*) extended this consideration to multicomponent mixtures. Using the concept of topological index (theorems by Kronecker and Hoppf) he obtained the generalized rule of azeotropy for n-component mixtures:

$$\sum_{k=1}^{n}\left[2^k(N_k^+ + S_k^+ - N_k^- - S_k^-)\right] = 1 + (-1)^{n-1} \tag{9}$$

where N_k^+ (N_k^-) is the number of k-component nodes with positive (negative) index, S_k^+ (S_k^-) is the number of k-component saddles with positive (negative) index. The index of the singular point can be determined from the signs of the eigenvalues of Equation (7). An index is positive (negative) if the number of negative eigenvalues is even (odd). Gurikov's Equation (8) is the specific case of Equation (9) for ternary mixtures. From the topological analysis of the singular points given in Section 4.2 we have for ternary mixtures that all nodes (stable or unstable, one-component, binary or ternary) have an index $+1$ and all saddles have an index -1. The numbers of negative nodes and positive saddles are equal to zero. Thus, for *ternary mixtures* Equation (9) has the form:

$$8(N_3^+ - S_3^-) + 4(N_2^+ - S_2^-) + 2(N_1^+ - S_1^-) = 2 \tag{10}$$

Excluding all the indices and taking into account that $S_1 = 3 - N_1$ we obtain Gurikov's rule of azeotropy given by Equation (8). For *quaternary mixtures*, the unstable and stable nodes have different indices, and the saddles can be positive or negative. Referring to Figure 9, where the different types of singular points are given for a quaternary mixture, we can determine the topological indices given in Table 2.

Table 2: *Topological indices for quaternary mixtures*

Case in Figure 9	Number of negative eigenvalues	Type of singular point	Topological index	Nomination
a, e, k, q	3	stable node	-1	N_k^-
b, f, l, r	0	unstable node	+1	N_k^+
c, g, i, m, o, s	2	saddle	+1	S_k^+
d, h, j, n, p, t	1	saddle	-1	S_k^-

Another approach to the analysis of topological restriction was independently performed by Serafimov (1968*d*; 1968*b*; 1968*c*; 1969*a*; 1969*b*; 1969*c*). The results of both authors were summarized in Serafimov *et al.* (1971) and Zharov and Serafimov (1975), and recently presented again in Serafimov (1996).

In conclusion, the rule of azeotropy simply means that a definite combination of singular points of the various types must lead to a definite system of residue curves. It is used in the topological classification of VLE diagrams that is presented in Section 7.

4.4 Structure of residue curve maps

Based on the rule of azeotropy and the postulate that residue curves must be closed (that is, originate and end in nodes), it has been found that if we know the type of all singular points (i.e., the direction of the residue curves near all points of pure components and azeotropes), then we can qualitatively construct the diagram of residue curves (Serafimov, 1968*d*; Zharov and Serafimov, 1975; Doherty, 1985). Some examples of qualitatively residue curve map construction are given in Figure 10 for various cases of azeotropy of a ternary mixture of component 1, 2 and 3, where the boiling points are $T_1 < T_2 < T_3$. We can see that in some cases (Cases 2, 3 and 5) the composition triangle is split into several residue curve regions. Recall that Schreinemakers (1901*c*) defines a residue curve region as a set of residue curves with common initial and final points. The residue curve boundaries are the singular residue curves that divide the composition space into these regions. Only saddle separatrices interior to the composition space can be residue curve boundaries.

Bushmakin and Molodenko (1957) and Doherty and Perkins (1978*a*) proposed to distinguish between *stable separatrices* (boundaries going from a saddle to a stable node), and *unstable separatrices* (boundaries going from an unstable node to a saddle). In Figure 10 we can see the unstable separatrices (Case 2 and 4, and the separatrices 1O and AO in Case 5), and the stable separatrices (Case 3, and the separatrices O2 and O3 in Case 5). Bushmakin and Molodenko (1957) assumed (correctly) that the composition triangle is split into residue curve regions only when there is at least one saddle binary azeotrope, or, in other words, when there is at least one separatrix interior to the composition triangle (necessary condition). However, we can see by the example of Case 4 in Figure 10 where we only have one residue curve region in spite of the existence of an unstable separatrix, that the existence of a binary saddle (A) and its separatrix (OA) is not a sufficient condition for the splitting of the composition space into several residue curve regions. This may cause confusion (see, for example, Safrit (1996)), but the ”contradiction” has a simple answer. Strictly speaking, the separatrix itself is a simple distillation region and the existence of the binary saddle leads to the splitting of the interior of the composition triangle into two regions with distinct final points: (1) the separatrix itself and (2) the set of the liquid compositions belonging to all other non-singular residue curves.

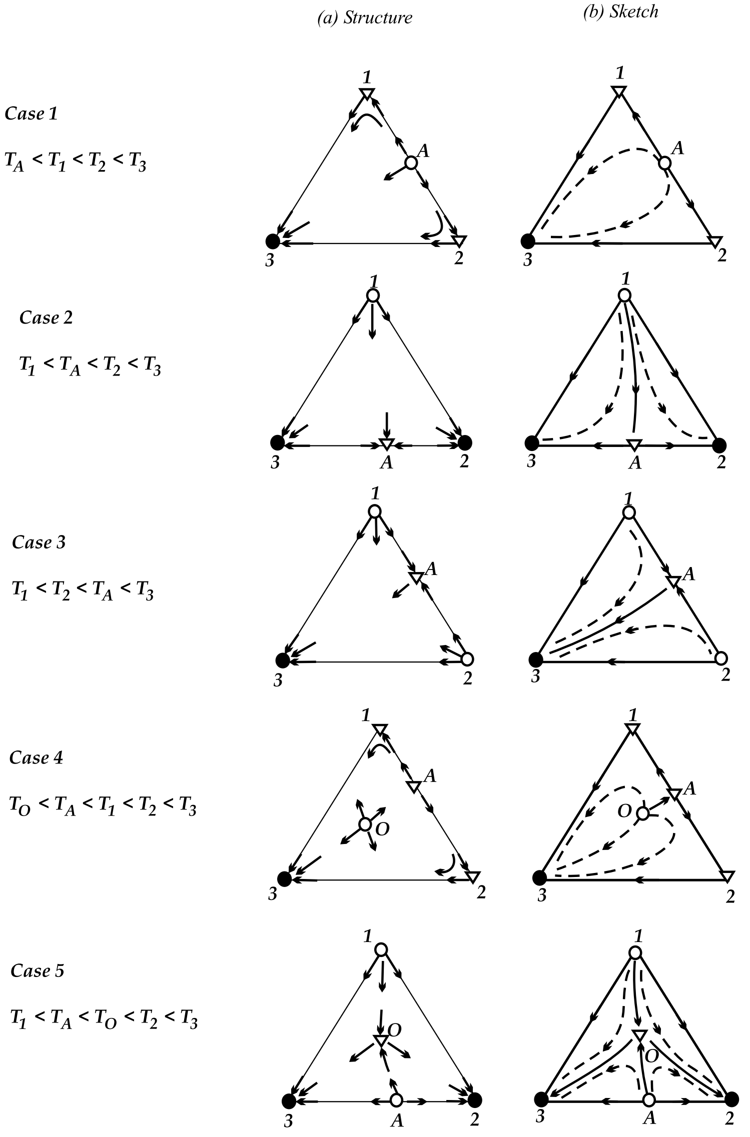


Figure 10: *Examples of qualitative residue curve map construction: (a) directions of residue curves near the singular points; (b) sketch of the residue curve diagram.*

Here, the separatrix is not a boundary because it does not correspond to the adopted definition of a boundary (it does not divide the family of the residue curves into different bundles).

Thus, a boundary is a separatrix but a separatrix is not necessarily a boundary. We can formulate the general rule:

- The composition space is split into several *residue curve regions* if there are several unstable or several stable nodes (necessary condition).
- The number of *residue curve regions* equals the total number of repeated nodes, that is, nodes of the same type (stable or unstable). For example, if we have three stable nodes and one unstable node the total number of repeated nodes is three and we have three residue curve regions. If we have two stable nodes and two unstable nodes the total number of repeated nodes is four and we have four residue curve regions.

Here, a residue curve region is defined as the set of residue curves with common initial and final points. Doherty and Perkins (1978*a*) proposed another definition of residue curve regions as the set of liquid compositions that belong to the residue curves with a common stable node. Thus, any unstable separatrix is a residue curve region boundary, and only unstable separatrices can be the boundaries of residue curve regions. We can see from Figure 10 that both statements are invalid. In Case 4 there is an unstable separatrix which is not a residue curve boundary. Furthermore, Case 3 has two residue curve regions separated by a stable separatrix boundary. The definitions were corrected by Doherty *et al.* (1985; 1993), but the error appeared again in Rev (1992) and in the review paper by Fien and Liu (1994).

It should be stressed that we cannot construct an exact map of residue curves for a given mixture without knowing the (exact) location and shape of the separatrices (in addition to knowing the initial and terminal points), and the exact location and shape of the ordinary residue curves. Thus, we hereafter distinguish between *a residue curve map*, *a sketch of the residue curve map* and *the structure of a residue curve map*. The first term means the exact representation of the residue curves and must be constructed by integration of the simple distillation residue curve Equation (7). The term ”sketch” means the qualitative diagram of residue curves representing the sign of curvature (convex/concave) and the existence (or nonexistence) of inflection points (qualitatively), but not the exact location of the residue curves. This is the focus in Section 7.4. Finally, the term *structure* of the residue curve map is the simplest graphical representation that characterizes the VLE and open evaporation of a given mixture (Serafimov, 1968*d*). The structural diagram represent the topology of the residue curve map as given by the residue curves' singular points (nodes and saddles), the residue curves going along the edges of the composition triangle, and the saddles separatrices located interior to the composition space (Serafimov, 1968*d*), that is, only the the singular residue curves. For example, the dashed residue curves in Figure 10 are unnecessary for the characterization of the structure.

As mentioned earlier, using information about the shape of the boiling temperature surface near the singular points we can only determine the *structure* of the residue curve map. Since the residue curves follow the direction of increasing boiling temperature, the structure of the residue curve map is also the structure of the boiling temperature surface. Representing the VLE diagram structure by an oriented graph of the boiling temperature increase allows us to determine the structure of the diagrams for multicomponent mixtures. Algorithms for this were proposed by Vitman and Zharov (1971*a*; 1971*b*) and Babich (1972). These oriented graphs may be visualized for quaternary mixtures, but not readily if the number of components is more than four. Instead, the graphs can be represented in matrix form and the determination of the VLE diagram structure can be computerized. Algorithms for computer-aided determination of multicomponent VLE diagrams structures were developed by Petlyuk *et al.* (1975*a*; 1975*b*; 1977*a*; 1977*c*; 1977*b*; 1978), and are also given by Julka and Doherty (1993), Rooks *et al.* (1998) and Safrit and Westerberg (1997) and others.

4.5 Separatrices of residue curves and flexure of the boiling temperature surface

A surface can be characterized by its topology. As just noted the topology of the residue curve diagram and the boiling temperature surface coincide. That is, their stable nodes (peaks), unstable nodes (pits) and saddle points are the same. Thus, it may appear that the stable separatrices of a residue curve diagram are coincident with the projections of the locus of the ridges in the boiling temperature surface onto the composition simplex, and the unstable separatrices with the valleys. This was claimed by Reinders and de Minjer (1940) based on the intuitive assumption that residue curves could not cross the ridges or valleys in the boiling temperature function $T_{bp}(\boldsymbol{x})$, since this would violate the Schreinemakers' rules. Opposed to this, Haase (1949) stated that the location of the flexures (ridges and valleys) in the boiling temperature surface cannot coincide with the boundaries of the simple distillation regions. Haase was right, however, this point was not immediately recognized.

Based on experiments, Bushmakin and Kish (1957) argued that for the mixture methyl acetate-chloroformmethanol the boundaries of simple distillation regions run along the projections of the flexures in the boiling temperature surface on the plane of the composition triangle *"within the limits of the experimental accuracy"*. However, they did not describe how they localized the flexures, nor did they give a quantitative comparison of the path of the boiling temperature surface flexures and the simple distillation region boundaries. It should be noted that Bushmakin and Kish did not vigorously claim the identity of the boundaries with the flexures in the boiling temperature surface in the general case, but wrote about the correspondence between them (Bushmakin and Molodenko, 1957). Nevertheless, these papers supported the hypothesis by Reinders and De Minjer resulting in its added confidence. Numerous attempts were subsequently made to prove the identity of the simple distillation boundaries with the flexures in the boiling temperature surface. The interest in this problem is understandable. Although a separatrix is the singular line of the residue curve family, its equation is not distinct from the equation of the ordinary residue curves. Under integration of Equation (7), the separatrix can be localized only as a line which arrives at ε-vicinity of a saddle at $\tau \to \infty$, or, starts from ε-vicinity of a saddle at $\tau \to -\infty$. In other words, the localization is only approximate. If the separatrix had the specific property that it coincides with the flexure of the boiling temperature function it could be exactly localized in a simple way.

Various ways to determine the flexure (ridges and valleys) in the boiling temperature surface have been proposed:

- As the locus of extremal boiling temperatures when moving along straight lines parallel to the edges of the composition triangle (see, for example, Doherty and Perkins, 1978*a*);
- As the separatrix of the steepest gradient lines (Malenko, 1970; Kogan and Kafarov, 1977*a*; Kogan and Kafarov, 1977*b*; Van Dongen and Doherty, 1984);
- As the locus of liquid composition points with maximum isotherm curvature (Boyarinov *et al.*, 1974). Path of the largest gradient on the boiling point surface (Stichlmair and Fair, 1998);
- As the locus of liquid composition points where the equilibrium vector is co-linear with the temperature gradient (Sobolev *et al.* (1980)).

However, as it was demonstrated by Van Dongen and Doherty (1984) and Rev (1992), these flexures do not coincide with the separatrices of residue curves. This finally confirmed the conclusion made by Haase as early as 1949.

This conclusion is not surprising since the pathways of the residue curves do not only depend on the boiling temperature surface, but also on the direction of the equilibrium vectors between the phases. The direction of the equilibrium vectors are not necessarily the same as that of the temperature gradient.

Kiva and Serafimov (1973) showed that residue curves crossing the valley or ridges of the boiling temperature surface do not violate Schreinemakers' rules since the residue curve *" [...] rises along the slope, intersects the fold [ridge] at an acute angle, and, [...] continues to rise, moving along the opposite slope of the curved fold [ridge] to its highest point"*. Even when a residue curve crosses a ridge or valley, the residue temperature is continuously increasing. Similar considerations are given in more detail by Rev (1992).

In conclusion, although the *structure* of a residue curve map can be determined solely from the shape of the boiling temperature surface, the exact location of the residue curve separatrices cannot.

4.6 Structure of distillate curve maps

The vapor composition trajectory during open evaporation can be represented graphically by the *vapor line* (Schreinemakers, 1901*c*), later named *distillate curve* by Doherty and Perkins (1978*a*). Each distillate curve is connected to a residue curve and moves along the condensation temperature surface $T_{dp}(\boldsymbol{y})$. The distillate curves are going through the vapor ends of the equilibrium vectors that are tangent to the corresponding residue curve. The projection of the distillate curve in the composition space is always positioned at the convex side of the corresponding residue curve projection. The less the curvature of the residue curve, the less is the gap between it and the corresponding distillate curve. The vapor condensation temperature is equal to the liquid boiling temperature at any instant and increases monotonically during the open equilibrium evaporation process. The system of distillate curves has the same singular points as the system of residue curves, and the singular point type is the same as the type of the corresponding singular point of the residue curves (Haase, 1950*b*; Storonkin, 1967).

5 Other Simple Equilibrium Phase Transformations

5.1 Open condensation

Open condensation is another equilibrium phase process that solely depends on the VLE, that is, no design or operating parameters, and can in turn characterize it. Open condensation is a hypothetical process where drops of condensate are continuously removed from a bulk of vapor in such a way that the composition of the condensate is in equilibrium with the still-pot vapor composition, at any instant. This process is symmetrical to the open evaporation process (Kiva and Serafimov, 1973c). It may appear that the *open condensation curves* are directed opposite to the open avaporation residue curves, but this is not correct. Only the structure is the same, but they do not coincide in general. This is evident from Figure 11 where open evaporation residue curves and open condensation curves going through points $\boldsymbol{x}$ and $\boldsymbol{y}$ of an arbitrary equilibrium vector are given. Nevertheless, open condensation and open evaporation are symmetrical processes with isomorphus (topologically equivalent) composition trajectory maps for *antipodal* VLE diagrams, that is diagrams with inverted signs of the nodes and opposite directed trajectories.

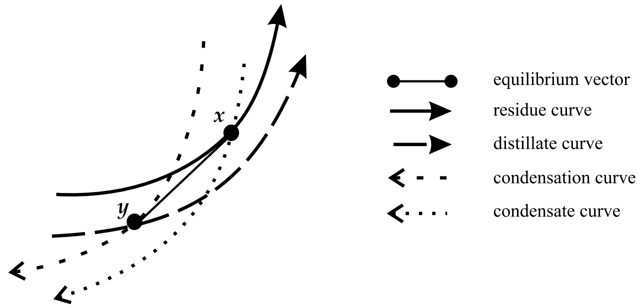


Figure 11: *Vapor and liquid composition trajectories of open evaporation and open condensation going through the points $\boldsymbol{x}$ and $\boldsymbol{y}$ of an equilibrium vector in the composition space.*

5.2 Repeated equilibrium phase mapping and distillation lines

Zharov (1968*c*; 1969*b*) proposed the use of repeated phase equilibrium E-mapping as a characterization of the VLE:

$$\boldsymbol{x}_1 \overset{E^1}{\to} \boldsymbol{y}_1; \;\; \boldsymbol{y}_1 = \boldsymbol{x}_2; \;\; \boldsymbol{x}_2 \overset{E^2}{\to} \boldsymbol{y}_2; \;\; ... \;\; ; \;\; \boldsymbol{x}_N \overset{E^N}{\to} \boldsymbol{y}_N \qquad (11)$$

Zharov named the sequence $E^N\boldsymbol{x}_1$ a *"chain of conjugated tie-lines [equilibrium vectors]"*, today often referred to as *tie-line curves* or *discrete distillation lines*. The repeated equilibrium phase mapping is illustrated in Figure 12. The chain describes the stepwise movement along both the boiling and condensation

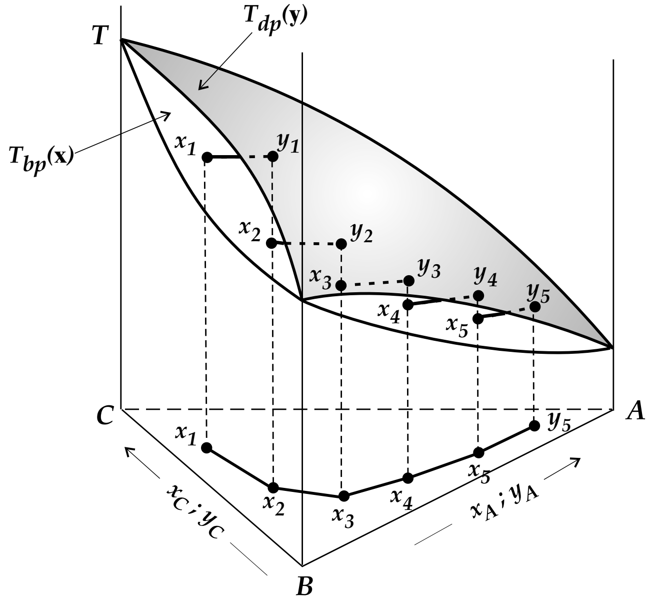


Figure 12: *Equilibrium distillation line (also named tie-line curve) is a chain of conjugated vapor-liquid equilibrium vectors in the composition space, that is, a sequence of repeated equilibrium phase mappings.*

surfaces similar to the McCabe-Thiele approach for binary mixtures at total reflux. Starting with a given liquid composition $\boldsymbol{x}_1$, the equilibrium relationship (E-mapping) determines the corresponding equilibrium vapor composition $\boldsymbol{y}_1$. The vapor is totally condensed and, thus, the vapor and liquid compositions are equal at each step, $\boldsymbol{y}_N = \boldsymbol{x}_{N+1}$, which gives the initial point $\boldsymbol{x}_2$ of the next step and so forth. The VLE describes movement horizontally (T constant) in Figure 12. Projection of a sequence of equilibrium phase mappings onto the composition plane is a discrete line. In a series of repeated mappings, the sequence strives to the component or azeotropic point that has a minimum boiling temperature. The sequence will follow the direction of decreasing boiling (condensation) temperature, that is, it has the same direction as the composition trajectories of open condensation. Choosing several different initial points $\boldsymbol{x}_1$, we will obtain a set of equilibrium vector chains. With the proper choice of the initial points we obtain a map of conjugated equilibrium vector chains in the composition space that characterizes the equilibrium mapping function $E : \boldsymbol{x} \rightarrow \boldsymbol{y}$. The set of these *equilibrium vector chains* is an organized selection from the equilibrium vector field. Zharov proposed to consider smooth *”connecting lines”* instead of the discrete chains of conjugated equilibrium vectors. The term connecting line (“c-line”) means a smooth line going in such a way that the vapor-liquid equilibrium vector at an arbitrary point is a chord of this line. As result, any connecting line is a common arc of infinite equilibrium mappings as illustrated in Figure 13. Today, these lines are commonly named *distillation lines*. For homogeneous mixtures the continuous distillation lines cannot intersect each other in contrast to the discrete chains of conjugated vectors in the composition space as shown in Figure 13, and qualitative differential equation theory can be used for their analysis. Based on this analysis, Zharov showed that the properties of distillation lines near the pure component and azeotropic points are identical with those of the residue curves, but the signs of the eigenvalues and indices of the singular points are inverted according to their opposite direction (which is just a matter of definition). As a result, the structure of the distillation line map (and conjugated vector chain map) can be determined from the shape of the boiling temperature surface in the same way as the structure of the residue curve map.

