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Research Article

Non-variant phenomena in heterogeneous systems. New type of solubility diagrams points

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Abstract

The article gives a general classification of non-invariant points in phase equilibrium diagrams of all possible types. The complete topological isomorphism of the diagrams of fusibility, solubility, and liquid-vapor equilibria in various sets of variables is demonstrated. The stability of mono-variant equilibria near the non-variant points is investigated. Recurrent formulas for calculating the number of topological elements of phase diagrams are given. A previously undescribed type of non-invariant points and phase processes in the solubility diagrams is described and characterized. The last ones have no topological analogs in other types of diagrams. Thus, we have carried out, as far as is available to the authors, a complete classification of invariant points and invariant processes in phase equilibrium diagrams of an arbitrary type and with an arbitrary number of components.

More Information

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Introduction

The main goal of the article is: to classify non-variant points in the different types of phase diagrams, regardless of component and equilibrium phase numbers; to consider the mono-variant equilibrium in the nearest neighborhood of non-variant points; and to deduce the rules for the calculation of different type phase diagrams elements (points, lines, surfaces – fields, volumes etc) from the data of components and phase numbers.

It is well-known, that non-variant points in the diagrams of phase equilibrium are characterized by the fact, that thermodynamic variance in these points or the number of thermodynamic freedom degrees (*f*) is equal to zero. *f* value is the number of independent state parameters of the system, which one can change without a change in the number or nature of equilibrium phases. Calculation of *f* values is produced with the help of Gibbs rule [1,2]:

$$f = n - k + 2 - l \quad (1),$$

where: n is a component number (or the number of substances, masses of which can change independently), k is the equilibrium phases number, and l is the number of independent limiting conditions, for example, $T = const$ $(l=1)$, or $P = const$ $(l=1)$, or $T,P = const$ $(l=2)$, or $X_i^{(j)} = const_{tr}^{(i)}$ - concentration *i*-th trim in *j*-th phase with variable composition $(l=1)$, or $X_i^{(j)} / X_k^{(j)} = const_{\sec}^{(i,j)}$ concentration plane *i-k-th* section in *j*-th phase with variable composition $(l=1)$, etc [1,2]. Additionally one believes, that external variable force fields are not superimposed on the heterogeneous system and also, that the system does not have many curved surfaces (with curvatures nano-radiuses units or tens nanometers [2]).

The classification of non-variant points in the different type phase diagrams earlier was considered sometimes. For example, in fusibility diagrams such classification (eutectics, *r*-kind peritectics, points of polymorph transitions) was fulfilled earlier [3,4]. For such purposes, the authors elaborated the most common and comfortable vector-matrix apparatus, which was applied in the full concentration range [3]. Later, in solubility diagrams classification of non-variant points (eutonics, *r*-kind peritonics, points of crystal-solvate transitions) was done [5]. Here authors adapted the vector-matrix apparatus from to the reduced (without solvent) concentration range. Classification of non-variant points in the liquid-vapor phase diagrams at *T = const* or *P = const* (congruent hetero-azeotropes, incongruent hetero-azeotropes in equilibrium diagrams: liquid$_1$-liquid$_2$-...-vapor) was also done sometimes as seen in a few works [2,4]. In delamination phase equilibrium diagrams liquid$_1$-liquid$_2$-...liquid$_k$ or solid$_1$-solid $_2$-... solid$_k$ at *T, P = const* (in vapor phases delamination is not prohibited, but sufficiently untypical) such classification was not done may be because of the relative rarity of the consideration. Meanwhile, all types of phase diagrams in different variables of state and different concentration spaces are absolutely equivalent in a topological sense [5–7]. Some types of non-variant equilibrium processes demand closed systems without system mass change, and some – open systems – with system mass change [1,2]. The different types of non-variant equilibrium phase processes are represented in Table 1.

Driving forces in non-variant process may be different

- External heat supply or removal at *P=const,* which is consumed in a non-variant phase process with phases masses change;
- External pressure supply or removal at *T=const,* which also consumed in heterogeneous system volume change in non-variant phase process;
- External component supply or removal at *T, P=const,* which is also consumed in the non-variant phase process (in these cases phase process becomes open).

The stability of mono-variant equilibrium in the nearest neighborhood of non-variant points was considered in the same articles [3,5]. However, common consideration, taking into account the topological isomorphism of phase diagrams, was not conducted. In this part of the article, we shall also use the criteria of the stability of heterogeneous phases complex relatively infinitely small state changes (or criterion of diffusional stability). Probably the first authors got these conditions, authors demonstrated the principle difference between them and similar conditions for the individual phase on the example of hetero-azeotropes in ternary three-phase system [2,8]. In a study, these criteria were generalized on the systems with arbitrary component numbers [9], arbitrary

Table 1: Characteristics of different types of non-variant phase processes (formal signs of stoichiometric coefficients of the resulting).