Zharov (1968*c*) noted that the discrete distillation line coincides with the composition profile of an equilib-

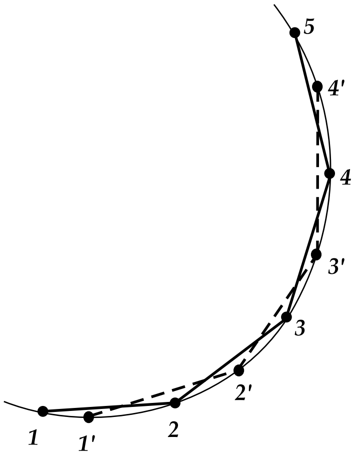


Figure 13: *Distillation line (smooth) and tie-line curves (chains of conjugated vapor-liquid equilibrium vectors).*

rium staged distillation column at total reflux. Based on this coincidence, Stichlmair (1988; 1989) uses the name *distillation line* for the smooth connection line through chains of conjugated vapor-liquid equilibrium vectors. Wahnschafft *et al.* (1992) named the discrete chain of conjugated equilibrium vectors a *tie-line curve*. Wahnschafft *et al.* (1992) and Widagdo and Seider (1996) define a tie-line curve and a distillation line as the liquid composition profile of a distillation column at total reflux. Distillation lines and (equilibrium) tie-line curves are defined uniquely from the VLE, regardless of their connection with the column composition profile. Thus, distillation lines are equivalent to residue curves as characteristics of the VLE in a thermodynamic sense. Stichlmair (1988) underlines that the (discrete) distillation lines give information about the lengths of the vapor-liquid equilibrium vectors which can characterize not only the qualitative course of distillation, but the distillation separability as well. The larger distance between the points on the distillation line, the easier is the separation. Residue curves do not bring this information.

Discrete distillation lines are readily constructed for any given mixture by computation if the mathematical description of the VLE is available. This computation is quicker than the computation of residue curves. However, the exact construction of the distillation lines is more ambiguous because the equation of this line is not uniquely defined. Various algorithms for the construction of continuous distillation lines, for example as given by Pöllmann *et al.* (1996), is not be simpler than the integration procedure for the construction of the residue curves. Eitherway, the *structure* of the distillation line maps does not differ from the residue curve map structures. Along with N-fold and infinity E-mappings, we can consider N-fold and infinite C-mappings, that is, the sequence $C^N \boldsymbol{y}_1$:

$$\boldsymbol{y}_1 \overset{C^1}{\to} \boldsymbol{x}_1; \;\; \boldsymbol{x}_1 = \boldsymbol{y}_2; \;\; \boldsymbol{y}_2 \overset{C^2}{\to} \boldsymbol{x}_2; \;\; \dots \;; \;\; \boldsymbol{y}_N \overset{C^N}{\to} \boldsymbol{x}_N \tag{12}$$

We name this chain of conjugated vapor-to-liquid vectors a *reverse* discrete distillation line, or, alternatively, reverse tie-line curve. It is apparent that the chains of conjugated vectors $\overrightarrow{\boldsymbol{yx}}$ and their smooth connecting lines will follow the direction of increasing boiling (condensation) temperature. Thus, they have the same direction as residue curves of open evaporation. For homogeneous mixtures the reverse distillation lines are direct inversions of distillation lines. In other words, distillation lines (discrete and continuous) are reversible.

Similar to residue curves, the system of distillation lines may split into distinct regions. A distillation line region is the set of compositions that belongs to distillation lines with the same initial and final points. The structure of a distillation line map is isomorphus (equal in form) to the structure of the open condensation curve maps, or, symmetric to the structure of the residue curve map for any given mixture. Distillation line region boundaries are saddle separatrices of the distillation line system.

5.3 Relationship between residue curves, distillation lines and condensation curves

It is apparent from simple geometric considerations that a residue curve and a distillation line that go through an arbitrary liquid composition point do not coincide (see for example Figure 3 in Wahnschafft *et al.* (1992), and Figure 7 in Widagdo and Seider (1996)). Fidkowski *et al.* (1993) write that *"the difference between these types of curves are negligible unless stated otherwise"*. Wahnschafft *et al.* (1992) were more subtle writing *"the difference between residue curves and distillation lines is normally not very significant"*. However, any general statements are not valid here because the difference between both types of lines depends on their curvature and the lengths of the equilibrium vectors. A residue curve is crossed by distillation lines and condensation curves at any point along the line. In the same way, a distillation line is crossed by residue curves and condensation curves at any points. Figure 14 shows the bands of residue curves and condensation curves that intersects an arbitrary distillation line for a ternary zeotropic mixture. The difference between these ordinary residue curves and distillation lines raises a concern regarding the difference between residue curve boundaries and distillation line boundaries. It is apparent that maps of the different lines have similar topology for a given mixture, and that the separatrices of all systems of lines have the same set of singular points. But, the exact location of the separatrix does generally not coincide for the different line systems. The relative location of the composition trajectory separatrices of open evaporation, open condensation and repeated phase mapping are considered by Kiva and Serafimov (1975; 1976) based on simple geometric considerations. The relationship between separatrices is shown in Figure 15. The relative location of boundaries of different simple phase transformations satisfies the following rules:

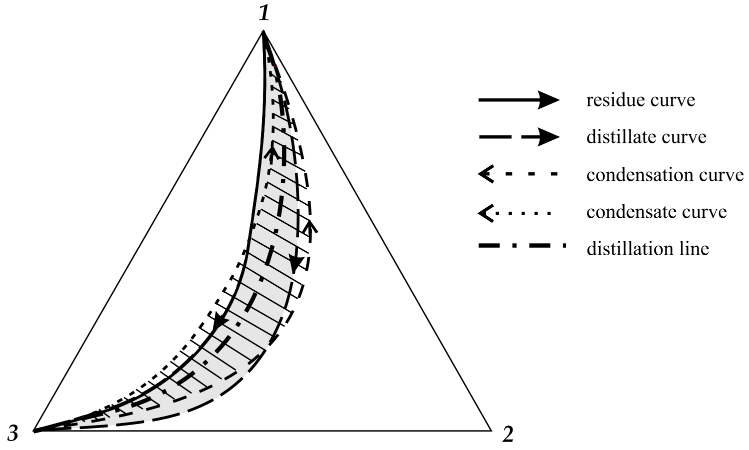


Figure 14: *Bands of residue curves and condensation curves crossing an arbitrary distillation line for a ternary zeotropic mixture.*

a) If the residue curve separatrix goes from an unstable node to a saddle (unstable separatrix), then the distillation line separatrix lies on its convex side. The condensation curve separatrix lies on the convex side of the distillation line separatrix. The distillate curve separatrix is located between the separatrices of residue curves and distillation lines, and the separatrix of the condensate curves lies on the convex side of the separatrix of condensation curves (see Figure 15 a).

b) If the residue curve separatrix goes from a saddle to a stable node (stable separatrix), then the distillation line separatrix lies on its concave side. The condensation curve separatrix lies on the concave side

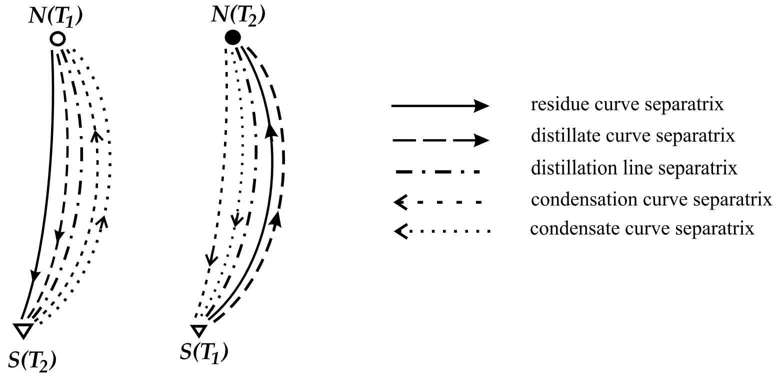


Figure 15: *Relative location of boundaries of different simple equilibrium phase transformations: • stable node, ○ unstable node, and ▽ saddle.*

of the distillation line separatrix. The separatrix of the condensate curves is located between the separatrices of the distillation lines and the condensation lines. The separatrix of the distillate curves lies on the convex side of the residue curve separatrix (see Figure 15 b).

6 Heterogeneous Mixtures

Heterogeneous mixtures include a composition region of two immiscible liquid phases as a result of molecular interaction or repulsion. Equilibrium between two liquid phases is considered in detail in textbooks and encyclopedia, for example Treybal (1963), Walas (1985), Müller (1988). An example of the vapor and liquid isotherm map and the connection between by the vapor-liquid equilibrium vectors for a heterogeneous mixture is shown in Figure 16. The compositions that belong to one liquid-liquid tie-line $\overrightarrow{\boldsymbol{x'x''}}$ have the same boiling temperature and are in equilibrium with the same vapor composition $\boldsymbol{y}^*$. The heterogeneous region is a flat fragment of the boiling temperature surface (liquid boiling envelope), and the liquid isotherms in this region coincide with the liquid-liquid tie-lines (Schreinemakers, 1901*a*). A *singular vapor line* corresponds to all phase complexes of the heterogeneous region (Haase, 1950*a*; Storonkin and Smirnova, 1963; Pham and Doherty, 1990)

6.1 Simple phase transformations in heterogeneous mixtures

The specific features of vapor-liquid-liquid phase equilibria lead to peculiarities of the simple phase transformations in heterogeneous mixtures. It has been shown by Haase (1950*a*) that Equation (6) for open evaporation residue curves for ternary mixtures can be applied to heterogeneous mixtures when x_i refers to the overall liquid composition. In the homogenous region, the tangents to the residue curves are the vapor-liquid equilibrium vectors. In the heterogeneous region, these tangents are the vapor-liquid equilibrium vectors connected to the *overall liquid composition*. Storonkin and Smirnova (1963) proved that the residue curves move continuously in the direction of increasing boiling temperature and cross the binodal curves without a gap or a discontinuity. Timofeev *et al.* (1970) proved that all the conclusions concerning the behavior of open evaporation residue curves are valid also for ternary and multicomponent heterogeneous mixtures. In other words, the residue curves are the same for homogeneous and heterogeneous azeotropic mixtures.

The main feature that distinguishes heterogeneous mixtures from homogeneous mixtures is that a hetero-

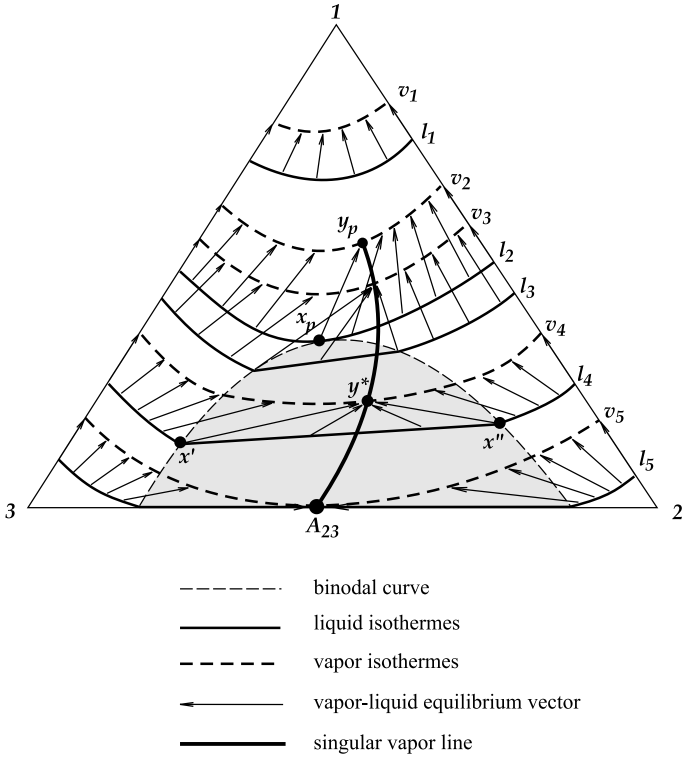


Figure 16: *An example of liquid and vapor isotherm map for a heterogeneous mixture.*

geneous azeotrope, hereafter called a *heteroazeotrope*, is either an unstable node or a saddle. It cannot be a stable node since heteroazeotropes cannot be maximum-boiling azeotropes. This is easily explained by physical reasoning: heterogeneity (liquid-liquid phase splitting) and minimum-boiling azeotropes are phenomena that occurs when the different components of the mixture repel each other, whereas maximum-boiling azeotrope occurs when the components attract each other.

The relationship between isotherms and residue curves for ternary heterogeneous mixtures presented by Timofeev *et al.* (1970) is shown in Figure 17. Unlike homogeneous mixtures, the isotherm passing through the point of a heteroazeotrope is always an *isotherm of final length*. Bushmakin's definition of the connection between an isotherm and the patterns of the residue curves (Section 4.2) should be reformulated as follows:

(a) A heteroazeotropic point is a saddle point if the isotherm passing through this point is a closed isotherm or an isotherm which ends at the edges of the composition triangle (see Figure 17a and b).

(b) A heteroazeotropic point is a nodal point if the isotherm passing through this point is an "isolated" isotherm surrounded by the closed isotherms or by the isotherms which end at the edges of the composition triangle (see Figure 17c and d).

Thus, the main relationship between the structure of the boiling temperature surface and the structure of the residue curve map applies to both homogeneous and heterogeneous mixtures. Pham and Doherty (1990) arrived at the same conclusions. The topology of a residue curve map of a heterogeneous mixture does not differ from that of a homogeneous mixture with the same set of singular points.

Distillate curves do not satisfy the uniqueness condition in the whole composition space. For the part of a residue curve in the heterogeneous region, the corresponding distillate curve moves along the singular vapor

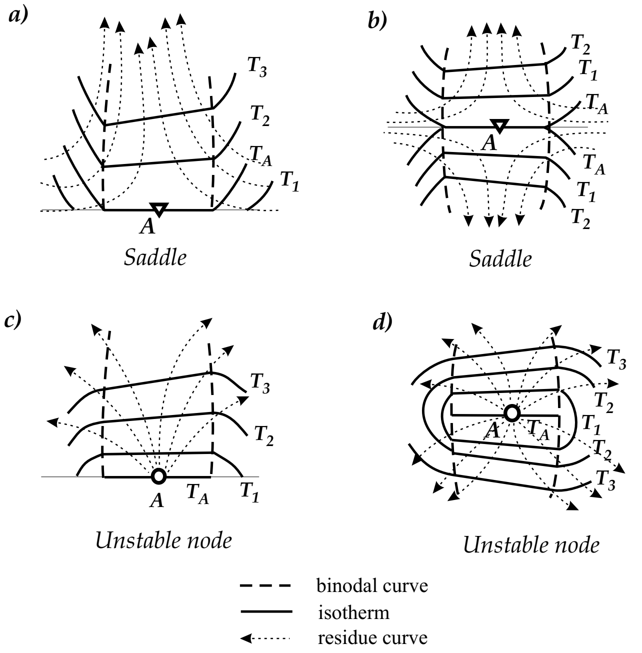


Figure 17: *Patterns of isotherms and residue curves near heterogeneous azeotropic points (Timofeev 1970).*

line. As a result, the distillate curves partially coincide with each other and with the singular vapor line (Storonkin and Smirnova, 1963; Pham and Doherty, 1990). This means that the behavior of the distillate curves will be somewhat different from that of the residue curves for the same mixture, namely:

(1) There is a singular vapor line in addition to the pure component and azeotropic points;

(2) If the composition space is split into residue curve regions and the boundary is related to the existence of the singular vapor line (this is not necessary), then the boundary of the distillate regions coincide partially or completely with the singular vapor line, and the coinciding part of both lines will be a manifold of contact for adjacent regions;

(3) The system of distillate curves can include a nonelementary singular point in addition to the component and azeotropic points.

Nevertheless, the global structure of the distillate curve map (initial and final points and splitting into regions) will be identical to the residue curve map.

6.2 Examples of simple equilibrium phase transformation maps

As an example, let us consider a mixture belonging to Serafimov's class 2.0-2b (Section 7.1). Three types of heterogeneity for this structure are presented in Figure 18. When the heterogeneous region includes both the unstable node A_{12} and the binary saddle A_{13}, the singular vapor line moves from the unstable node to the saddle inside the heterogeneous region (Type A). When the heterogeneous region only includes the unstable node A_{12}, the singular vapor line moves from the unstable node in the direction of increasing temperature and has the end point $\boldsymbol{y}_P$ inside the heterogeneous region (Type B). When the heterogeneous region only includes the saddle A_{13}, the singular vapor line moves from the saddle in the direction of decreasing temperature and has the end point $\boldsymbol{y}_P$ outside the heterogeneous region (Type C).

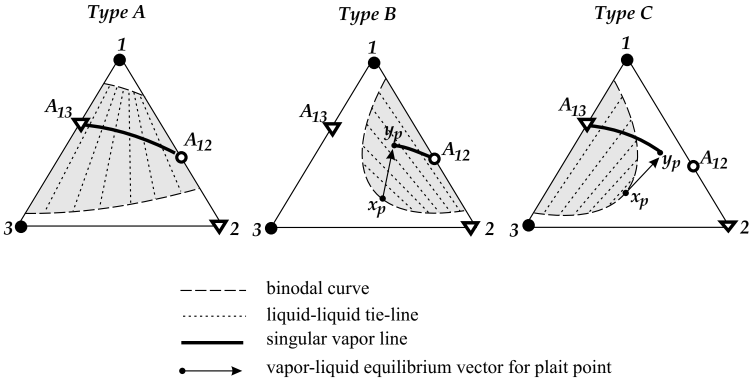


Figure 18: *Three possible types (A, B, C) of heterogeneity for a mixture with the boiling temperature structure of Serafimov's class 2.0-2b. The singular points are indicated by • stable node, ○ unstable node, and ▽ saddle.*

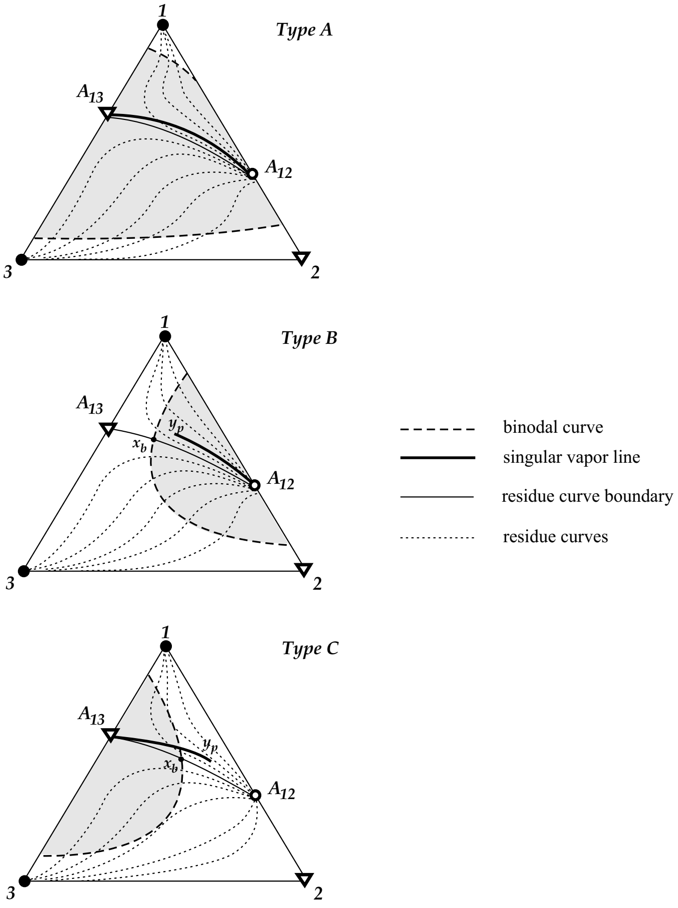


Figure 19: *Residue curve maps for the three types of heterogeneity given in Figure 18.*

The structures of the residue curve maps for these cases are presented in Figure 19. In all the cases the residue curve maps have the same structure, though the shapes of the residue curves will differ from one another. In all cases the residue curve boundary is located at the concave side of the singular vapor line.

The structures of the distillate curve maps are presented in Figure 20. For the mixture of Type A all equilibrium vectors that extend from the residue curve separatrix terminate at the singular vapor line. Hence, the

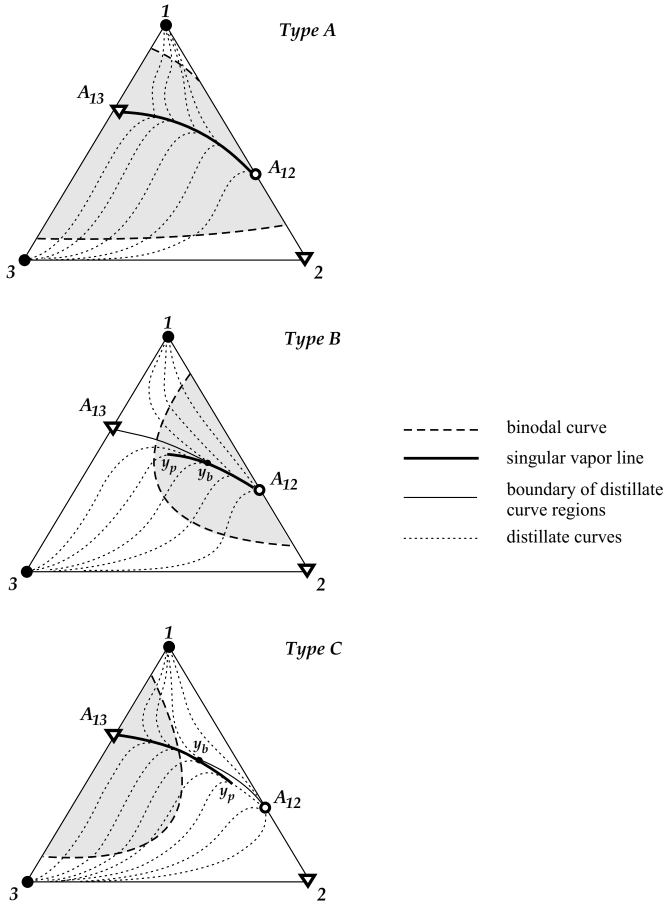


Figure 20: *Distillate curve maps for the three types of heterogeneity in Figure 18.*

singular vapor line is a separatrix (region boundary) of the distillate curves.

For the mixture of Type B, the equilibrium vectors arrive at the singular vapor line for the part of the residue curve separatrix that is located in the heterogeneous region (that is, from the point A_{12} to the point of intersection of the separatrix with the binodal curve $\boldsymbol{x}_b$). Hence, the part of the singular vapor line from A_{12} to $\boldsymbol{y}_b$ will coincide with the boundary of the distillate regions, where point $\boldsymbol{y}_b$ is the end point of the equilibrium vector which is tangential to the separatrix of the residue curves at the point $\boldsymbol{x}_b$.

For the mixture of Type C, the equilibrium vectors arrive at the singular vapor line for the part of the residue curve separatrix that is located in the heterogeneous region (that is, from the point A_{13} to the point of intersection of the separatrix with the binodal curve $\boldsymbol{x}_b$). Hence, the part of the singular vapor line from A_{13} to $\boldsymbol{x}_b$ will coincide with the boundary of the distillate regions, where point $\boldsymbol{y}_b$ is the end point of the equilibrium vector which is tangential to the separatrix of the residue curves at the point $\boldsymbol{x}_b$. For both diagrams of Types B and C, point $\boldsymbol{y}_b$ is a point of bifurcation of the singular vapor line and the separatrix of the distillate curves.

One can see that, unlike the residue curves, the behavior of distillate curves depends not only on the structure of the boiling temperature surface but on the location of the binodal curve as well. The peculiarities of the inner topology of the distillate curve maps include:

(1) Distillate curves may coincide with each other along the singular vapor line;

(2) The coinciding part of singular vapor line and the distillate curve boundary is a manifold of contact for adjacent regions;

(3) The system of distillate curves can include a nonelementary singular point in addition to the pure component and azeotropic points.

The global structure of the distillate curve map (initial and final points and splitting into regions) is similar to that of the residue curve map.

Analysis of the structure of the *distillation line map* and of the composition trajectory map for *open condensation* has not been made yet. We assume that the ”inner” topology of these maps will be more complex than the topology of the residue curve map. Nevertheless, it is reasonably safe to suggest that the topology in general (that is, the initial and final points of the composition trajectories and the splitting into regions) will depend on the shape of the boiling temperature surface in a similar way as of homogeneous mixtures.

7 Ternary VLE Diagrams. Classification, Occurrence and Structure Determination

7.1 Classifications of ternary VLE diagrams

From the previous discussions we concluded that the *structure* of simple phase transformations maps is determined, in general, by the shape of the boiling temperature surface for both homogeneous and heterogeneous mixtures. As a consequence, knowledge of the shape of the boiling temperature surface alone permits us to characterize, distinguish and classify any ternary mixture. Feasible structures must satisfy the Rule of azeotropy (Section 4.3), and this may be used to classify ternary VLE diagrams. Such a classification was first proposed by Gurikov (1958). Gurikov considers ternary mixtures with no more than one binary azeotrope for each binary pair of the components and no more than one ternary azeotrope (that is, no bi-azeotropy), i.e., $N_3 + S_3 \leq 1$ and $N_2 + S_2 \leq 3$. He denotes the total number of binary azeotropes as being M where $M = N_2 + S_2$. Substitution into Equation (8) gives:

$$2S_3 + M + 2 = 2N_3 + 2N_2 + N_1 \tag{13}$$

Both M and N_1 can take the values 0, 1, 2 or 3. From Equation (13) we see that the quantities M and N_1 are bound to be of equal parity. If M is an even number (0 or 2), then N_1 is also even. If M is an odd number (1 or 3), then N_1 is also an odd number. Gurikov uses the quantity M as a classification parameter. Specifying the value of M he considers feasible structures of residue curve maps for each of the two corresponding values of N_1. A structure is considered feasible if it does not violate the set of Schreinemakers’ Rules (Section 4.1), and the condition of closed sets of the residue curves (i.e. extending from and terminating in pure component and azeotropic singular points). From this analysis Gurikov revealed 22 feasible topological structures of residue curve maps (or boiling temperature surfaces).

Serafimov (1968*d*; 1970*b*) extended the work of Gurikov and used the total number of binary azeotropes M and the number of ternary azeotropes T as classification parameters. Serafimov’s classification denotes a structure class by the symbol ”M.T” where M can take the values 0, 1, 2 or 3 and T can take the values 0 or 1 (i.e. same assumption as Gurikov that the ternary mixture does not exhibit biazeotropy). These classes are further divided into types and subtypes denoted by a number and a letter. As a result of this detailed analysis, four more feasible topological structures, not found by Gurikov, were revealed. Thus Serafimov’s classification includes 26 classes of feasible topological structures of VLE diagrams for ternary mixtures. The foundation of this work is also presented more recently (Serafimov, 1996).

Both the classifications of Gurikov and Serafimov consider *topological* structures and thus do not distinguish between antipodal (exact opposite) structures since they have the same topology. Thus, the above classifications include ternary mixtures with opposite signs of the singular points and opposite direction of the residue curves (antipodal diagrams). Serafimov's classification is presented graphically in Figure 21. The transition from one antipode to the other (e.g. changing from minimum- to maximum-boiling azeotropes) can be made by simply changing the signs of the nodes and inverting the direction of the arrows. As discussed in Sections 3 to 5, all the representations of the VLE (isotherm map, residue curve map, vector field

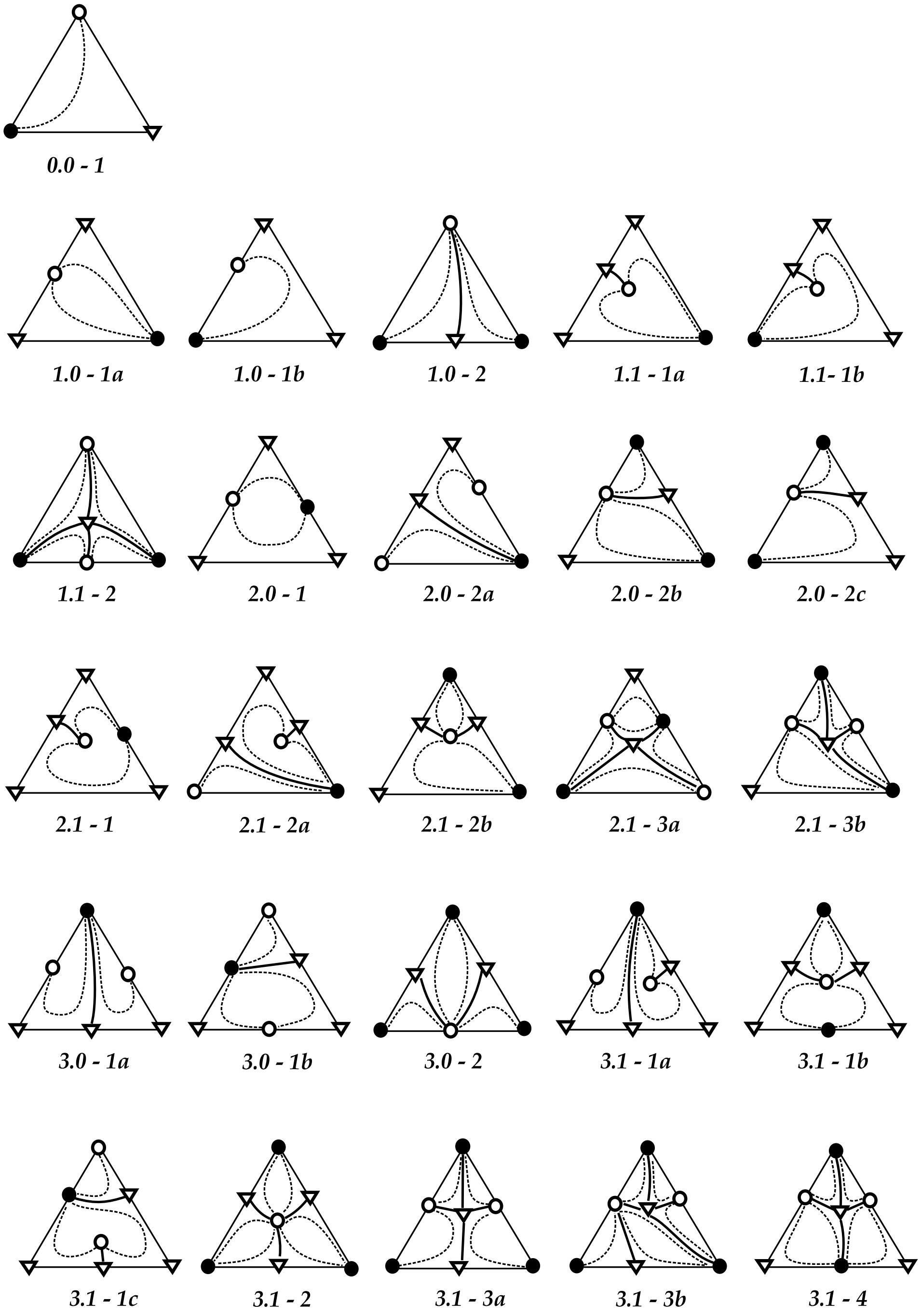


Figure 21: *Feasible topological structures of VLE diagrams for ternary mixtures according to classification by Serafimov (1970*b*): ● - stable (unstable) node, ○ - unstable (stable) node, ▽ - saddle.*

of equilibrium vectors in the composition space) are related and are equally capable of classifying the mixtures. Feasible structures of residue curve maps, isotherm maps and vector fields for ternary mixtures are presented by Serafimov (1971; 1973).

The classification of ternary mixtures may be refined by distinguishing between antipodes inside each structure class, based on the reasoning that *”minimum- and maximum-boiling azeotropes have dissimilar physical nature and dissimilar behavior during distillation”* (Zharov and Serafimov, 1975). This refined classification includes a total of 49 types of feasible VLE diagrams (p. 96-98 in Zharov and Serafimov, 1975). An even more detailed classification is proposed by Matsuyama and Nishimura (1977). This classification is founded on the same principles, but the diagrams are further distinguished according to the relative location of the binary azeotropic points on the edges of the composition triangle. The components are ranked in the order of their boiling temperature (“light”, “intermediate” and “heavy”). The classification includes 113 diagram classes of which 87 are presented graphically by Doherty and Caldarola (1985). Nevertheless, among these 113 classes there are still only the 26 topologically distinct structures of Serafimov. Matsuyama and Nishimura’s classes are denoted by three digits according to the existence and type of binary azeotropes at the edges 12, 23 and 13. The digits can take values 0 (no azeotrope), 1 (minimum-boiling azeotrope, unstable node), 2 (minimum-boiling azeotrope, saddle), 3 (maximum-boiling azeotrope, stable node) or 4 (maximum-boiling azeotrope, saddle). When a ternary azeotrope exists, a letter follows the three-digit classification code: m (minimum-boiling ternary azeotrope, unstable node), M (maximum-boiling ternary azeotrope, stable node) and S (intermediate-boiling ternary azeotrope, saddle).

In this connection we want to emphasize that the relative volatility of the components in an azeotropic mixture change within the composition space. The terms ”light”, ”intermediate” and ”heavy” component have little meaning in general for nonideal and azeotropic mixtures. This distinction made in Matsuyama and Nishimura’s classification does not give any additional information. Actually, it is sometimes ambiguous, as some of Matsuyama and Nishimura’s classes where a ternary saddle azeotrope is present have two or even three possible topological structures. For example, code 112-S can be either of Serafimov’s topological class 3.1-3a or 3.1-3b depending on whether there is a saddle - saddle separatrix or not. This ambiguity was also pointed out by Foucher *et al.* (1991) who recommend an extension of the Matsuyama and Nishimura’s classification code name in these cases. This issue is further discussed in Section 7.4.

The relationship between the different classifications is presented in Table 3 where the classes are ordered according to Serafimov’s classification (1970*b*) with increasing number of azeotropes occurring in the ternary mixture. Hereafter we use Serafimov’s (1970*b*) nomenclature for the topological classes and Zharov and Serafimov’s (1975) nomenclature for the antipodal structure types (referred to as the ZS-type).

Table 3: *Correspondence between different classifications of ternary VLE diagrams*

Gurikov (1958) 22 classes	Serafimov (1970) 26 classes	ZS-type [a] 49 classes	Matsuyama & Nishimura (1977) 113 classes
1	0	1	000
4a	1.0-1a	3a	100
		7a	030
4b	1.0-1b	3b	001
		7b	003
3	1.0-2	4	020
		8	400
2a	1.1-1a	2a	200-m
		6a	040-M
2b	1.1-1b	2b	002-m
		6b	004-M
5	1.1-2	5	010-S
		9	300-S
9	2.0-1	15	031, 103, 130
8a	2.0-2a	17	023, 320
		18	401, 410
8c	2.0-2b	11a	102, 120, 021
		21a	043, 430, 403
8b	2.0-2c	11b	201, 210, 012
		21b	034, 304, 340
7	2.1-1	13	032-m, 230-m, 203-m
		14	041-M, 140-M, 104-M
-	2.1-2a	16a	420-m, 402-m
		16b	024-m, 420-M
6	2.1-2b	10	022-m, 220-m, 202-m
		20	044-M, 440-M, 404-M
10a	2.1-3a	19	013-S, 310-S, 301-S
10b	2.1-3b	12	011-S, 110-S, 101-S
		22	033-S, 330-S, 303-S
14a	3.0-1a	29	411
		33	323
14b	3.0-1b	28	123, 321, 132, 213, 312, 231
		34	413, 314, 431, 341, 134, 143
13	3.0-2	24	212, 122, 221
		37	434, 344, 443
-	3.1-1a	27b	421-m, 412-m
		32b	423-M, 324-M
12	3.1-1b	26	232-m, 223-m, 322-m
		31	414-M, 441-M, 144-M
-	3.1-1c	27a	142-M, 241-M, 124-M, 214-M, 421-M, 412-M
		32a	423-m, 324-m, 432-m, 342-m, 234-m, 243-m
11	3.1-2	23	222-m
		36	444-M
15	3.1-3a	25a	121-S, 112-S, 211-S
		38a	343-S, 334-S, 433-S
-	3.1-3b	25b	121-S, 112-S
		38b	343-S, 334-S, 433-S
16	3.1-4	30	131-S, 113-S, 311-S
		35	133-S, 313-S, 331-S

[a] ZS-type refers to the refined classification on antipodal structures by Zharov and Serafimov (1975)

7.2 Completeness of classifications

The classifications presented above do not include (by assumption) biazeotropic mixtures, i.e. mixtures where two binary azeotropes exist for one or more of the binary constituents or where there exists two ternary azeotropes. Kogan (1971) suggested that the rule of azeotropy is not valid for biazeotropic mixtures. However, this is not true, because the rule of azeotropy is a topological rule based on the combination of singular points of different types for continuous surfaces (without a gap), and its validity does not depend on the number of singular points of one element of the surface. This fact has been proved by Komarova *et al.* (1974) and by Matsuyama and Nishimura (1977), and is also discussed in Serafimov (1996). An example of a hypothetical biazeotropic mixture is given in Figure 22. The set of singular points in the mixture is $S_3 = 1$, $N_3 = 1$, $N_2 = 2$, $S_2 = 2$, $S_1 = 1$ and $N_1 = 2$, which satisfies the rule of azeotropy.

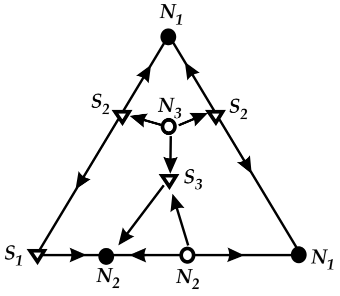


Figure 22: *The rule of azeotropy also applies to biazeotropic mixtures: Hypothetical mixture with two ternary azeotropes and two binary azeotropes for one of the binary pairs.*

The classifications do not take into account structures with nonelementary singular points. The existence of biazeotropy and nonelementary singular points of the residue curves is closely connected to tangential azeotropy. The structure of residue curve maps and the rule of azeotropy for such mixtures are considered in the papers by Serafimov (1971*a*; 1971*b*; 1971*c*; 1971*d*; 1974), Doherty and Perkins (1979*a*), Kushner *et al.* (1992) and Serafimov *et al.* (1996). It is beyond the scope of this survey to review these papers, though they touch upon interesting aspects. For example, structures with biazeotropic elements and nonelementary singular points are encountered in the transition from one topology to another with pressure (or temperature) change. At bifurcation pressures, one or more of the singular points will be nonelementary. The fact that the classifications do not include such transient structures, which usually exist over only very small pressure (temperature) intervals, does not limit their practical use.

7.3 Occurrence of predicted structures

Experimental VLE data indicates the natural occurrence of ternary mixtures for at least 16 of Serafimov's 26 topological classes, and 28 of the 49 antipodal types given by Zharov and Serafimov (1975). Serafimov (1968*d*) analyzed the occurrence of different types of VLE diagrams among 418 reported data on azeotropic mixtures. Later, Reshetov made a similar study for 1609 ternary mixtures (in which 1365 are azeotropic) based on thermodynamic data published during the period from 1965 to 1988 (Reshetov, 1998). The occurrence of the various classes and types of ternary mixtures based on these data are presented in Table 4, and a graphical representation is given in Figure 23.