Number; “Producing phase” (p-ph$_1$)	Phase process ↔ “Producing phase” ↔ ” ± resulting phases” $p-ph_1 \leftrightarrow \pm ph_2 \pm ph_3 \pm ... \pm ph_r$	Diagram of phase equilibrium	Limiting conditions	Concentration space	Components number (n); Phases number (r)	Opened or closed system (N system)
I. liquid (l)	$l \leftrightarrow \pm s_i \pm s_k \pm s_n \pm ... \pm s_m$	fusibility	P=const	full	$r = n+1$ $n \geq 2$	closed
II. vapor (v)	$v \leftrightarrow \pm l_i \pm l_k \pm l_n \pm ... \pm l_m$ $v \leftrightarrow \pm s_i \pm s_k \pm s_n \pm ... \pm s_m$	liquid-vapor solid-vapor	P=const	-“-	-“-	-“-
III. (v)	$v \leftrightarrow \pm l_i \pm l_k \pm l_n \pm ... \pm l_m$ $v \leftrightarrow \pm s_i \pm s_k \pm s_n \pm ... \pm s_m$	liquid-vapor solid-vapor	T=const	-“-	-“-	-“-
IV. (l)	$l \leftrightarrow \pm s_i \pm s_k \pm s_n \pm ... \pm s_m$	solubility	P=const; T=const	reduced, without solvent (w)	$r = n$ $n \geq 3$	opened
V. (l)	$l \leftrightarrow \pm l_k \pm l_n \pm ... \pm l_m$	delamination	P=const	full	$r = n+1$ $n \geq 2$ -“-	closed
VI. solid (s)	$s \leftrightarrow \pm s_k \pm s_n \pm ... \pm s_m$	-“-	-“-	-“-	-“-	-“-
VII. (l)	$l \leftrightarrow \pm l_k \pm l_n \pm ... \pm l_m$	-“-	P=const; T=const	reduced, without one component	$r = n$ $n \geq 3$	opened
VIII. (s)	$s \leftrightarrow \pm s_k \pm s_n \pm ... \pm s_m$	-“-	-“-	-“-	-“-	-“-
IX. (v)	$v \leftrightarrow \pm l \pm s$	single component	Absence	Absence	r = 3 n =1	indifferently
X. (v)	$v \leftrightarrow \pm s_i \pm s_k$	-“-	-“-	-“-	-“-	-“-
XI. (l)	$l \leftrightarrow \pm s_i \pm s_k$	-“-	-“-	-“-	-“-	-“-
XII. (s)	$s \leftrightarrow \pm s_i \pm s_k$	-“-	-“-	-“-	-“-	-“-

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phases in heterogeneous complex, as in the metric of full Gibbs potential in the whole concentration space, as in the metric incomplete Gibbs potentials (Korjinskiy potential) in reduced concentration space [10].

The goal to predict recurrently the number of phase diagram elements (points, lines, surfaces – fields, volumes, etc) from the data of components and phase numbers, as authors know, earlier was not set. Although, for example, the well-known "azeotrope rule", for phase equilibrium diagrams liquid-vapor allows the calculation of the number of special diagram points – knots, saddles, focuses (in the role of which are points of individual components, binary azeotrope, ternary azeotropes, etc [11]).

1. Classification of non-variant points and non-variant phase processes in the different types of phase diagrams, according to their topological features of the location in concentration spaces

Full concentration space

Let us consider full concentration space and *r*-phase equilibrium in the arbitrary *n*-component system with thermodynamic variance *f=0* (the non-variant process is closed). Renumber phases: 1 phase $p\text{-}ph_1$ is the "producing phase"; 2, 3…*r* – ph_2, ph_3, ... Ph_r are "resulting phases". The main requirement, applicable to $p\text{-}ph_1$, is, that it is the phase with variable composition. This phase, as a rule, should differ according to the aggregation state from ph_2, ph_3, ... Ph_r (this requirement is not valid only for delamination phase equilibrium diagrams types V, VI, VII, and VIII in Table 1). So, we consider I, II, III, V, and VI non-variant phase processes at *T=const* or *P=const.* Without loss of generality will assume that the mass of the $p\text{-}ph_1$ phase is equal to 1 mole:

$$p - ph_1 \leftrightarrow \alpha_2 ph_2 + \alpha_3 ph_3 + ...\alpha_r ph_r \quad (1.1).$$