Table 4: *Occurrence of classes of ternary VLE diagrams found in published mixture data*

No.	Serafimov's Class	Occurrence Serafimov (until 1968)	ZS-type of Antipodal Structure	Set of Azeotropes	Occurrence Reshetov (1965-1988)
0	0	-	1	zeotropic	244
1	1.0-1a	13	3a	min	283
			7a	max	12
2	1.0-1b	2	3b	min	4
			7b	max	1
3	1.0-2	20	4	min	95
			8	max	21
4	1.1-1a	None	2a	min + min A_3	None
			6a	max + max A_3	None
5	1.1-1b	None	2b	min + min A_3	None
			6b	max + max A_3	None
6	1.1-2	7	5	min + S_3	8
			9	max + S_3	8
7	2.0-1	1	15	min + max	9
8	2.0-2a	None	17	min + max	2
			18	max + min	3
9	2.0-2b	77	11a	min + min	280
			21a	max + max	6
10	2.0-2c	2	11b	min + min	10
			21b	max + max	2
11	2.1-1	None	13	min + max + min A_3	None
			14	min + max + max A_3	None
12	2.1-2a	None	16a	min + max + min A_3	None
			16b	min + max + max A_3	None
13	2.1-2b	3	10	min + min + min A_3	55
			20	max + max + max A_3	None
14	2.1-3a	14	19	min + max + S_3	37
15	2.1-3b	5	12	min + min + S_3	2
			22	max + max + S_3	1
16	3.0-1a	None	29	min + min + max	None
			33	max + max + min	None
17	3.0-1b	None	28	min + min + max	9
			34	max + max + min	3
18	3.0-2	85	24	min + min + min	114
			37	max + max + max	None
19	3.1-1a	3	27b	min + min + max + min A_3	None
			32b	max + max + min + max A_3	None
20	3.1-1b	None	26	min + min + max + min A_3	None
			31	max + max + min + max A_3	None
21	3.1-1c	None	27a	min + min + max + max A_3	None
			32a	max + max + min + min A_3	None
22	3.1-2	171	23	min + min + min + min A_3	355
			36	max + max + max + max A_3	None
23	3.1-3a	None	25a	min + min + min + S_3	None
			38a	max + max + max + S_3	None
24	3.1-3b	None	25b	min + min + min + S_3	None
			38b	max + max + max + S_3	None
25	3.1-4	15	30	min + min + max + S_3	41
			35	max + max + min + S_3	4

min - minimum-boiling binary azeotrope, max - maximum-boiling binary azeotrope

A_3 - ternary node azeotrope, S_3 - ternary saddle azeotrope

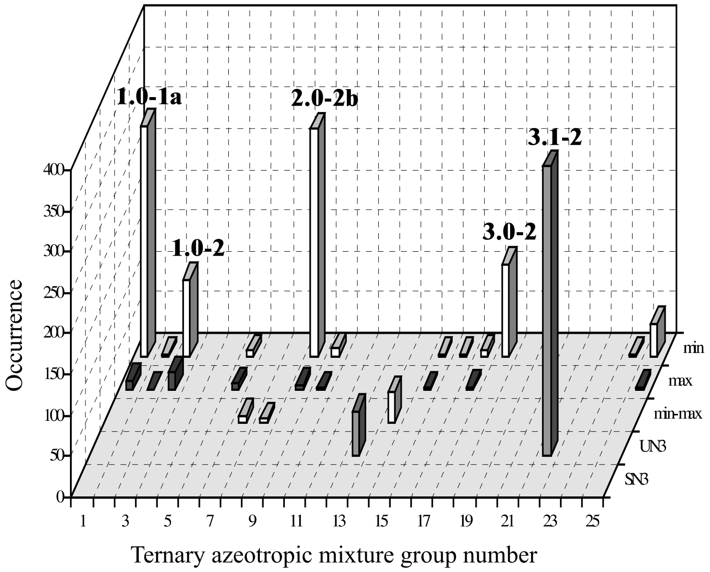


Figure 23: *Occurrence of classes among published data for ternary mixtures (Reshetov's statistics 1965-1988).*

using the mixture group number (No.) in Table 4. The structures are divided into groups including only or mostly minimum-boiling azeotropes (”min”), only or mostly maximum-boiling azeotropes (”max”), equal number of minimum- and maximum-boiling azeotropes (”min-max”), and minimum- and maximum-boiling ternary azeotropes (”UN3” and ”SN3”, respectively).

Obviously, the distribution reported in these studies does not necessarily reflect the real occurrence in nature. The azeotropic data selection is small and occasional. Moreover, the distribution can be distorted compared to the unknown “natural” distribution since the published components data are the results of a deliberate search for entrainers for specific industrial separation problems. Nevertheless, these data are interesting and can be used for some deductions.

Both statistics, from Serafimov (1968*d*) and Reshetov (1965-1988) show the same trend. Serafimov's class 3.1-2 with three minimum-boiling binary azeotrope and one minimum-boiling ternary azeotrope has the largest number of reported mixtures. About 26 % of the 1365 ternary azeotropic mixtures in the study by Reshetov, and 41 % of 418 mixtures in the study by Serafimov, are of this class. In the statistics by Reshetov, the second largest class (1.0-1a) has one minimum-boiling binary azeotrope, and the third largest class (2.0-2b) has two minimum-boiling binary azeotropes.

Baburina *et al.* (1983; 1988) claimed that some types of the VLE diagrams are thermodynamically inconsistent, namely Serafimov's classes 1.0-1a, 1.0-1b, 2.1-1, 3.0-1a, 2.0-2a, 3.0-1a, 3.0-1b, 3.1-3a and 3.1-3b. Thus, according to Baburina, the number of feasible classes of topological VLE diagram structures is only 15 rather than 26. This statement was based on the reasoning that: (a) mixtures of these classes were not reported in Serafimov's statistics (Serafimov, 1968*d*); (b) these diagrams cannot be described by the Wilson activity coefficient equation; (c) theoretical analysis by the authors confirms the inconsistency of these diagrams. All these arguments appear to be incorrect: (a) real mixtures representing the classes 1.0-1a, 1.0-1b, 2.0-2a, and 3.0-1b are found as shown in the statistics given above; (b) Zhvanetskij *et al.* (1993) demonstrated that all the 26 classes of VLE diagrams can be simulated by the Wilson activity coefficient equation; (c) it has been shown that the theoretical analysis by Baburina *et al.* is not valid (Reshetov *et al.*, 1990; Zhvanetskij *et al.*, 1993). Later, accepting Baburina's claims, Pöllmann and Blass (1994) and Pöllmann *et al.* (1996) proposed to reduce the number of ternary VLE diagrams to consider only ”physically meaningful” structures. The list of ”physically meaningful” structures in Pöllmann and Blass (1994) includes 19 structures of Serafimov's classes 0, 1.0-1a, 1.0-1b, 1.0-2, 1.1-2, 2.0-1, 2.0-2a, 2.0-2b, 2.0-2c, 2.1-2b, 2.1-3a, 2.1-3b, 3.0-1a, 3.-1b, 3.0-2, 3.1-1b, 3.1-2, 3.1-3a, 3.1-4.

However, in our opinion, it is impossible in principle to state that some classes of ternary mixtures cannot exist in nature or are "physically meaningless" because all the structures predicted by the rule of azeotropy are thermodynamically and topologically consistent by definition. We can only discuss the *probability* of the existence of some types of the VLE diagram structure. It is well-known that binary maximum-boiling azeotropes are less abundant than minimum-boiling azeotropes. According to Lecat (1949) the ratio of the minimum-boiling versus maximum-boiling azeotropes that occur in nature is about 9 to 1, and the statistics of Reshetov confirms this approximate rule, see Figure 24. In particular, no ternary mixture with three binary maximum-boiling azeotropes has been found among the selection of 1365 mixtures, and no ternary maximum-boiling azeotrope has been found. As a result, even for the topological structures where existence is beyond question, the occurrence of antipodes with maximum-boiling azeotropes is much less common than that of antipodes with minimum-boiling azeotropes, see Table 5.

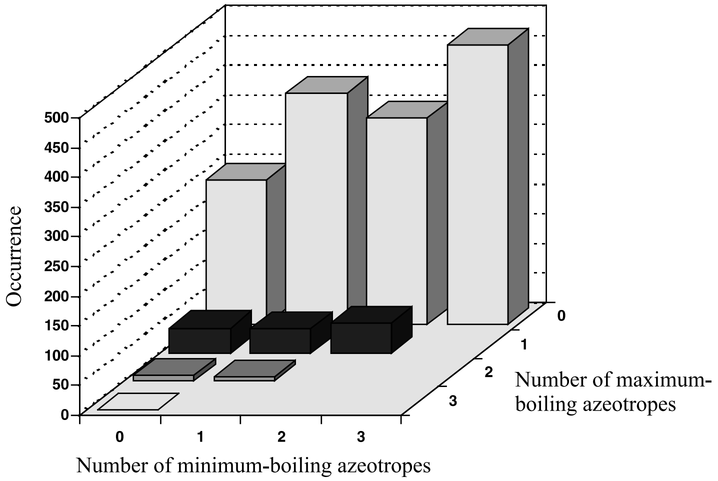


Figure 24: *Occurrence of various combination of binary azeotropes in ternary mixtures.*

Table 5: *Occurrence of antipodes of the most common topological classes of ternary VLE diagrams*

Serafimov's Class	Reshetov's Statistics (1965-1988) min. azeotrope(s)	max. azeotrope(s)
1.0-1a	283	12
1.0-2	95	21
2.0-2b	280	6
2.1-2b	55	None

We propose to consider some conditions that limit the natural occurrence of certain VLE diagram structures. First, we find for maximum-boiling azeotropes:

1A low probability of three binary maximum-boiling azeotropes occurring in a ternary mixture

1B low probability of the occurrence of a ternary maximum-boiling azeotrope.

Second, the following structures require unlikely molecular interactions:

- **2A** low probability that there is a saddle separatrix that is not a boundary of the residue curve region
- **2B** low probability that there is a ternary node in a mixture with binary azeotropes of different signs
- **2C** low probability that there is a ternary saddle in a mixture with binary azeotropes of the same sign.

Based on these assumptions, we can reveal the structures that are expected to be rare. These “improbable” structures are presented in Table 6. The table includes two structures that are on the list of ”physically meaningful” structures given by Pöllmann and Blass (classes 3.1-1b and 3.1-3a). None of the structures in Table 6 are reported to occur in real mixtures according to the statistics presented in the previous section. Low probability does not mean that these structures do not exist, but Table 6 can be used as an Ockham’s Razor in analysis of VLE and azeotropic distillation. It is conceivable that some of these structures occur in nature but only as tangential azeotropes (i.e., the singular points responsible for these structures are close to an edge of the composition triangle to such an extent that they have not been detected experimentally or through modeling). For practical purposes the existence of such singular points can be neglected in such cases. The mixtures in the collection by Reshetov are ranked in the order of decreasing occurrence in Table 7. Most common VLE diagram structures are given in Group A. Group B structures are also common, and Group C can be considered as rare structures.

Table 6: *Improbable types of topological classes of ternary VLE diagrams*

Serafimov’s Class	ZS[a]-type	Matsuyama and Nishimura’s Class	Probability (1-low, 2-very low, 3-improbable)	Limiting Factors
1.1-1a	2a	200-m	1	2A
	6a	040-M	3	2A + 1B
1.1-1b	2b	020-m	1	2A
	6b	004-M	3	2A + 1B
2.1-1	13	032-m, 230-m, 203-m	1	2B
	14	041-M, 140-M, 104-M	3	2B + 1B
2.1-2a	16a	420-m, 402-m	1	2A
	16b	024-m, 420-M	3	2A + 1B
2.1-2b	20	044-M, 440-M, 404-M	3	1B
3.1-1a	27b	421-m, 412-m	1	2A + 2B
	32b	423-M, 324-M	3	2A + 2B + 1B
3.1-1b	26	232-m, 223-m, 322-m	1	2B
	31	414-M, 441-M, 144-M	3	2B + 1B
3.1-1c	27a	142-M, 241-M, 124-M, 214-M, 421-M, 412-M	3	2A + 2B
	32a	423-m, 324-m, 423-m, 342-m, 234-m, 243-m	1	2A + 2B + 1B
3.1-2	36	444-M	3	1A + 1B
3.1-3a	25a	121-S, 112-S, 211-S	1	2C
	38a	343-S, 334-S, 433-S	2	2C + 1A
3.1-3b	25b	121-S, 112-S	1	2C
	38b	343-S, 334-S, 433-S	2	2C + 1A

[a] ZS-type refers to the refined classification on antipodal structures by Zharov and Serafimov (1975)

Table 7: *Identified structures of ternary VLE diagrams among real mixtures according to Reshetov's statistics (1965 to 1988)*

		Structure of Ternary VLE Diagram			
	No.	Serafimov's Class	ZS[a]-type	Matsuyama & Nishimura's Class	Occurence %
Group A $>$ 5 %	1	3.1-2	23	222-m	26.0
	2	1.0-1a	3a, 7a	100, 030	21.6
	3	2.0-2b	11a, 21a	102, 120, 021, 043, 430, 403	21.0
	4	1.0-2	4, 8	020, 400	8.5
	5	3.0-2	24	212, 122, 221	8.4
Group B 1 - 5 %	6	2.1-2b	10	022-m, 220-m, 202-m	4.0
	7	3.1-4	30, 35	131-S, 113-S, 311-S, 133-S, 313-S, 331-S	3.3
	8	2.1-3a	19	013-S, 310-S, 301-S	2.7
	9	1.1-2	5, 9	010-S, 300-S	1.2
Group C $<$ 1 %	10	2.0-2c	11b, 21b	201, 210, 012, 034, 304, 340	0.9
	11	3.0-1b	28	123, 321, 132, 213, 312, 231	0.88
	12	2.0-1	15	031, 103, 130	0.66
	13, 14	2.0-2a	17, 18	023, 320, 401, 410	0.36
	13, 14	1.0-1b	3b, 7b	001, 003	0.36
	15	2.1-3b	12, 22	011-S, 110-S, 101-S, 033-S330-S, 303-S	0.22

[a] ZS-type refers to the refined classification on antipodal structures by Zharov and Serafimov (1975)

7.4 Determination of the structure

The question of whether it is possible to determine the VLE diagram structure of a mixture solely from the boiling temperatures of the pure components and azeotropes has been discussed since the first publications in this field. It was claimed by Gurikov (1958) and later confirmed by Serafimov (1968*a*), and Zharov and Serafimov (1975) that, in general, pure component and azeotropic boiling temperature data only are *not* sufficient to construct the diagram uniquely and that additional information about the *direction* of increasing boiling temperature near some singular points is needed. It has been proposed using ebulliometric measurements to obtain this additional information experimentally (Serafimov, 1968*a*; Zharov and Serafimov, 1975). Obviously, a mathematical description of the VLE may be used for this purpose too.

Doherty (1985) stated that the residue curve maps can be uniquely and explicitly determined from the components and azeotropes boiling points only. This concept is used by Bernot (1990), Foucher *et al.* (1991) and Peterson and Partin (1997). However, this assumption is not theoretically founded and is not valid in general. On the other hand, as noted by Foucher *et al.* (1991) and as we show below, in most cases the simple ranking of singular points (components and azeotropes) in order of increasing boiling points is sufficient to construct the structure of the residue curve map. In specific cases we have indeterminacy (Foucher *et al.*, 1991), but this is really a result of the lack of data required for a unique solution. The cases where different structures of VLE diagrams correspond to the same order of the boiling temperatures of the singular points are presented in Figures 25 and 26.

In Cases 1 and 2 the indetermination occurs for one topological class (antipodes). Case 1 is described by Foucher *et al.* (1991). For all the cases in Figure 25 the real structure of the given mixture can be easily determined experimentally. Depending on the direction of the increasing temperature b or c near the singular point in the triangle given in column a) the mixture has a structure as given in column b) or c). A more complex situation presented in Figure 26 is also described by Foucher *et al.* (1991) and named "global" indeterminacy. The real structure cannot be identified from additional investigation of the boiling

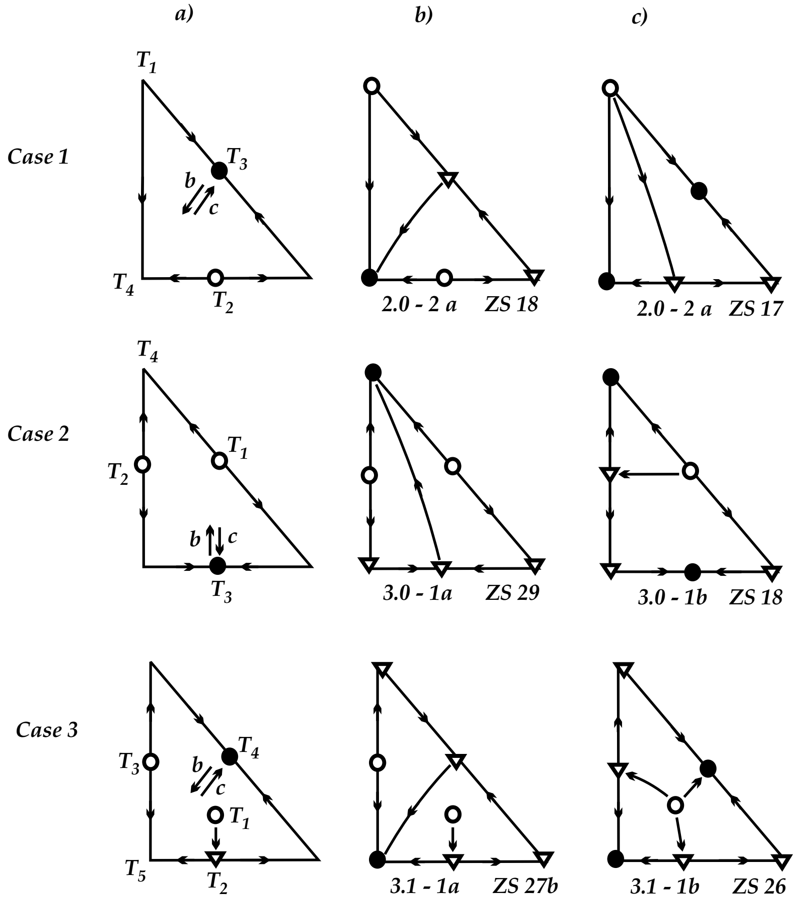


Figure 25: *Indeterminacy of the residue curve map structure for a ternary mixture with the given order of the components and azeotropic temperature points: a) the given set of temperature ordered singular points; b,c) feasible structure alternatives.*

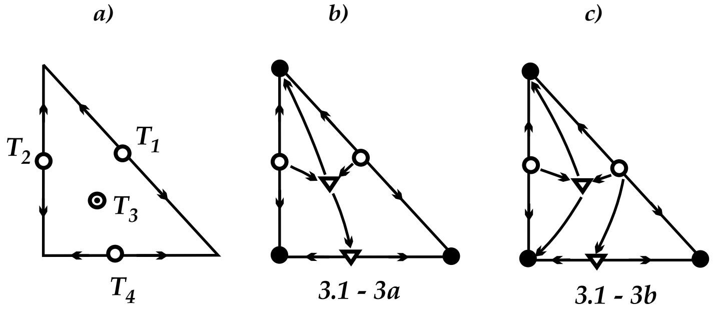


Figure 26: *Global indeterminacy of the residue curve map structure for a given order of the components and azeotropic points (according to Foucher, 1991): a) the given order of the singular points; b,c) feasible structure alternatives.*

temperature surface, and computing the actual residue curve map is required. Fortunately, this type of structure has low probability (no mixtures reported yet, see Table 6).

There are some cases where identification of the structure of VLE diagram can be made with a high degree of probability from the data on the components and binary azeotropes. These cases are presented in Table

8. In all other cases, binary data are not sufficient for the precise identification of the structure. By way of example let us consider the mixtures with two and three binary minimum-boiling azeotropes where we know all singular points at the edges of triangle (Figure 27 a, cases 1 and 2). Three feasible structures are shown in Figure 27 (b, c, d for each case). All feasible alternatives are likely to occur and it is very risky to assign a structure to the given mixture based on information about the singular points at the edges of triangle only.

Table 8: *Window of prediction of ternary VLE diagram structures from binary data only*

Singular points on the edges 12-23-13 (Matsuyama's nomination)	Structure Alternatives				Most probable structure		
	Serafimov's Class	ZS-type	Serafimov's Class	ZS-type	Serafimov's class	ZS-type	Comment
100	1.0-1a	3a	1.1-1a	2a	1.0-1a	3a	
030	1.0-1a	7a	1.1-1a	6a	1.0-1a	7a	almost certain
001	1.0-1b	3b	1.1-1b	2b	1.0-1b	3b	
003	1.0-1b	7b	1.1-1b	6b	1.0-1b	7b	almost certain
103 (or 130, or 031)	2.0-1	15	2.1-1 2.1-1	13 14	2.0-1	15	

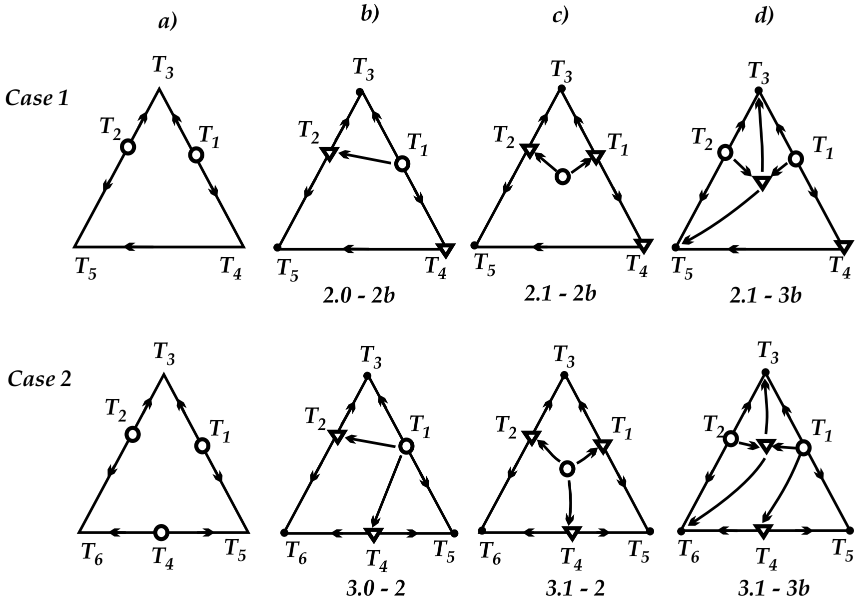


Figure 27: *Feasible alternatives of the residue curve map structure for the given ranking of the singular points at the edges of the composition triangle: a) the given set of ranking of the components and azeotropic points at the edges of the composition triangle; b) structure without ternary azeotrope; c) structure with a ternary unstable node azeotrope; d) structure with a ternary saddle azeotrope.*

This is also pointed out by Westerberg (1997): *Generally, we cannot construct a unique diagram if we only know the existence of the azeotropes and their boiling point temperatures. If we know the temperature and also the nature of all the pure component and azeotrope points (type of saddle, stable node, unstable node), then we can sketch a unique diagram.*

It has been stated by Matsuyama and Nishimura (1977), Yamakita *et al.* (1983) and Foucher *et al.* (1991) that the rule of azeotropy can be used to check the consistency of azeotropic data. It is appropriate to emphasize that this only applies to the consistency of the experimentally determined ternary azeotropic points. Furthermore, only when the boiling temperature of this point lies between the temperatures of the singular point of a separatrix or a line between an unstable node and a stable node, can an erroneous ternary azeotrope be singled out and excluded. If the experimentally determined singular point has a boiling point temperature outside these intervals it cannot be excluded on the basis of the rule of azeotropy. This is demonstrated in Figure 28.

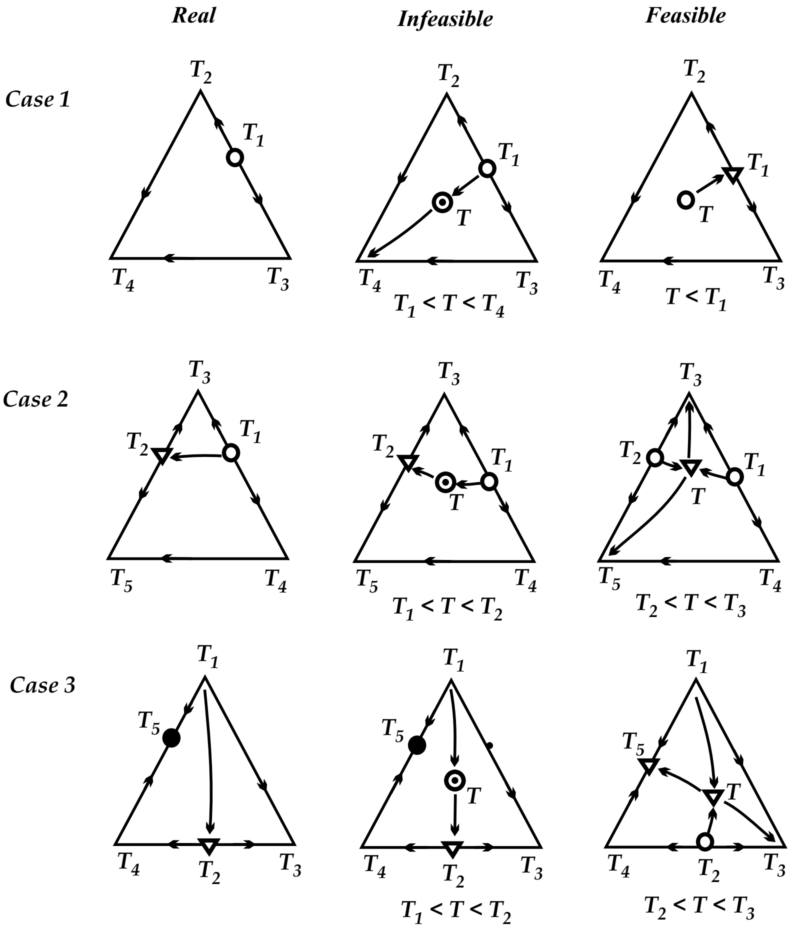
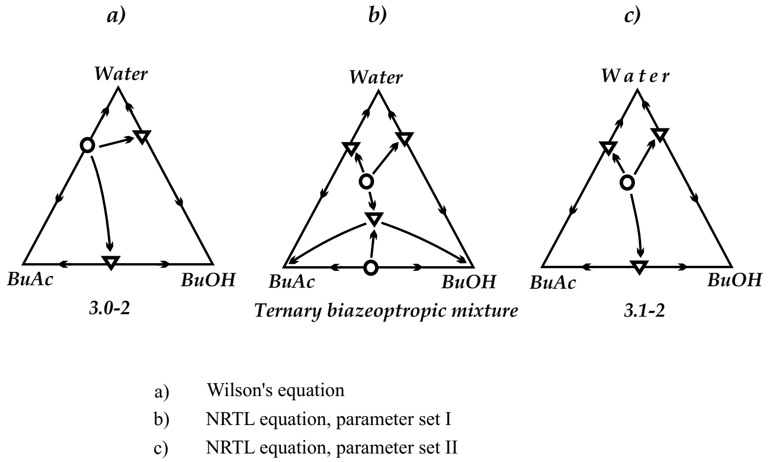


Figure 28: *Consistency test based on the rule of azeotropy may fail to detect an erroneous experimentally determined ternary azeotrope (⊙): a) real structure; b) infeasible structure (existence of the false ternary azeotrope is excluded); c) feasible structure (existence of the false ternary azeotrope obeys the rule of azeotropy and cannot be excluded).*

The issues concerning the identification of the VLE diagram structure on the basis of incomplete information (and indeterminacy and inconsistency of such identification) were of great significance before the mathematical modeling of VLE became widely applicable. Today we can obtain an appropriate mathematical description of the ternary VLE, find all singular points and construct the diagram of residue curves or distillation lines based on data for the binary constituents. It is also possible to predict the binary parameters from the characteristics of the pure components (e.g., by means of the group contribution models). VLE diagrams obtained by modeling are determined and consistent by definition (but they do not necessarily represent the behavior of the real mixtures properly). The real issue today is the accuracy of the model description. The description of a ternary mixture can be wrong even with reliable binary data because the ternary azeotrope can be found (or not found) mistakenly by the model. For example, modeling the VLE for the mixture of n-butanol, n-butyl acetate and water by means of the Wilson and NRTL activity coefficient equations may give different topological structures of the diagrams depending on the binary parameters sets that were chosen, see Figure 29. A ternary azeotrope is known to exist for this mixture. With the given binary data, the Wilson equation does not predict a ternary azeotrope. However, the Wilson equation itself is capable of predicting all the feasible ternary diagrams in Figure 21.



a) Wilson's equation
b) NRTL equation, parameter set I
c) NRTL equation, parameter set II

Figure 29: *Prediction of the VLE diagram structure for the mixture butanol-butyl acetate - water based on thermodynamic models.*

The parameters for the model can be readily corrected if experimental data on the ternary azeotrope are available. However, topological or thermodynamic considerations do not help to select the correct model in such a situation if only binary data are available.

8 Unidistribution and Univolatility Lines

This section deals with the *geometry* of the simple phase transformation trajectories. The very essence is given in Section 8.2).

8.1 Distribution coefficient and relative volatility

The distribution coefficient and relative volatility are well-known characteristics of the vapor-liquid equilibrium. The distribution coefficient K_i is defined by:

$$K_i = y_i/x_i \tag{14}$$

As the name implies, K_i characterizes the distribution of component i between the vapor and liquid phases in equilibrium. The vapor is enriched with component i if $K_i > 1$, and is impoverished with component i if $K_i < 1$ compared to the liquid. The ratio of the distribution coefficients of components i and j gives the relative volatility of these components, usually denoted by α_{ij}:

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{y_i/x_i}{y_j/x_j} \tag{15}$$

The relative volatility characterizes the ability of component i to transfer (evaporate) into the vapor phase compared to the ability of component j. Component i is more volatile than component j if $\alpha_{ij} > 1$, and less volatile if $\alpha_{ij} < 1$. For ideal and nearly ideal mixtures, the relative volatilities for all pair of components are nearly constant in the whole composition space. The situation is different for nonideal and in particular azeotropic mixtures where the composition dependence can be complex. The qualitative characteristics of the distribution coefficient and relative volatility functions are also considered in a general form by the ”pen-and-paper” approach that is typical for the thermodynamic topological analysis.

Serafimov (1970*a*) considered the behavior of these functions for binary mixtures. Based on Serafimov’s approach and the paper by Kushner *et al.* (1992), we present in Figure 30 the feasible patterns of the distribution coefficient functions $K_i(\boldsymbol{x})$ and $K_j(\boldsymbol{x})$ for *binary mixtures* according to the feasible paths of the equilibrium line $\boldsymbol{y}(\boldsymbol{x})$. The distribution coefficients of azeotrope-forming components are equal to unity in the points of the pure components and the azeotrope. One of these distribution coefficient functions has an extremal point when the equilibrium line $\boldsymbol{y}(\boldsymbol{x})$ has an inflection point, and both distribution coefficient functions have extrema when there is an azeotrope in the mixture. The relative volatility function $\alpha_{ij}(\boldsymbol{x})$ intersect the line $\alpha = 1$ at the azeotrope points(s). The transitions from one type of diagram to another is caused by the change of the molecular interactions of the components resulting in positive or negative deviations from ideality given by Raoult’s law.

In conclusion, the composition dependence of the distribution coefficients are qualitative and quantitative characteristics of the VLE for the given mixture. The patterns of these functions determines not only the *class* of binary mixture (zeotropic, minimum- or maximum-boiling azeotrope, or biazeotropic), but the individual behavior of the given mixture as well, as will be shown in the following section.

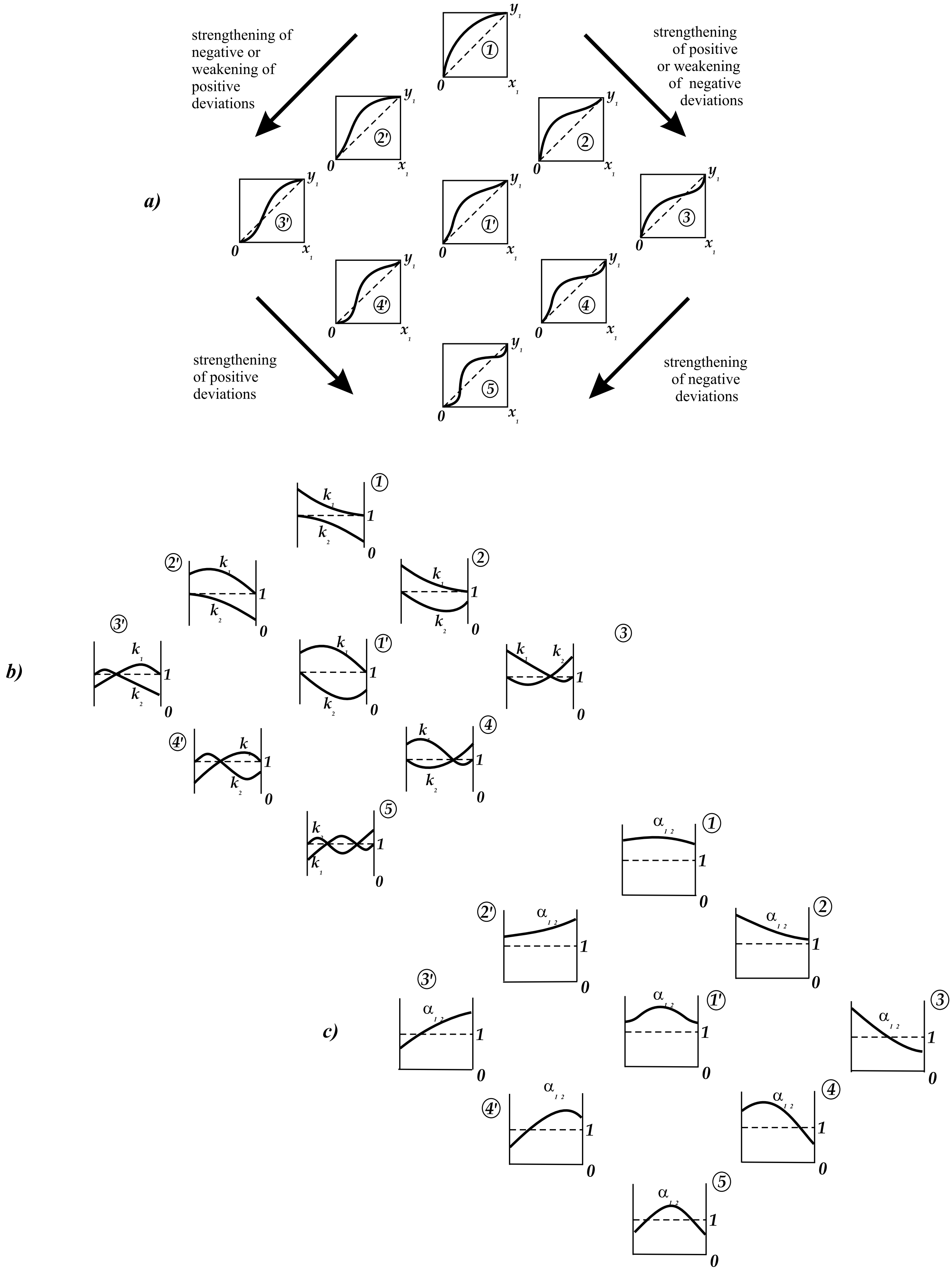


Figure 30: *Correspondence between the feasible patterns of the VLE functions for binary mixtures of components 1 and 2: a) Equilibrium line $\boldsymbol{y}(\boldsymbol{x})$; b) Distribution coefficients $K_i(\boldsymbol{x})$ and $K_j(\boldsymbol{x})$; c) Relative volatility $\alpha_{ij}(\boldsymbol{x})$.*

8.2 Univolatility and unidistribution line diagrams

The composition dependence of the distribution coefficients of a ternary mixture of components 1, 2 and 3 can be represented by three surfaces $K_1(\boldsymbol{x})$, $K_2(\boldsymbol{x})$ and $K_3(\boldsymbol{x})$. Serafimov (1970*a*) proposed to consider the system of *unidistribution lines* in the composition space where the distribution coefficient of the given component i equals unity $K_i(\boldsymbol{x}) = 1$.

The dynamic system of open evaporation residue curves given in Equation (7) can be represented as:

$$\frac{dx_i}{d\tau} = x_i\,(1 - K_i) \qquad i = 1, ..., n-1 \tag{16}$$

The singular points of this system are related to the unidistribution lines, because:

(a) in the point of pure component i $\quad K_i = 1,\ x_j = 0,\ x_h = 0$

(b) in the point of binary azeotrope A_{ij} $\quad K_i = K_j = 1,\ x_h = 0$

(c) in the point of ternary azeotrope A_{ijh} $\quad K_i = K_j = K_h = 1$

Thus, the existence of a binary azeotrope gives rise to two unidistribution lines ($K_i = 1$ and $K_j = 1$), and the existence of a ternary azeotrope gives rise to three unidistribution lines ($K_i = 1$, $K_j = 1$, $K_h = 1$). The point of pure component i may (or may not) give rise to an unidistribution line of component i. Serafimov (1970*b*; 1970*a*; 1973) showed that a given residue curve map corresponds to a given set of feasible diagrams of unidistribution lines.

In a similar way, the relative volatility function can be represented by *isovolatility lines*, that is, contour lines in the composition plane of the three surfaces $\alpha_{ij}(\boldsymbol{x})$ for all pairs of the components. It is difficult to interpret all three isovolatility lines (α_{ij}, α_{ih}, α_{jh}) in the same diagram. Serafimov *et al.* (1972) propose to use the system of *univolatility lines* where $\alpha_{ij} = 1$. In addition, isovolatility lines for other values than unity are useful to evaluate the influence of a component h on the relative volatility of the other two components ij given by α_{ij}^{h}, in the search for an entrainer for extractive distillation (Laroche *et al.*, 1993; Wahnschafft and Westerberg, 1993). We use the term *univolatility lines* to distinguish between the lines where $\alpha_{ij} = 1$ from other isovolatility lines where $\alpha_{ij} \neq 1$. It is evident that the point of a binary azeotrope Az_{ij} gives rise to an α_{ij}-univolatility line and that the point of a ternary azeotrope gives rise to the three univolatility lines ($\alpha_{ij} = 1$, $\alpha_{ih} = 1$, and $\alpha_{jh} = 1$). Serafimov *et al.* (1972) showed that there are also univolatility lines which are not connected to azeotropic points, and that such lines can occur even in zeotropic mixtures.

Analysis of feasible diagrams of unidistribution and univolatility lines is given by Serafimov (1970*b*; 1970*a*; 1972). The main aim of this work was to consider feasible structures of the residue curve maps in more detail, and in fact the approach helped to construct more refined classification of the ternary diagrams. Later, the diagrams of unidistribution lines were used as a main tool for analysis of tangential azeotropy and biazeotropy (Serafimov, 1971*a*; Serafimov, 1971*b*; Serafimov, 1971*c*; Serafimov, 1971*d*; Kushner *et al.*, 1992; Serafimov *et al.*, 1996). The diagrams of univolatility lines were used for the same purpose by Zhvanetskij and Reshetov *et al.* (Zhvanetskij *et al.*, 1988; Zhvanetskij *et al.*, 1989; Zhvanetskij *et al.*, 1993; Reshetov *et al.*, 1990; Sluchenkov *et al.*, 1990). In addition, Zhvanetskij *et al.* (1988) noted that univolatility lines split the composition triangle into regions of certain order of volatility of components which they named "regions of K-ranking", or, "K-ordered regions".

In this paper we consider the feasible structures unidistribution and univolatility line diagrams given by Serafimov for the purpose of sketching the simple phase transformation trajectories such as residue curves and distillation lines.

The unity lines are *road signs* for the pathway of residue curves and distillation lines, that is, they give the exact direction of the equilibrium vectors in the composition space (Kiva and Serafimov, 1973):

1. Along the unidistribution line ($K_i = 1$) all equilibrium vectors in the composition space $\overrightarrow{\boldsymbol{xy}}$ are parallel to the edge jh of the composition triangle (see Figure 31).
2. Along the univolatility line ($\alpha_{ij} = 1$) the equilibrium vector $\overrightarrow{\boldsymbol{xy}}$ lies on the secant going from the vertex H through the given point $\boldsymbol{x}$ (see Figure 32).
3. At an intersection of a residue curve with the unidistribution line ($K_i = 1$) there is an extremal point of the composition x_i ($dx_i/d\tau = 0$) (see Figure 31).

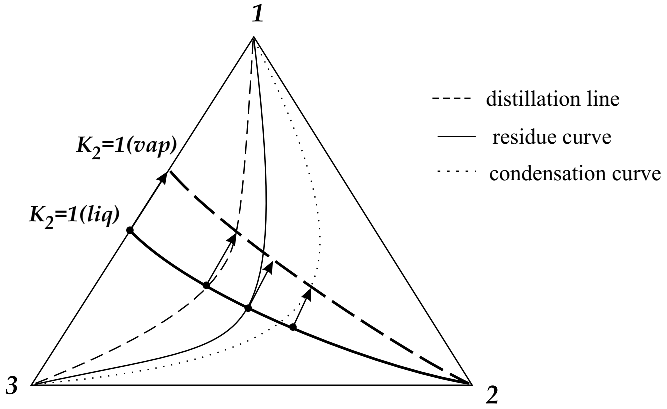


Figure 31: *The simple phase transformation trajectories have extremal compositions along the unidistribution lines (here shown for a zeotropic mixture).*

4. If there are no univolatility lines, there are no inflection points of the simple phase transformation trajectories (see Figure 31).
5. The univolatility line α_{ij} gives rise to an inflection point of the residue curves (and the other simple phase transformation trajectories) if there is no K_i or K_j unidistribution lines along the residue curve between the univolatility line in question and the stable or unstable nodes of the residue curves.