Let us rewrite phase process (1.1) through the molar fraction of *i*-th components in the *j*-th phase - $X_i^{(j)}$:

$$\begin{array}{l} \alpha_2 X_1^{(2)} + \alpha_3 X_1^{(3)} + ...\alpha_r X_1^{(r)} = X_1^{(1)} \\ \alpha_2 X_2^{(2)} + \alpha_3 X_2^{(3)} + ...\alpha_r X_2^{(r)} = X_2^{(1)} \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ \alpha_2 X_n^{(2)} + \alpha_3 X_n^{(3)} + ...\alpha_r X_n^{(r)} = X_n^{(1)} \end{array} \quad (1.2).$$

If one sums all equations of the (1.2) system, he will get the balance mass equation:

$$\sum_{i=2}^{r} \alpha_i = 1 \quad (1.3).$$

Solve system (1.2):

$$\alpha_i = \Delta_i^{(r-1)} \Big/ \Delta^{(r-1)}; \alpha_r = 1 - \sum_{i=2}^{r-1} \Delta_i^{(r-1)} \Big/ \Delta^{(r-1)} \quad (1.4),$$

Where:

$$\Delta^{(r-1)} = \begin{vmatrix} X_1^{(2)} X_1^{(3)} ... X_1^{(r)} \\ X_2^{(2)} X_2^{(3)} ... X_2^{(r)} \\ \dots\dots\dots\dots\dots \\ X_n^{(2)} X_n^{(3)} ... X_n^{(r)} \end{vmatrix}; \Delta_i^{(r-1)} = \begin{vmatrix} X_1^{(2)} X_1^{(3)} ... X_1^{(i-1)} X_1^{(1)} X_1^{(i+1)} ... X_1^{(r)} \\ X_2^{(2)} X_2^{(3)} ... X_2^{(i-1)} X_2^{(1)} X_2^{(i+1)} ... X_2^{(r)} \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ X_n^{(2)} X_n^{(3)} ... X_n^{(i-1)} X_n^{(1)} X_n^{(i+1)} ... X_n^{(r)} \end{vmatrix} \quad (1.5),$$

So, the non-variant phase process in the full concentration range may be rewritten:

$$\Delta^{(r-2)} * p - ph_1 \leftrightarrow \sum_{i=2}^{r} \Delta_i^{(r-2)} * ph_i \quad (1.6).$$

Reduced concentration space

Let us consider reduced concentration space (without taking into account one component, for example, solvent, so one can add or remove this component to or from the system) and *r*-phase equilibrium in the arbitrary *(n+1)*-component system with thermodynamic variance *f=0* (non-variant process is open). Also renumber phases: 1 phase $p\text{-}ph_1$ is "producing phase"; 2, 3…*r* – ph_2, ph_3 ..... ph_r are "resulting phases". The requirement that $-p\text{-}ph_1$ is the phase with variable composition is valid. This phase, as a rule, should differ according to the aggregation state from ph_2, ph_3 ..... ph_r (this requirement is not valid only for delamination phase equilibrium diagrams types V, VI, VII, and VIII in Table 1). We consider IV, VII, VIII, and non-variant phase processes at *T,P=const* in Table 1. Without loss of generality will assume that the mass of the $p\text{-}ph_1$ phase is equal to 1 mole (without taking into account one of the components with number 1):

$$p - ph_1 \leftrightarrow \tilde{\alpha}_2 ph_2 + \tilde{\alpha}_3 ph_3 + ...\tilde{\alpha}_r ph_r \quad (1.7).$$

Let us rewrite phase process (1.7) through the molar fraction of *i*-th components in the *j*-th phase in reduced concentration space without 1-component (such molar fractions, as a rule, are named indexes Yaenecke - $Y_i^{(j)}$):

$$Y_i^{(j)} = n_i^{(j)} \Big/ \sum_{k=2}^{n+1} n_k^{(j)}; \sum_{i=2}^{n+1} Y_i^{(j)} = 1 \quad (1.8),$$

Where: $n_i^{(j)}$ - mole number of *i*-th components in *j*-th phase.

$$\begin{array}{l} \tilde{\alpha}_2 Y_1^{(2)} + \tilde{\alpha}_3 Y_1^{(3)} + ...\tilde{\alpha}_r Y_1^{(r)} = Y_1^{(1)} \\ \tilde{\alpha}_2 Y_2^{(2)} + \tilde{\alpha}_3 Y_2^{(3)} + ...\tilde{\alpha}_r Y_2^{(r)} = Y_2^{(1)} \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ \tilde{\alpha}_2 Y_{n-1}^{(2)} + \tilde{\alpha}_3 Y_{n-1}^{(3)} + ...\tilde{\alpha}_r Y_{n-1}^{(r)} = Y_{n-1}^{(1)} \end{array} \quad (1.9).$$

Sum all equations of the (1.2) system, and get the balance mass equation:

$$\sum_{i=2}^{r} \tilde{\alpha}_i = 1 \quad (1.10).$$

Solve system (1.9):

$$\tilde{\alpha}_i = \tilde{\Delta}_i^{(r-1)} \Big/ \tilde{\Delta}^{(r-1)} ; \tilde{\alpha}_r = 1 - \sum_{i=2}^{r-1} \tilde{\Delta}_i^{(r-1)} \Big/ \tilde{\Delta}^{(r-1)} \qquad (1.11),$$