   This rule is illustrated in Figure 32 for a zeotropic mixture of components 1-2-3 with two univolatility lines ($\alpha_{12} = 1$ and $\alpha_{23} = 1$). It can be seen that there is no unidistribution line between the unstable node 1 and the α_{23}univolatility line, and there is an inflection point on the residue curves between the unstable node and the univolatility line. In a similar way, there is no unidistribution line between the α_{12}univolatility line and the stable node 3, and there is an inflection point of the residue curves between this univolatility line and the stable node too. There is a K_2 unidistribution line between the α_{23} univolatility line and the α_{12} univolatility line, and there are no inflection points between the univolatility lines.
6. The inflection points for all lines on the residue curve bundle intersecting the univolatility line are located on the *inflection line*, that is, the locus of inflection points. A rule of the relative location of the inflection lines for various simple phase transformations can be determined from simple geometric considerations. This rule is illustrated for an example mixture in Figure 33.
7. The inflection line of the distillation lines coincides with the univolatility line if the inflection exists between the univolatility line and the maximum-boiling node. The inflection line of the distillation lines coincides with the E-mapping (Section 2) of the univolatility line if the inflection exists between

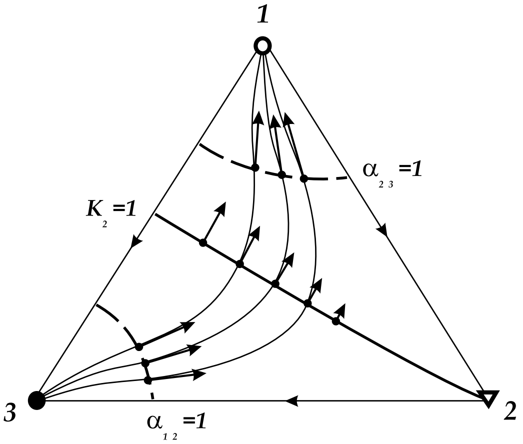


Figure 32: *Residue curve map with two inflection points on the residue curves for a zeotropic mixture with two univolatility lines. The mixture is of Serafimov's class 0.0-1 with two-sided arc-wise univolatility lines.*

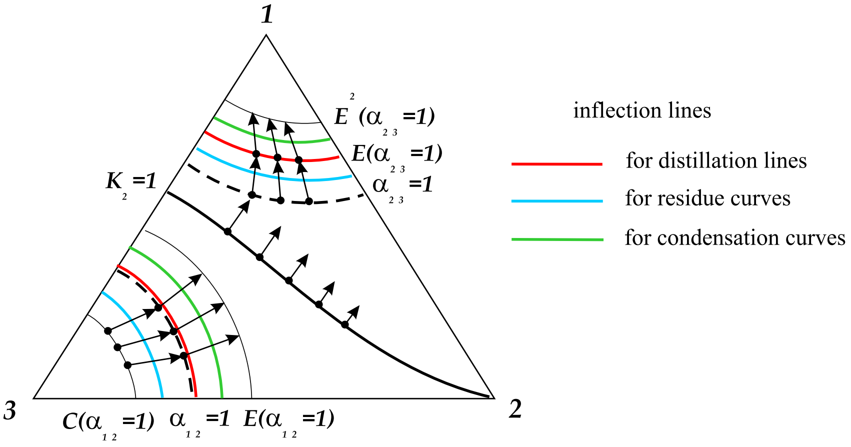


Figure 33: *Relative location of the inflection lines for various simple phase transformations relative to the location of the univolatility lines and their equilibrium vectors.*

the univolatility line and the minimum-boiling node. The inflection line of the residue curves is shifted from the inflection line of the distillation lines in the direction of the residue curves movement (the shift is less than one equilibrium vector). The inflection line of the condensation curves is shifted from the inflection line of the distillation lines in the direction of the condensation curves movement (the shift is less than one equilibrium vector). In addition, the inflection points occur if the line of the simple phase transformation intersects the unidistribution lines of the same index (component(s)) or the same univolatility lines twice in succession. Examples of these situations are given in Figure 34 and 35.

For the mixture represented in Figure 35 some of the distillation lines have two inflection points (between the minimum-boiling node 1 and the α_{23} univolatility line, and between two intersections of the α_{23} univolatility line.

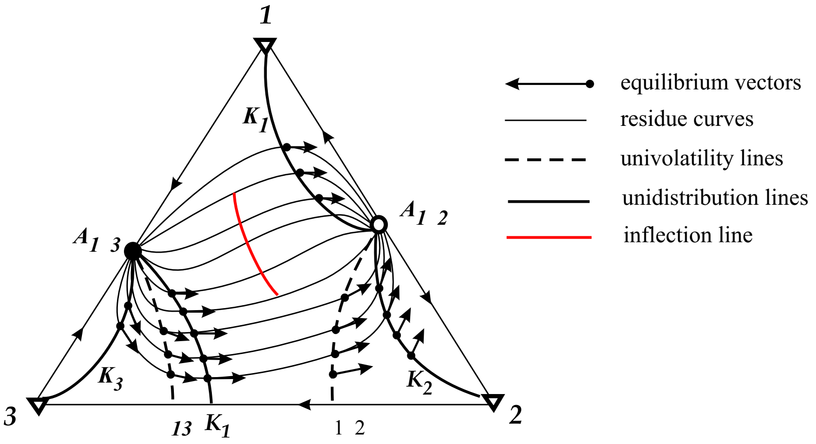


Figure 34: *Existence of inflection points between two unidistribution lines of the same index* K_1*. The mixture is of Serafimov's class 2.0-1.*

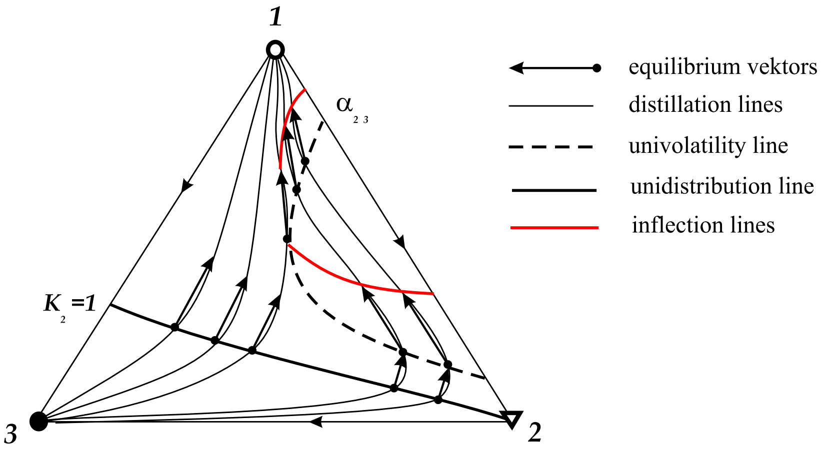


Figure 35: *Appearance of inflection points between two intersections of the same univolatility line. The mixture is of Serafimov's class 0 with single-sided arc-wise univolatility line.*

Figure 36 illustrates how, on the basis of unidistribution and univolatility lines, we can make a complete sketch of the residue curve map.

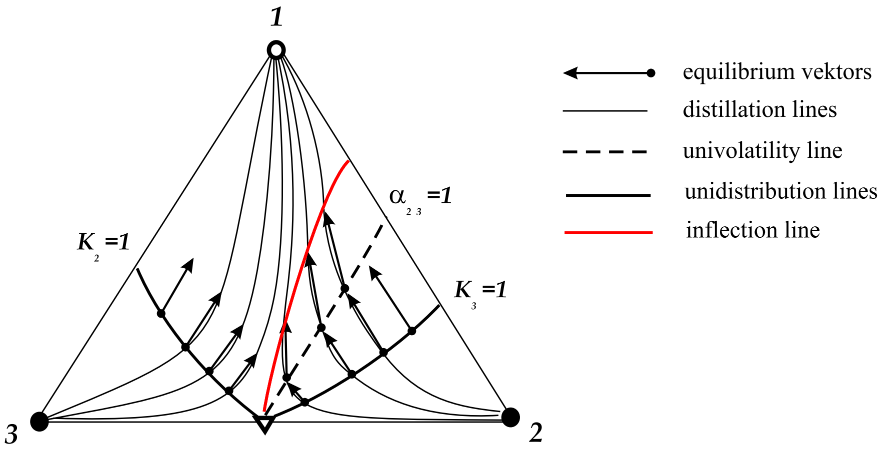


Figure 36: *Sketch of the distillation line map for a mixture of Serafimov's Class 1.0-2 based on the unity line roadmap.*

The splitting of the composition space into regions of volatility ranking (K-ranking) is shown in Figure 37 for the examples presented in Figure 32 and 34-36. The regions are determined by the combination of three digits corresponding to the number of components. The order of the digits gives order of decreasing volatility, that is, 123 means that 1 is the most volatile and 3 the least.

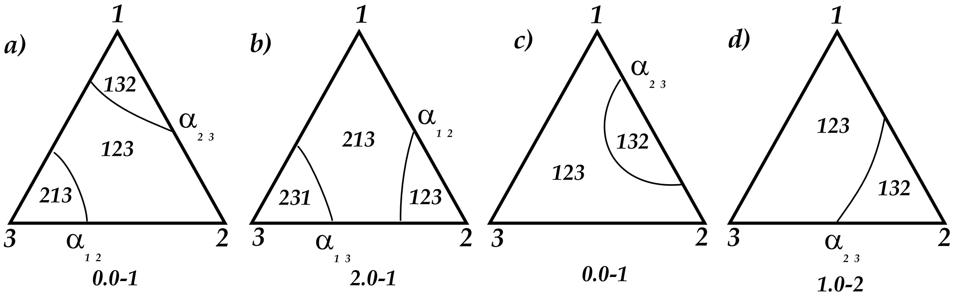


Figure 37: *Examples of how the composition space is split into regions of K-ranking (according to Zhvanetskij et al., 1988): (a) mixture given in Figure 32; (b) mixture given in Figure 34; (c) mixture given in Figure 35; (d) mixture given in Figure 36*

The diagrams in Figure 37 clearly illustrate that the volatility order of the components cannot coincide with their boiling point temperatures in the whole composition space even for zeotropic mixtures if the diagram includes univolatility lines. The combined diagram of unidistribution and univolatility lines permits us to construct the sketch of the simple phase transformation maps. It not only characterizes the topology of the maps but their geometry as well. The unidistribution and univolatility lines can be readily determined numerically based on a VLE model of the given mixture (see for example Bogdanov and Kiva (1977)), and their computation is much easier than the computation of the residue curves or especially the distillation lines.

8.3 Structure of unidistribution and univolatility line diagrams

The motivation of this section is that a combined diagram of unidistribution and univolatility lines can characterize the VLE for any given mixture, and enable us to sketch residue curves and distillation lines maps without any computation.

An overview of the unity line diagrams for the most common classes of ternary mixtures (according to Reshetov's statistics given in Table 7, Section 7.3) is presented in Figure 38, where only the intrinsic univolatility lines are shown.

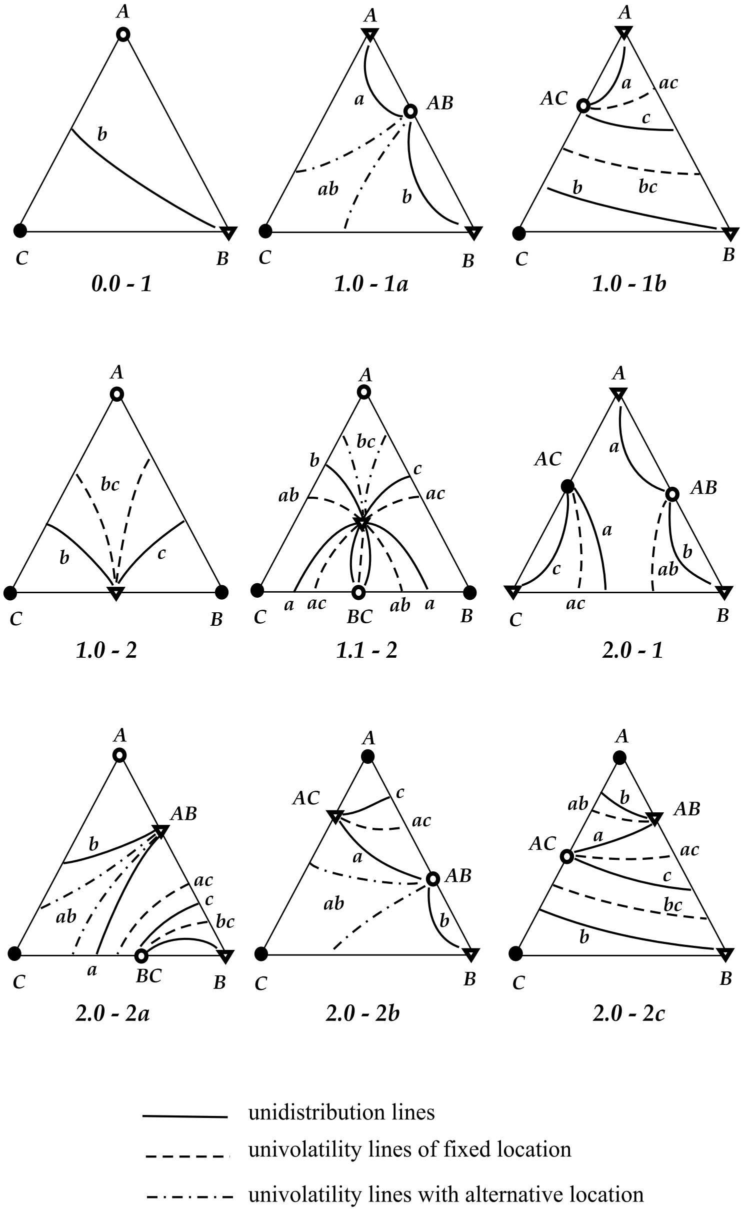


Figure 38: *Unidistribution and univolatility line diagrams for the most common classes of ternary mixtures according to Reshetov's statistics (Section 7.3).*

To elaborate on the ideas presented in the two previous sections (8.1 - 8.3) we can study an unfolded triangle shown in Figure 39 where each binary composition diagram is presented in detail. Such unfolded diagrams illustrate how the various combinations of binary constituents and shapes of the $K_i(\boldsymbol{x})$ surfaces lead to various structures of the ternary diagrams. Thus, by considering each binary pair of a ternary mixture we can understand the phenomena behind its ternary VLE behavior as well. This is shown in more detail in the following five examples.

Example 1. Zeotropic mixture 1-2-3

a) Let us assume that all three binary constituents are mixtures of Type 1. Unfolding the prism, we draw the curves $K_i(x)$ at the edges of the prism and determine the values $K^{\infty}_{i(j)}$ (infinite dilution of i in j) at the edges of the prism (Figure 39). Here:

$$\begin{array}{rcl} (K_1 = 1) > & K^{\infty}_{2(1)} & > K^{\infty}_{3(1)} \\ K^{\infty}_{1(2)} > & (K_2 = 1) & > K^{\infty}_{3(2)} \\ K^{\infty}_{1(3)} > & K^{\infty}_{2(3)} & > (K_3 = 1) \end{array}$$

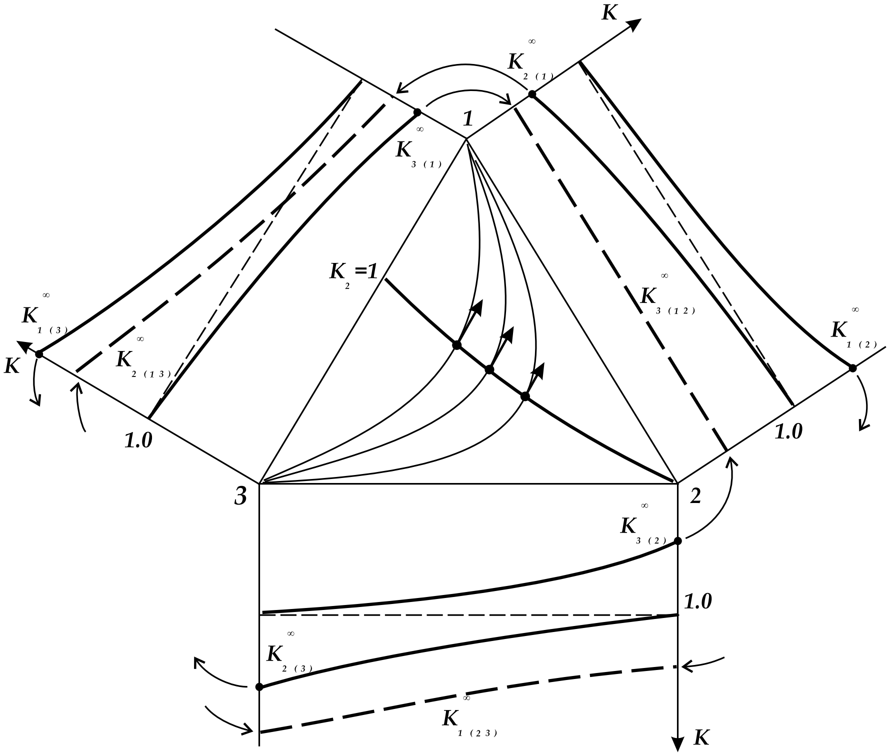


Figure 39: *The construction of the ternary VLE diagram for a zeotropic mixture 1-2-3 where all the binary constituents are mixtures of Type 1 (C-shaped residue curves).*

Assuming that the functions $K^{\infty}_{i(jh)}$ are monotonous, we construct their feasible trajectories at the edges of the prism. We can see that line $K^{\infty}_{2(13)}$ intersects line $K = 1$ and there are only two points with the value $K_2 = 1$ at the edges of the triangle. These points are connected by the K_2-unidistribution line. There are no univolatility lines and, consequently, there are no inflection points at the residue curves or distillation lines. A sketch of the diagram is made based on the location of unidistribution line. This cell of residue curves (distillation lines) is C-shaped.

b) Let us assume that the binary mixture 1-3 is the mixture of Type 2’, i.e. it becomes more negative or less positive than the mixture 2-3 (Figure 40).

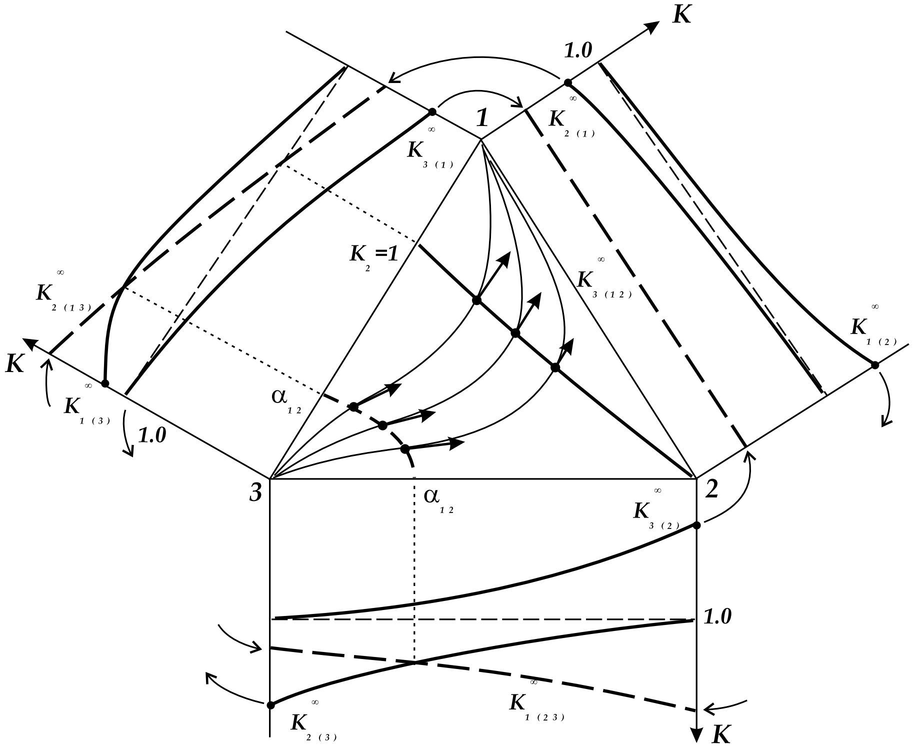


Figure 40: *Univolatility and unidistribution line diagram and phase portrait of the residue curve map for a zeotropic mixture 1-2-3 where the binary constituents 1-3 are a mixture of Type 2’ (S-shaped residue curves).*

Then $K^{\infty}_{2(3)} > K^{\infty}_{1(3)} > (K_3 = 1)$, and there are points of intersection of the lines $K_1(x)$ and $K_2(x)$ at the edges 13 and 23. As a result, the α_{12}-univolatility line connects edges 13 and 23 of the composition triangle (Figure 40), and there is not a unidistribution line between this line and the stable node of residue curves. This univolatility line gives rise to inflection points of residue curves and distillation lines. A sketch of the diagram is determined based on the position of unidistribution and univolatility lines. This cell of residue curves (distillation lines) is S-shaped.

c) Let the binary mixture 1-3 be a mixture of Type 2, i.e. it becomes more positive than the mixture 12. In the similar way we find that there is an α_{23}-univolatility line connecting edges 12 and 13 and no unidistribution lines between it and the unstable node of the residue curves (Figure 41). This univolatility line gives rise to inflection points of residue curves and distillation lines. A sketch of the diagram is determined basing on the position of unidistribution and univolatility lines. This cell of residue curves (distillation lines) is S-shaped too but with opposite sign of the curvature.

d) Let the binary mixture 1-3 be a mixture of Type 1’, i.e., it has a mixed deviation from ideal mixtures. The diagram of unidistribution and univolatility lines and the sketch of the RC (DL) map here is given above in Figure 32. In this case there are both an α_{12}-univolatility line connecting edges 13 and 23 and an α_{23}-univolatility line connecting edges 12 and 13. Any line of the simple phase transformations has two inflection points, and the lines are Ω-shaped.

e) Let the binary mixture 1-2 be a mixture of Type 1’ . The diagram of unidistribution and univolatility lines and the sketch of the RC (DL) map here is given above in Figure 35. Here, there is the α_{23}-univolatility line as an arc at edge 12 of the composition triangle. A part of the residue curves or distillation lines

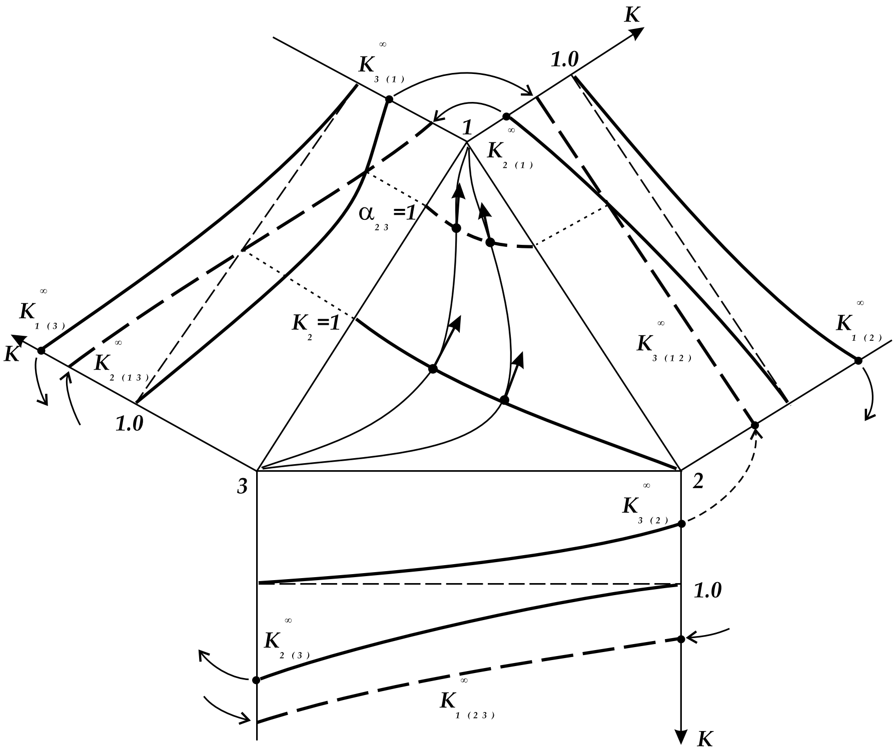


Figure 41: *Unidistribution and univolatility line diagram and the sketch of residue curves for a zeotropic mixture 1-2-3 where the binary constituents 1-3 are a mixture of Type 2 (S-shaped residue curves).*

intersects this univolatility line twice in succession. Each of these lines of a bunch will have two inflection points (one point between the intersection points and other between the univolatility line and the Apex 1. These lines have a specific Ω-shape and other lines are C-shaped.

It can be seen from these examples that the single unidistribution line going from the saddle point is an inherent characteristic of zeotropic mixtures (Serafimov's Class 0). Univolatility lines can optionally exist if the mixture is nonideal, and there is a diversity of the diagrams of univolatility lines caused by various combinations of the deviation from ideality in the binary constituents.

Detailed analysis of all feasible types of the univolatility lines for ternary zeotropic mixtures was made later by Zhvanetskij et al., 1988, and 33 variants of these diagrams were revealed. Though the occurrence of most of these types is questioned, all these types are possible theoretically.

Example 2. Mixture 1-2-3 with minimum-boiling azeotrope A_{12} (Serafimov's Class 1.0-1a)

a) The mixture 1-2 in this ternary mixture must be the mixture of Type 3. Let both mixtures 2-3 and 1-3 be mixtures of Type 1. The diagram of unidistribution and univolatility lines and the sketch of the RC (DL) map are presented in Figure 42 a. The -univolatility line goes from the point of azeotrope to the edge 13. The lines of the simple phase transformations have inflection points between the univolatility line and Apex 3. A part of the lines in this cell are C-shaped, ant the other lines are S-shaped.

b) Let the mixture 1-3 be a mixture of Type 2', i.e., it is more negative (or less positive) than mixture 2-3. Here the -univolatility line goes from the point of azeotrope to edge 23. The lines of the simple phase transformations have another sign of curvature (Figure 42 b).

Let us consider now various trajectories of the functions $K_i(x)$ at edge $K-1-2$ of the prism. In the case

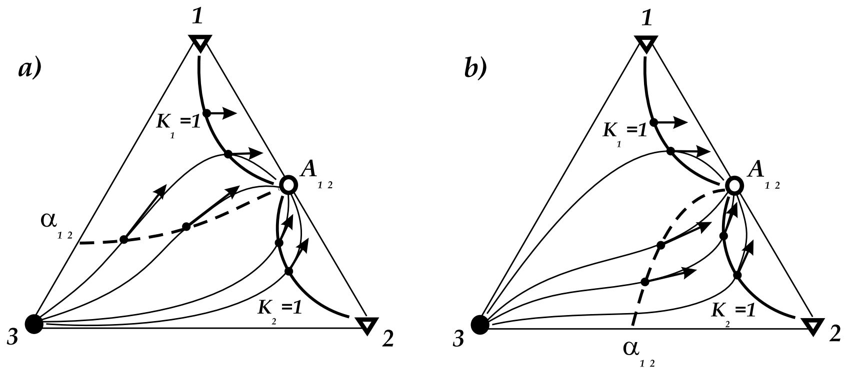


Figure 42: *Unidistribution and univolatility line diagram and the sketch of residue curves for a mixture 1-2-3 with a minimum-boiling azeotrope A_{12} for various types of the binary constituents: a) both mixtures 1-3 and 2-3 are mixtures of Type 1; b) mixture 1-3 is a mixture of Type 2.*

where mixtures 1-3 and 2-3 are the mixtures of Type 1, the only intersection of K-lines corresponds to the point of binary azeotrope, and it leads to the structure presented in Figure 42 a. Other cases are presented in Figure 43.

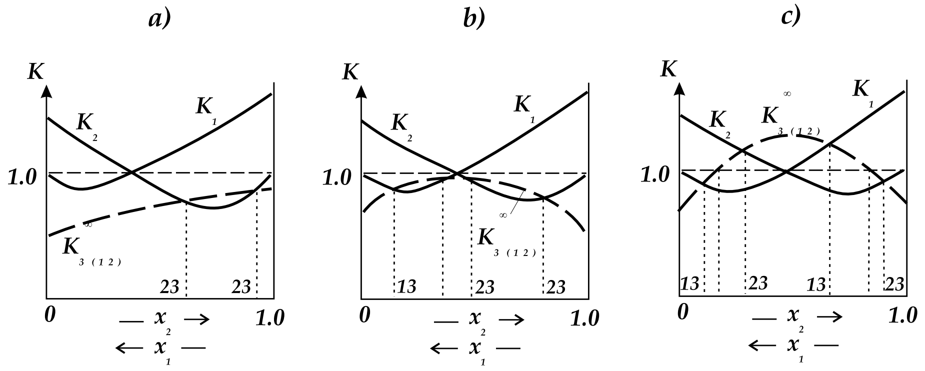


Figure 43: *Distribution coefficient trajectories $K_i(x)$ at the edge $K - 1 - 2$ for a mixture 1-2-3 with minimum-boiling azeotrope 1-2: a) Mixture 2-3 is a mixture of Type 2; b) both mixtures 2-3 and 1-3 are the mixtures of Type 2; c) additional positive deviations at the ternary mixture.*

In Figure 43a, the mixture 2-3 becomes more positive (Type 2), and the line $K^\infty_{3(12)}$ intersects twice in succession with the line $K_2(12)$. It leads to the appearance of two points $\alpha_{12} = 1$ at edge 1-2. The lines of the simple phase transformation have two inflection points when they intersect twice in succession with the α_{23}-univolatility line and there is a local deformation of the residue curves or distillation lines. The corresponding ternary diagram is presented in Figure 44a.

In Figure 43b, both mixtures 1-3 and 2-3 are mixtures of Type 2 (more positive). Line $K^\infty_{3(12)}$ intersects twice in succession with the line $K_2(12)$, and intersects twice in succession with the line $K_1(12)$. It leads to the appearance of two points $\alpha_{12} = 1$ and $\alpha_{13} = 1$ two points at the edge 1-2. The lines of simple phase transformation have two inflection points where they intersect these arc-wise univolatility lines, and the map has two local deformations (Figure 44 b).

Both these diagrams are diagrams of Serafimov's Class 1.0-1a but they have more complex geometry in the simple phase transformation lines than the mixtures represented in Figure 42, corresponding to a more complex diagram of univolatility lines.

It can be seen that the inherent characteristic of the diagram of Class 1.0-1a is just existence of two unidistribution lines going from the azeotrope point to tops 1 and 2 and the α_{12}-univolatility line going between them to one of sides 13 or 23. The movement of the α_{12}-univolatility line and the existence of other univolatility lines are the specific characteristics of the given mixture.

Let us consider the situation where both mixtures 1-3 and 2-3 are mixtures of Type 2, but the positive deviations in the ternary mixture are so strong that line $K^{\infty}_{3(12)}$ has a maximum with the value $K > 1$ (Figure 43 c). Here we have in addition two points at edge 12. This changes the diagram of unidistribution and univolatility lines totally and, consequently, changes the RC (DL) map (Figure 44 c). We can see that strengthening of positive deviations leads to appearance of ternary minimum-boiling azeotrope, and this diagram is a diagram of another class (Serafimov's Class 1.1-1a).

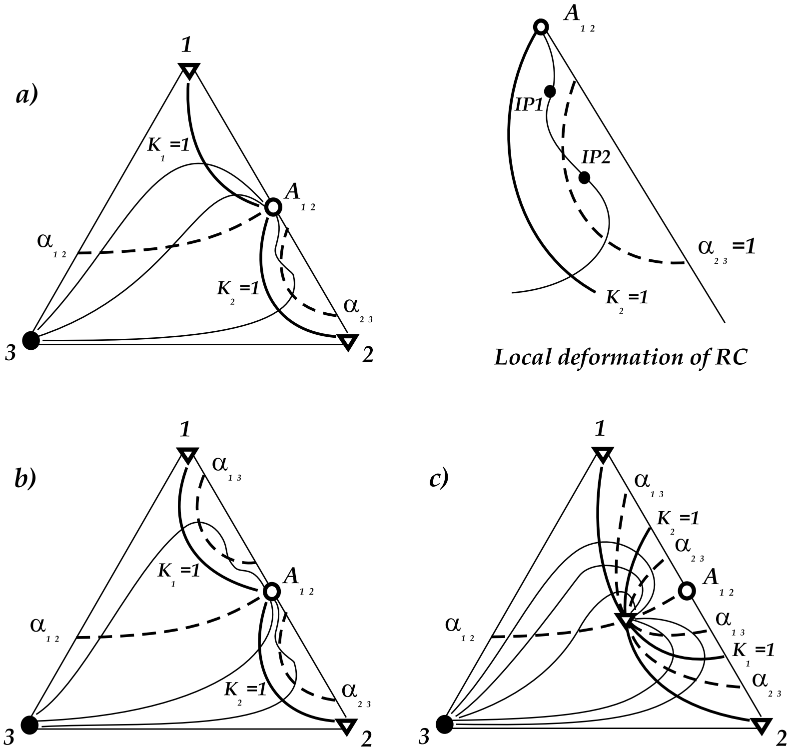


Figure 44: *Unidistribution and univolatility line diagram and the sketch of the residue curve (distillation line) map for the cases presented in Figure 42.*

Example 3. Mixture 1-2-3 with the minimum-boiling azeotrope 13 (Serafimov's Class 1.0-1b)

a) The mixture 1-3 in this ternary mixture must be a mixture of Type 3. Let the mixtures 1-2 and 2-3 be mixtures of Type 1. The diagram of unidistribution and univolatility lines and the sketch of the RC (DL) map are presented in Figure 45.

This diagram includes two univolatility lines, one which (α_{23}-univolatility line) is not connected with an azeotrope. Both univolatility lines are blocked from each side by the corresponding unidistribution lines, and its existence does not lead to the inflection points of the lines of simple phase transformations. These lines are U-shaped. This structure is a diagram of Serafimov's Class 1.0-1b. This set of unidistribution and univolatility lines is an inherent characteristic of the diagrams of this class. The feasible types of the diagram of this class are presented in Figure 46 where additional univolatility lines exist, optionally depending on the combination of the binary constituents.

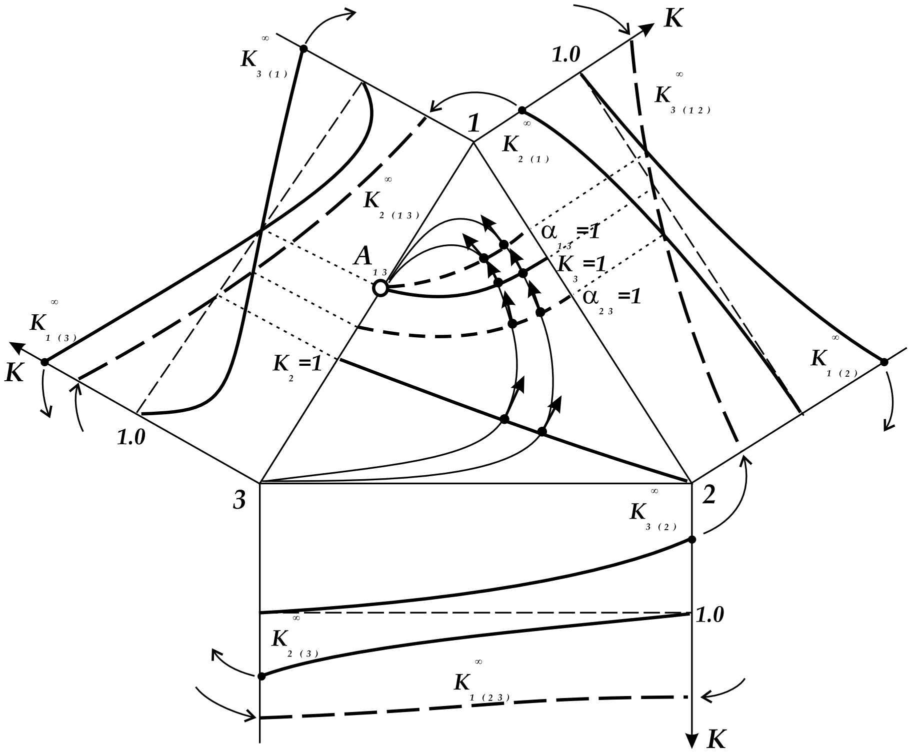


Figure 45: *Unidistribution and univolatility line diagram and the sketch of the residue curve map for the mixture of Class 1.0-1b (U-shaped residue curves).*

We can see that optional (additional) univolatility lines lead to the local deformation of the lines of the simple phase transformations. They change the geometry of the diagram, but do not change the topological structure.

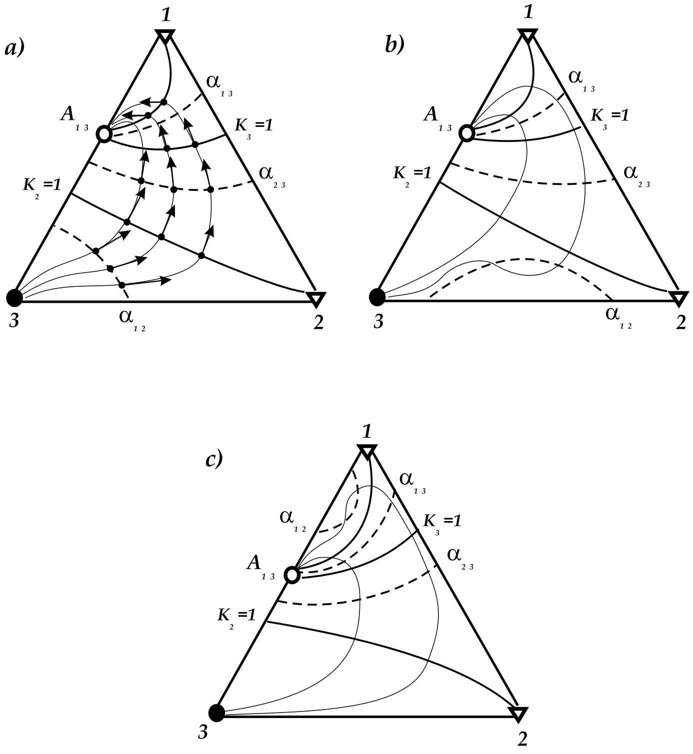


Figure 46: *Types of unidistribution and univolatility line diagrams and of the sketch of residue curve map for mixture of Class 1.0-1b: a) mixture 1-3 is the Type 4 mixture; b) mixture 2-3 is the Type 1' mixture; c) mixture 1-2 is the Type 2 mixture.*

Example 4. Mixture 1-2-3 with minimum-boiling azeotrope 12 and maximum-boiling azeotrope 23 (Serafimov's Class 2.0-1)

Let mixture 1-2 be a mixture of Type 3, mixture 1-3 be a mixture of Type 3', and mixture 2-3 be a mixture of Type 1. The diagram of unidistribution and univolatility lines and the sketch of residue curves (distillation lines) was presented in Figure 34. The univolatility lines are blocked from both sides by the corresponding unidistribution lines and do not give rise to any inflection points. However, part of the lines of simple phase transformations intersect the unidistribution line of the same index (K1) twice in succession, and it leads to the existence of inflection points for these lines. Some feasible variations of this diagram at the different combinations of the binary constituents are presented in Figure 47. Any or both of the additional univolatility lines at side 1-2 can appear when mixture 23 is Type 2' mixture (Figure 47 a, b). Case (c) can appear when mixture 2-3 is Type 2 mixture, and the case (d) can appear when the mixture 2-3 is Type 2 mixture and the mixture 1-3 is Type 4' mixture.

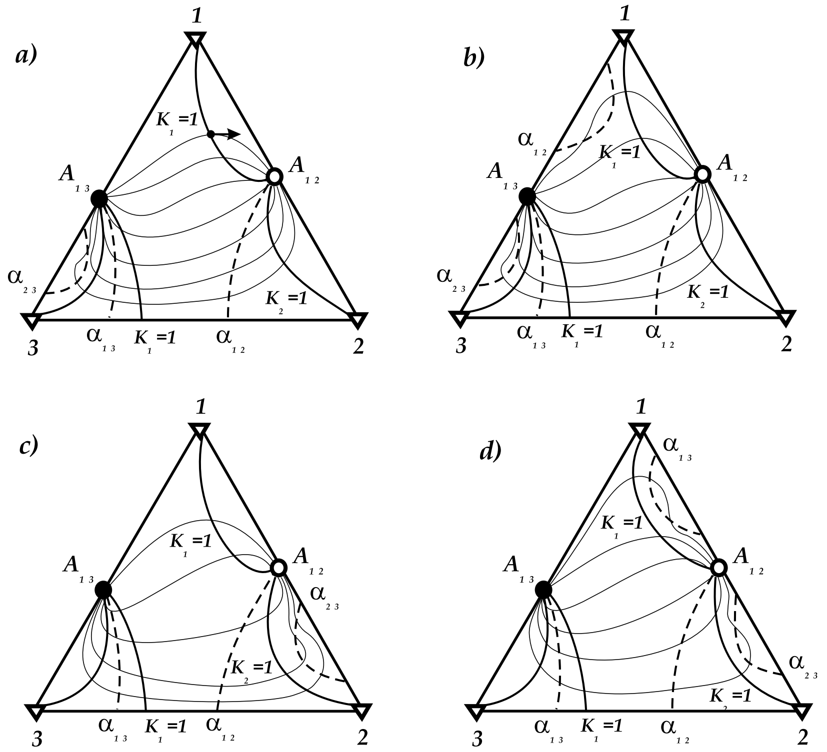


Figure 47: *Types of the diagram of unidistribution and univolatility lines and of the sketch of the residue curve map for a mixture of Class 2.0-1.*

The additional univolatility lines lead to the local deformation of the residue curves or distillation lines. However, we can see that the set of the unidistribution and univolatility lines of the "basic" diagram (Figure 34) is an inherent characteristic of this class of the topological structures (Serafimov's Class 2.0-1).