Where:

$$\tilde{\Delta}^{(r-1)} = \begin{vmatrix} Y_1^{(2)} Y_1^{(3)} \ldots Y_1^{(r)} \\ Y_2^{(2)} Y_2^{(3)} \ldots Y_2^{(r)} \\ \ldots\ldots\ldots\ldots\ldots\ldots \\ Y_{n-1}^{(2)} Y_{n-1}^{(3)} \ldots Y_{n-1}^{(r)} \end{vmatrix} ; \tilde{\Delta}_i^{(r-1)} = \begin{vmatrix} Y_1^{(2)} Y_1^{(3)} \ldots Y_1^{(i-1)} Y_1^{(1)} Y_1^{(i+1)} \ldots Y_1^{(r)} \\ Y_2^{(2)} Y_2^{(3)} \ldots Y_2^{(i-1)} Y_2^{(1)} Y_2^{(i+1)} \ldots Y_2^{(r)} \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ Y_{n-1}^{(2)} Y_{n-1}^{(3)} \ldots Y_{n-1}^{(i-1)} Y_{n-1}^{(1)} Y_{n-1}^{(i+1)} \ldots Y_{n-1}^{(r)} \end{vmatrix} \qquad (1.12).$$

So, the non-variant phase process in a reduced concentration range may be rewritten:

$$\tilde{\Delta}^{(r-2)} * p - ph_1 \leftrightarrow \sum_{i=2}^{r-1} \tilde{\Delta}_i^{(r-2)} * ph_i \qquad (1.13).$$

Let us classify non-variant points.

1.1 Linear independent phases compositions: Let us consider the case when equilibrium phase compositions in the full concentration space or reduced concentration space are linearly independent. The number of components in this case *n≥1 [n≥2]* in full [reduced] concentration space for different types of diagrams from Table 1 I, II, III, V, VI (IV, VII, VIII). So, determinants $\Delta^{(r-1)} \neq 0$ or $\tilde{\Delta}^{(r-1)} \neq 0$. Determinants: $\Delta_i^{(r-1)}$; $\Delta^{(r-1)}$ $\tilde{\Delta}_i^{(r-1)}$; $\tilde{\Delta}^{(r-1)}$ with the dimension *(r-1)* and *(r-2)* matching columns have one (different) sign, if figurative points of $p\text{-}ph_1$ – phase and ph_i – phase lie *cis (trans)* of hyper-plane, passing through the figurative points of all other resulting phases: $ph_2, ph_{3,...,} ph_{i-1,} ph_{i+1...} ph_r$, according to the study by Modenov [12]. Sometimes in multidimensional geometry one says, that points $p\text{-}ph_1$ – phase and ph_i – phase lie in the position of conjunction (opposition) to each other. So, we can formulate the common rule:

Rule I: Stoichiometric coefficients $\alpha_i[\tilde{\alpha}_i]$ in the equations of non-variant phase process (1.1) ((1.7)) *are positive*, if in full [reduced] concentration space figurative points of producing phase and *i*-th resulting phase lie *cis* hyper-plane, passing through the figurative points of the rest resulting phases and *are negative*, if figurative points of producing phase and *i*-th resulting phase lie *trans* this hyper-plane.

According to the signs of $\alpha_i[\tilde{\alpha}_i]$, there is possibly the realization of the following types of non-variant points:

A. All $\alpha_i[\tilde{\alpha}_i] > 0$. In this case one says, that $p\text{-}ph_1$ forms congruently, and the non-variant point is named eutectic (Type I in Table 1.), eutonic (Type IV), congruent azeotrope (Type II, III), congruent liquid delamination (Type V, VII) or solid delamination (Type VI, VIII) points.

B. For some $\alpha_j[\tilde{\alpha}_j] < 0$ *(j = 2, 3...r)*, for the rest ones: $\alpha_i(\tilde{\alpha}_i) > 0$. $p\text{-}ph_1$ forms incongruently, and non-variant point is named *k*-type peritectic (Type I in Table 1.), *k*-type peritonic (Type IV), *k*-type incongruent azeotrope (Type II, III), *k*-type incongruent liquid delamination (Type V, VII) or solid delamination (Type VI, VIII) points. *k*-number is a multiplicity of incongruent processes or a number of $\alpha_j[\tilde{\alpha}_j] < 0$. The maximal multiplicity of the incongruent process is *(r-2)*, the rest is geometrically impossible.

C. One more type of non-variant point corresponds to the linear dependence of equilibrium phase compositions and will be considered later.

Let us consider all types of non-variant points in the systems with component numbers:

- *n=2* (types I, II, III, V, VI), *n=3* (IV, VII, VIII);
- *n=3* (types I, II, III, V, VI), *n=4* (IV, VII, VIII);
- *n=4* (types I, II, III, V, VI), *n=5* (IV, VII, VIII).

Different types of the locations of non-variant points and $p\text{-}ph_1$, ph_i equilibrium phase figurative points in the systems with the different component numbers are represented in Figure 1.

- In a single-component system *(n=1)* in full concentration space without limiting conditions *(l=0)* the variant of linear independence of the 3 equilibrium phases composition is impossible because the composition of all coexisting phases in the whole concentration range is the same. In the binary system *(n=2)* in reduced concentration space (without 1-component), phase compositions are also the same in Jaenecke indexes [2,5]. So, for example, the solubility diagram in the binary system at *T,P=const* is a non-variant point. In both cases, concentration spaces are non-dimensional (geometric points). So, Figure 1. A can not generate specific non-variant points, considered earlier. Phase diagram types IX, X, XI, and XII in this case can not be realized.
- In the systems, *n=2* (types I, II, III, V, and VI) at *T* or *P= const*, *n=3* (IV, VII, and VIII) at *T,P= const* – Figure 1B,1C concentration space is mono-dimensional (cut in strict line). It is possible to realize only two types of non-variant points – E and P_I;
- In the systems *n=3* (types I, II, III, V, VI) at *T* or *P= const*, *n=4* (IV, VII, VIII) at *T,P= const* – (Figure 1D-1F) concentration space is bi-dimensional (triangle plane). It is possible to realize three types of non-variant points – E, P_I, P_{II};
- In the systems *n=4* (types I, II, III, V, VI) at *T* or *P= const*, *n=5* (IV, VII, VIII) at *T,P= const* – (Figure 1G-1J) concentration space is three-dimensional (tetrahedron volume). It is possible to realize four types of non-variant points – E, P_I, P_{II}, P_{III};
- In the multi-component systems *n=N* (types I, II, III, V,