Example 5. Mixtures with three minimum-boiling binary azeotropes.

Let us consider the diagrams of unidistribution and univolatility lines and the sketches of the residue curves (distillation lines) for the ternary mixture 1-2-3 with minimum-boiling azeotrope in any binary constituent. The diagrams are presented in Figures 48 - 50 assuming that in all cases we have the same functions $K_i(ij)$. We can see that the different types of behavior of the curves $K^{\infty}_{i(jh)}$ lead to different diagrams of unidistribution and univolatility lines and also to a different topological class of the residue curve (distillation line) map. It is interesting to note that the simplest behavior of the curves $K^{\infty}_{i(jh)}$ leads to the the appearance of ternary minimum-boiling azeotrope (Class 3.1-2, Figure 48, and this type of mixture is the most common. More complex behavior of the curves $K^{\infty}_{i(jh)}$ leads to the appearance of the diagram of Serafimov's Class 3.0-2 (Figure 49), and the mixtures of this class occur more rarely. The most complex behavior of the curves $K^{\infty}_{i(jh)}$ leads to the appearance of a ternary saddle azeotrope (Class 3.1-3b, Figure 50), and the occurrence of such mixtures is almost negligible.

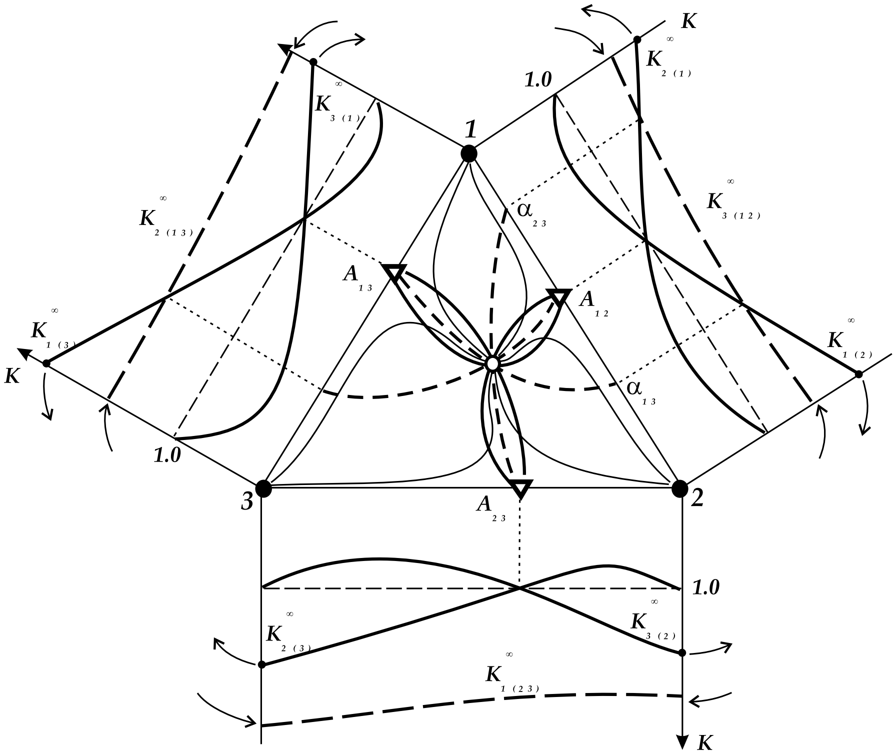


Figure 48: *Unidistribution and univolatility line diagram and sketch of the residue curve map for a mixture of Class 3.1-2.*

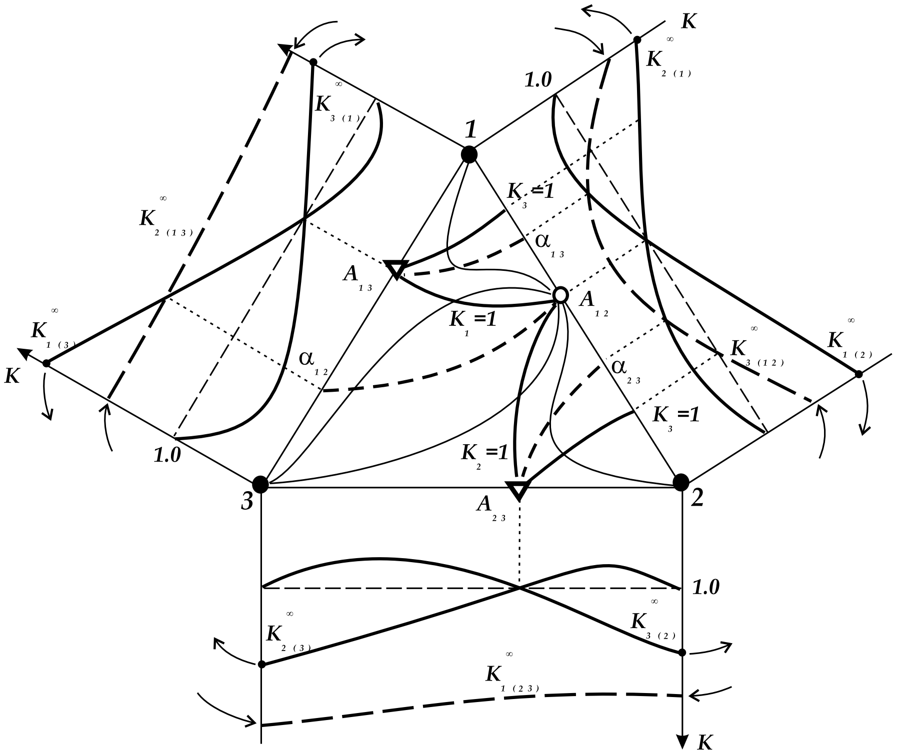


Figure 49: *Unidistribution and univolatility line diagram and sketch of the simple phase transformation line map for a mixture of Class 3.0-2.*

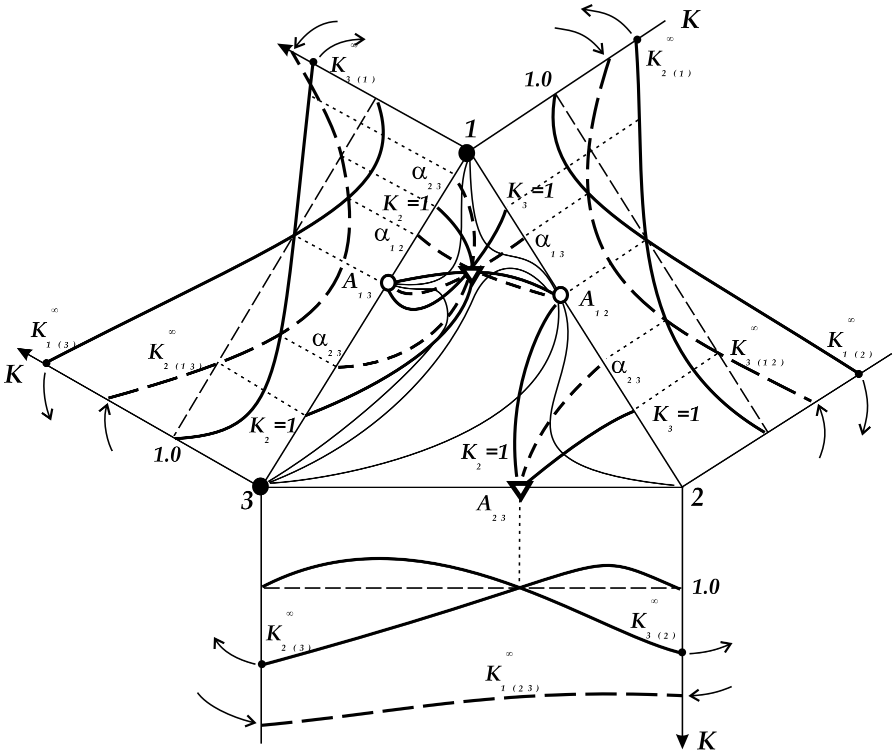


Figure 50: *Unidistribution and univolatility line diagram and sketch of the simple phase transformation line map for a mixture of Class 3.1-3b.*

9 Conclusions

The main conclusions that can be made from the literature on qualitative analysis of the VLE diagrams and the additional investigations presented in this paper are:

1. Vapor-liquid equilibrium can be characterized by various means; first and foremost by simple phase transformation maps, among which open evaporation residue curve maps and distillation line maps have received broad acceptance. Note that distillation lines (discrete and continuous) have a well-defined thermodynamical meaning. These lines are rigorously defined by the VLE and, in turn, characterize it, as well as the residue curves.

   The VLE can also be qualitatively characterized by unidistribution line diagrams and univolatility line diagrams. Univolatility line diagrams give additional information about the regions of the composition space with different volatility order of the components. The combined diagram of unidistribution and univolatility lines characterizes the shape (geometry) of the trajectories of simple phase transformations.

2. We recommend that a distinction is made between the *topological structure* of simple phase transformation maps (i.e., the set of singular points and the splitting into regions of the simple phase transformation trajectories), the *sketch* of the map (i.e., the qualitative pattern of the trajectories with representation of their shape), and the *exact map* of simple phase transformation trajectories like residue curves and distillation lines.

3. The structures of VLE diagrams of azeotropic mixtures are limited by rigorous topological constraints. The structures for ternary mixtures without biazeotropy are classified into 26 possible topological structures. All types of the classified diagrams are topologically and thermodynamically feasible, but their occurrence in nature is determined by the probability of certain combinations of molecular interactions. Data on the natural occurrence of various mixture classes permit us to exclude rare or improbable diagrams from consideration in the investigation of the correlation between VLE diagram structures and feasible separations upon distillation.

4. Usually the (topological) structure of the VLE diagram for a given mixture can be uniquely determined based solely on information about the existence and boiling point temperature of all singular points (pure components and azeotropes). It should be noted however, that there are some cases of indeterminate diagram structures.

5. The (topological) structure of the VLE diagram identifies the class of a given mixture, but not its specific characteristic like the shape of the singular and ordinary simple phase transformation trajectories.

6. A sketch of the simple phase transformation map (residue curve or distillation line map), including the specific features of a given mixture (i.e., the shape of the trajectories), can be determined from the localization of the unidistribution and univolatility lines. These lines give complete information about the curvature (path) of singular and ordinary trajectories of the simple phase transformation.

7. Generating an exact map including the localization of simple phase transformation trajectory boundaries (separatrices) requires numerical calculation. Often, only the boundaries are located by appropriate simulation rather than generating a complete trajectory map.

8. It is reasonable to use the combined diagram of unidistribution and univolatility lines as a representative qualitative characteristic of the VLE.

Acknowledgments

Dr. S.A. Reshetov at the Karpov Institute of Physical Chemistry in Moscow is greatfully acknowledged for providing the statistics on the occurrence of Serafimov's topological classes for reported ternary azeotropic mixtures. Assistance by Dr. Bella Alukhanova in drawing the figures is also greatfully acknowledged.

Definitions of Terms

This section contains an alphabetic listing with definitions of central terms as they are used in this text. Note also that Table 1 in the Introduction gives an overview and quick reference of the different terms used for key concepts in the azeotropic distillation literature and may be helpful in particular when reading Russian publications that are translated into English.

Antipode - exact opposite, but topological equivalent structure.

Azeotrope - mixture whose equilibrium vapor and liquid compositions are equal at the given system temperature and pressure. Mathematically: a singularity in the VLE manifold that does not correspond to a pure component.

Azeotropic distillation - distillation that involves azeotropic mixtures. Note that this is a much broader definition than traditionally used in the distillation literature where the term is frequently used as an abbreviation of heteroazeotropic distillation.

Azeotropic mixture - mixture that forms one or several azeotrope(s).

Biazeotropic mixture - mixture that forms two binary azeotropes for a binary pair or two ternary azeotropes.

Composition space - for an n-component mixture the composition space contains all the n-dimensional vectors of $\mathcal{R}^n$ where the elements sum to unity and are nonnegative.

Composition trajectory - the steady state or instantaneous composition profile of a distillation column, or the trajectory of composition change during batch distillation.

Condensate curve - open condensation liquid composition trajectory.

Condensation curve - open condensation vapor composition trajectory.

Conjugate - an element of a mathematical group that is equal to a given element of the group multiplied on the right by another element and on the left by the inverse of the latter element. *[Britannica]*

Distillate curve - composition trajectory of the vapor during open evaporation.

Distillation - the process of separating a liquid mixture by successive evaporation and condensation.

Distillation boundary - locus of compositions that cannot be crossed by the given distillation process. The existence and location of such boundaries depend critically on the type of distillation in question. Distillation boundaries are thermodynamic barriers for multicomponent distillations in the same way that azeotropes are barriers to binary distillation. They split the composition space into distillation regions.

Distillation line - the set of points $\boldsymbol{x}$ for which the vapor composition in equilibrium $\boldsymbol{y}$ also lies on the same line in the composition space (Zharov and Serafimov, 1975). A discrete distillation line is drawn as a piecewise linear curve through a sequence of conjugated vapor-liquid equilibrium vectors in the composition space. Continuous (smooth) distillation lines interpolate the same sequence of equilibrium points and are not mathematically unique.

Distillation line map - diagram that shows distillation lines for different initial conditions for a given mixture in the composition space.

Distillation region - a subspace of the composition space defined by a family of distillation trajectories that join a stable and unstable node.

Distribution coefficient - ratio of mole fractions in vapor and liquid phase for the given species. Commonly referred to as vapor-liquid equilibrium ratio or K-value.

Entrainer - material (liquid component) that acts as a mass separating agent.

Equilibrium vector - composition vector between two phases in equilibrium, also named *tie-line*.

Equilibrium staged distillation - staged distillation column where vapor-liquid equilibrium is assumed between the phases on all trays.

Heteroazeotrope - azeotrope where the vapor phase coexists with two or more liquid phases.

Heterogeneous mixture - mixture with more than one liquid phase.

Homoazeotrope - azeotrope where the vapor phase coexists with one liquid phase.

Homogeneous mixture - mixture with a single liquid (and vapor) phase.

Ideal mixture - mixture that obeys Raoult's law (or Henry's law), i.e., the activity coefficients for all components of the liquid are equal to unity. Ideal mixtures are a special case of zeotropic mixtures.

Inflection point - root of the second order derivative of a given function, point of change of function curvature.

Inflection point curve - locus of inflection points.

Injective - being a one-to-one mathematical function.

Isodistribution line - locus of points in the composition space where the distribution coefficient for a particular component is constant.

Isomorphic - being of identical or similar form, shape, or structure. Antipodal topological VLE diagrams are isomorphous.

Isotherm - locus of points in the composition space where the temperature for a given mixture at vapor-liquid equilibrium is constant. Liquid isotherms are lines of constant value of the boiling temperature and vapor isotherms are lines of constant value of the condensation temperature.

Isotherm map - diagram that shows isotherms for a given mixture in the composition space. Contour plot of one or both of the vapor-liquid equilibrium temperature surfaces for a given mixture.

Isovolatility line - locus of points in the composition space where the relative volatility of a pair of components is constant.

K-value - see distribution coefficient.

Liquid-liquid tie-line - equilibrium vector between two liquid phases.

Mapping - to assign (as a set or element) in a mathematical correspondence.

Mapping function - function that gives the mathematical correspondence between two sets of elements.

Monoazeotropic mixture - mixture that forms only one azeotrope at each element of the composition simplex (only one binary azeotrope for each binary pair in an azeotropic mixture).

Node (*mathematically*) **-** critical point with all paths either approaching (stable) or departing (unstable).

Nonideal mixture - mixture that exhibits deviations from Raoult's law (or Henry's law). Nonideal mixtures may be zeotropic or azeotropic.

Ockham's Razor - principle stated by English philosopher William of Ockham (1285-1347/49) that the simplest of competing theories should be preferred to the more complex, and that entities are not to be multiplied beyond necessity.

Open condensation - condensation of a vapor phase where the liquid formed is removed continuously.

Open distillation - distillation with input and/or output mass streams.

Open evaporation - evaporation of a liquid phase where the vapor formed is removed continuously. Also referred to as simple distillation or Rayleigh distillation.

Open evaporation distillate curve - see distillate curve.

Relative volatility - the ratio of distribution coefficients for pair of components in a mixture.

Residue curve - composition trajectory of the residue liquid in the still during open equilibrium evaporation. Sometimes referred to as "distillation line" in Russian and old German-language literature.

Residue curve map - diagram that shows residue curves for different initial still compositions for a given mixture in the composition space.

Residue curve region - set of liquid compositions in the composition space that belong to a family of residue curves with common initial and final points.

Saddle - singular point with finitely many paths both approaching and departing. Only separatrices extends or terminate in the saddle point. All other paths have a hyperbolic course in the vicinity of the singular point.

Separatrix - locus of bifurcation points of differential equations, i.e., points at which an infinitesimal perturbation causes at least one of the integration endpoints to change. A separatrix may be stable or unstable dependent on whether solutions in its vicinity approach or depart as the value of the independent (integration) parameter goes to infinity.

Simple distillation - see open evaporation.

Simple distillation region - see residue curve region.

Simple distillation residue curve - see residue curve.

Simple equilibrium phase transformation - process where the composition of one phase changes according to its phases equilibrium and where the other phase is continuously removed. Open evaporation and open condensation are such processes.

Simplex - spatial configuration of (n-1) dimensions determined by n points in a space of dimension equal to or greater than (n-1). A triangle together with its interior determined by its three vertices is a two-dimensional simplex in the plane.

Singular point - root to the first order derivative of a function. The singular points of the residue curve Equations (7) are given by the solution of $\boldsymbol{x} = \boldsymbol{y} = 0$. Azeotropes and pure components are singular points of Equations (7).

Singular vapor line - equilibrium vapor compositions that correspond to the liquid compositions lying on the heterogeneous liquid boiling envelope.

Tie-line - see equilibrium vector.

Tie-line curve - sequence of conjugated vapor-liquid equilibrium vectors (tie-lines) in the composition space. In this paper also referred to as a *discrete distillation line*. See distillation line.

Topology - a branch of mathematics concerned with those properties of geometric configurations (as point sets) which are unaltered by elastic deformations (as a stretching or a twisting).

TTA - thermodynamic topological analysis.

Unidistribution line - locus of points in the composition space where the distribution coefficient of the given component equals unity. At each point along the unidistribution line of component i, the equilibrium vector in the composition space has a direction normal to the component i vertex of the composition simplex.

Unity lines - collective term for unidistribution and univolatility lines.

Univolatility line - locus of points in the composition space where the relative volatility of pair of components equals unity. In ternary systems, a univolatility line of the components i and j is the locus where the equilibrium vectors in the composition space point directly at the third component h vertex.

VLE - vapor-liquid equilibrium.

VLE manifold - union of all possible vapor-liquid equilibrium pairs in a mixture.

VLE diagram - graphical presentation of the vapor-liquid equilibrium functions of a mixture like isotherm maps, residue curve maps and distillation lines maps.

Zeotropic mixture - mixture that does not form azeotropes. A mixture may be zeotropic, but still nonideal.

Authors' Note Concerning the References

The following three Russian scientific journals have been published in English-language editions since about 1957:

Theoretical Foundations of Chemical Engineering
English edition of *Teoreticeskie Osnovy Khimiceskoj Technologii*, Maik nauka, Interperiodica Publ., Moscow. A comprehensive journal covering all aspects of theoretical and applied research in chemical engineering. Published 6 times per year.

Russian Journal of Physical Chemistry
English edition of *Zurnal Fiziceskoj Khimii*, Akademija Nauk SSSR, Moscow. Published monthly by The British Library Document Supply Centre in cooperation with the Royal Society of Chemistry, London.

Russian Journal of Applied Chemistry
English edition of *Zurnal Prikladnoi Khimii*, Akademija Nauk SSSR, Moscow. Previously *Journal of Applied Chemistry of the USSR* (until 1992). Published monthly by Consultants Bureau, New York.

The papers in the English-language editions are translations of papers originally written in Russian. The early translations are often poor and the titles sometimes inadequate and ambiguous. Therefore, we have given corrected English titles in square brackets for some of the references. For example, we have added corrected words in brackets in the subtitle of Serafimov (1968*b*)"II. The Form [*Pattern*] of Distillation Lines [*Residue Curves*] in the Region of Singular Points Near Four-Component Singular Points" to show that the Russian term *distillation line* is what is residue curve in most English-language publications.

Furthermore, the page numbers refer to the page numbering in the English edition, whereas the page numbers given in brackets correspond to the page numbering in the original Russian edition of the journals. If a reference is *only* available in Russian language this is marked by (in Russian). This also applies to other references that are not available in English-language translations.

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