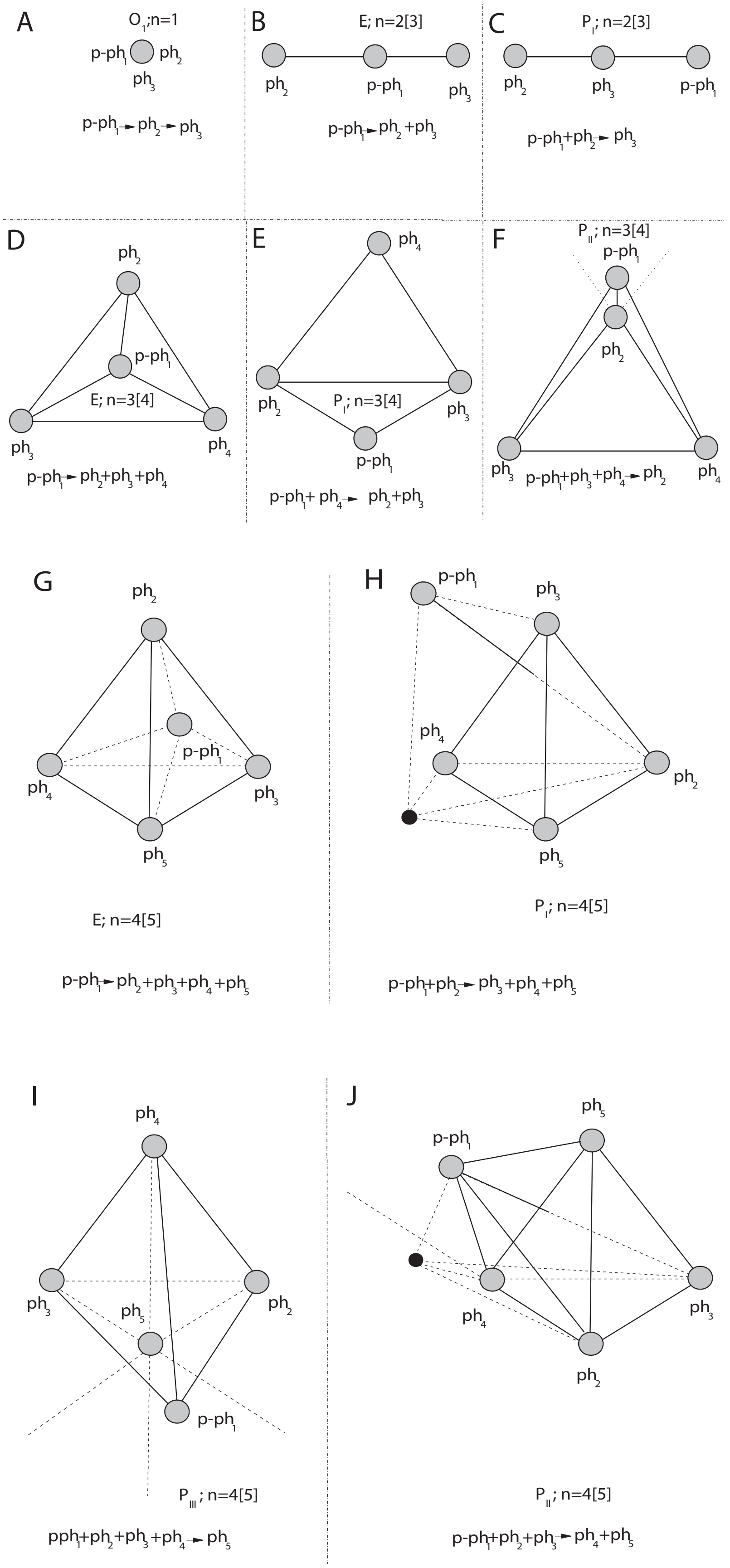

Figure 1: Different types of the location of non-variant points and *p-ph*$_1$, *ph*$_i$ equilibrium phase figurative points in the systems with the different components numbers: gray circles – phases points, black circles – auxiliary projections; dot lines – extensions and invisible faces. Symbols: E (eutectics, eutonics, congruent azeotropes, congruent liquid or solid delamination points); P_K (*K*-th type peritectics, peritonics, incongruent azeotropes, incongruent liquid or solid delamination points). Component numbers *n*: 1.A *(n=1[2]),* 1.B-1.C *(n=2[3]),* 1.D-1F *(n=3[4]),* 1.G-1.J *(n=4[5]).*

VI) at *T* or *P= const*, *n=N+1* (IV, VII, VIII) at *T,P= const* concentration space is multidimensional (simplex hyper-volume). It is possible to realize *N* types of non-variant points – E, P_I, P_{II}...P_{N-1}.

It is also important to note, that usual phase diagrams (without reversible chemical reactions between system substances) and phase diagrams of mutual systems (with one or more reversible chemical reactions between system substances) from the point of view of non-variant points classification are equivalent. The only difference is in the fact, that concentration simplex in mutual systems is the other, but has the same dimension. For example, in the systems with *n=3(4)* it is not a triangle, but a square, in the systems with *n=4(5)* it is not a tetrahedron, but a cube, etc.

1.2 Linear dependent phases compositions

One can see, that maximal common linear dependence of phase composition is virtually impossible. Really, belonging to 3 figurative phase points to 1 strict line in a bi-variant concentration space, or belonging to 4 figurative phase points to 1 plane in a three-variant concentration space, belonging to 4 figurative phase points to 1 volume in a four-variant concentration space, all these cases are incredible. This fact reflects the absence of any additional causes of lowering the dimensions of concentration space in the conditions of *r*-phase equilibrium.

The only real case of the realization of such linear dependence is in the coincidence of figurative points of 2 and 3 different equilibrium phases in full or reduced concentration space. According to the reasons, mentioned above, the case of two different pairs of equilibrium phases coincidence in full or reduced concentration space is incredible.

Different types of the location of non-variant points and $p\text{-}ph_1$, ph_i equilibrium phase figurative points in the systems with the different component numbers (case of coincidence of the composition of two phases in full or reduced concentration space) are represented in Figure 2.

- In a single-component system *(n=1)* in full concentration space without limiting conditions *(l=0)* the composition of all coexisting phases in the whole concentration range is the same. This case corresponds to ternary points in single-component diagrams, the last ones may be formed by vapor-liquid-solid (Type IX in Table 1), vapor-solid-solid (Type X in Table 1), liquid-solid-solid (Type XI in Table 1), solid-solid-solid (Type XII in Table 1). Several different solid phases with the same composition correspond to different polymorph modifications. One additional moment is in the fact, that as a rule, for the realization of such equilibrium, one should use relatively high pressures. Non-variant points we shall denote *T* in Figure 2A. In these points, when heat is supplied, it is consumed to phase transitions: evaporation and melting (Type IX); evaporation and polymorph transformation (Type X); melting and polymorph transformation (Type XI); polymorph transformation (Type XII). If the driving force of the non-variant process is external pressure the same processes occur: the efforts of pressure increase will start non-variant processes, decreasing the sum phase volume. In the cases of reverse driving forces reverse phase processes will start.

Topologically similar in the diagrams of solubility in reduced concentration space (without solvent), phase compositions of two different crystal-solvates of one compound are also the same in Jaenecke indexes (Type IV). In the process of the solvent removing crystal-solvate with a larger number of solvent molecules will transfer to crystal-solvate with a smaller number of solvent molecules.

- In the systems, *n=2* (types I, II, III, V, VI) at *T* or *P= const*, *n=3* (IV, VII, VIII) at *T,P= const* – Figure 2B, concentration space is mono-dimensional (cut in strict line). It is possible to realize only one type of non-variant transition point – T_I;
- In the systems *n=3* (types I, II, III, V, VI) at *T* or *P= const*, *n=4* (IV, VII, VIII) at *T,P= const* – Figure 1C concentration space is bi-dimensional (triangle plane). It is possible to realize only one type of non-variant transition point – T_{II};
- In the systems *n=4* (types I, II, III, V, VI) at *T* or *P= const*, *n=5* (IV, VII, VIII) at *T,P= const* – Figure 1D concentration space is three-dimensional (tetrahedron volume). It is possible to only one type of non-variant transition point – T_{III};
- In the multi-component systems *n=N* (types I, II, III, V, VI) at *T* or *P= const*, *n=N+1* (IV, VII, VIII) at *T,P= const* concentration space is multidimensional (simplex hyper-volume). It is also possible to realize one type of non-variant transition point T_{N-1}.

2. Stability of mono-variant equilibrium in the nearest neighborhood of non-variant points

Now we shall consider the questions, concerning the stability of mono-variant equilibria in the nearest neighborhood of non-variant points, in the process of state parameters change. The mono-variant equilibria states have a geometrical image, as mono-variant curves, come into non-variant points). The problem was solved for fusibility diagrams in a time-consuming manner, using some additional relations in particular as demonstrated in a few works [3,6]. We shall try to solve this problem considerably easily, using criteria of the stability of heterogeneous phases complex relatively infinitely small state changes [2].

Then we write differential van der Waals equations system for the equilibria of the phases pairs *(p-ph*$_1$ (give it number 1),

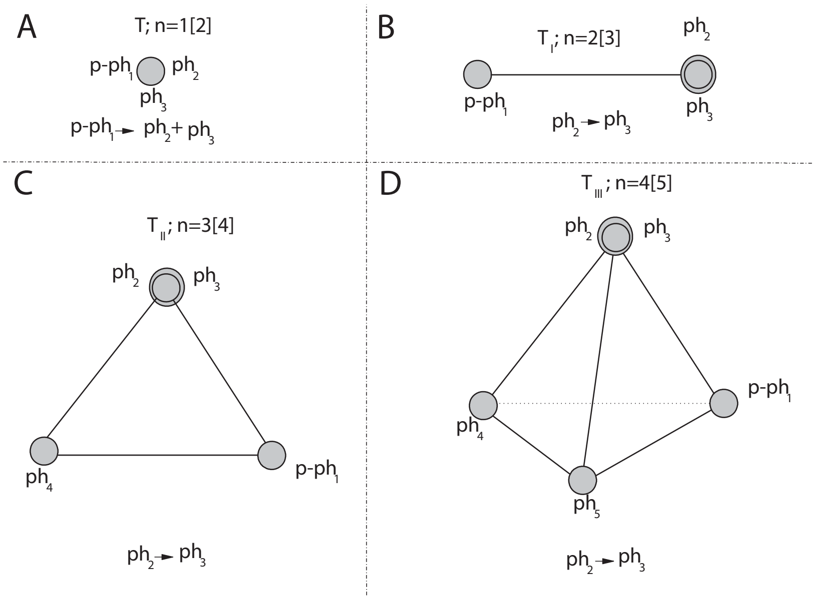

Figure 2: Different types of the location of non-variant points and *p-ph$_1$, ph$_i$* equilibrium phase figurative points in the systems with the different components numbers (case of coincidence of the composition of two phases in full or reduced concentration space): gray circles – phases points, dot line – invisible tetrahedron face. Symbols: T_K (*k*-type transition points in full or in reduced concentration ranges). Component numbers *n*: 2.A *(n=1[2])*, 2.B *(n=2[3])*, 2.C *(n=3[4])*, 2.D *(n=4[5])*.

ph$_2$, ph$_3$, ...ph$_r$ (give them numbers *2,3,...r*) in the *n*-component system in the variables of 1 phase in the metric of Gibbs potential in full concentration range [3,5-7]:

$$\begin{aligned}
&(\vec{X}^{(2)} - \vec{X}^{(1)})\hat{G}^{(1)} d\vec{X}^{(1)} = S^{(1\to 2)} dT - V^{(1\to 2)} dP \\
&(\vec{X}^{(3)} - \vec{X}^{(1)})\hat{G}^{(1)} d\vec{X}^{(1)} = S^{(1\to 3)} dT - V^{(1\to 3)} dP \qquad (2.1). \\
&\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\
&(\vec{X}^{(r)} - \vec{X}^{(1)})\hat{G}^{(1)} d\vec{X}^{(1)} = S^{(1\to r)} dT - V^{(1\to r)} dP
\end{aligned}$$

Here: $V^{(\tau)}$and $S^{(\tau)}$ – molar phase volumes and entropies of phase $\tau; \nabla V^{(\tau)}$ and $\nabla S^{(\tau)}$ – concentration gradients of $V^{(\tau)}$and $S^{(\tau)}$ with the elements $(\partial V^{(\tau)} / \partial X_i^{(\tau)})_{T,P,X_k^{(\tau)} \neq X_{i,n}^{(\tau)}}$ and $(\partial S^{(\tau)} / \partial X_i^{(\tau)})_{T,P,X_k^{(\tau)} \neq X_{i,n}^{(\tau)}}$, correspondingly; $\vec{X}^{(\tau)}$ – vector of the state of figurative point of τ phase in concentration space with elements $X_i^{(\tau)}; d\vec{X}^{(\tau)}$ – vector $\vec{X}^{(\tau)}$ shift at (*α-β*) equilibrium shift with elements $dX_i^{(\tau)}; \hat{G}^{(\tau)}$ – operator, corresponding to the matrix of second derivatives $G_{ij}^{(\tau)}$:

$$G_{ij}^{(\tau)} = \left(\frac{\partial^2 G^{(\tau)}}{\partial X_i^{(\tau)} \partial X_j^{(\tau)}} \right)_{T,P,x_{k \neq j,n}} \qquad (2.2),$$

Where: $G^{(\tau)}$ – molar Gibbs free energy of τ phase. Note, that, according to the conditions of diffusional stability of τ phase, matrices of operators $\hat{G}^{(\tau)}$ are nondegenerate, and corresponding quadratic bilinear forms are determined positively, according to Sylvester's criterion.

Physical sense of the parameters $S^{(\alpha\to\beta)} = [S^{(a)} - S^{(\beta)} + (\vec{X}^{(\beta)} - \vec{X}^{(\alpha)})\nabla S^{(a)}]$ and $V^{(\alpha\to\beta)} = [V^{(a)} - V^{(\beta)} + (\vec{X}^{(\beta)} - \vec{X}^{(\alpha)})\nabla V^{(a)}]$ are entropy and volume changes in the process of isotherm-isobaric formation of 1 mole of β phase from infinitely large mass of α phase.

Then we write differential van der Waals equations for the equilibria of the phases pairs *(p-ph$_1$* (give it number 1), *ph$_2$, ph$_3$, ...ph$_r$* (give them numbers *2, 3, ... r*) in the metric of incomplete Gibbs potential in *(n+1)*-component system in the reduced concentration range (without 1 component) [3,5-7]:

$$\begin{aligned}
&(\vec{Y}^{(2)} - \vec{Y}^{(1)})\hat{G}_{[1]}^{(1)} d\vec{Y}^{(1)} = \tilde{S}^{(1\to 2)} dT - \tilde{V}^{(1\to 2)} dP + n_1^{(1\to 2)} d\mu_1 \\
&(\vec{Y}^{(3)} - \vec{Y}^{(1)})\hat{G}_{[1]}^{(1)} d\vec{Y} = \tilde{S}^{(1\to 3)} dT - \tilde{V}^{(1\to 3)} dP + n_1^{(1\to 3)} d\mu_1 \qquad (2.3). \\
&\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\
&(\vec{Y}^{(r)} - \vec{Y}^{(1)})\hat{G}_{[1]}^{(1)} d\vec{Y} = \tilde{S}^{(1\to r)} dT - \tilde{V}^{(1\to r)} dP + n_1^{(1\to r)} d\mu_1
\end{aligned}$$

Designations here are similar to the equations (2.1), but functions: $G_{[1]} = G - n_1\mu_1 = \sum_{i=2}^{n+1} n_i\mu_i$ (where μ_1, μ_i are chemical potentials of the solvent and dissolved components), $\tilde{S}, \tilde{V}$ are calculated relative to one mole of *n* components without 1 component-solvent, and vectors $\vec{Y}^{(\tau)}$ characterize the position of a figurative point of τ phase in reduced (*n*)-dimensional concentration space:

$$Y_i^{(\tau)} = n_i^{(\tau)} \Big/ \sum_{j=1}^{k} n_j^{(\tau)} \quad \left(\sum_{i=2}^{n+1} Y_i^{(\tau)} = 1 \right) \qquad (2.4).$$

In this case, matrices $G_{[1]ij}^{(\tau)}$ are also nondegenerate, and corresponding quadratic bilinear forms are determined positively, according to Sylvester's criterion [6,7].

$$G_{[1]ij}^{(\tau)} = \left(\frac{\partial^2 G_{[1]}^{(\tau)}}{\partial Y_i^{(\tau)} \partial Y_j^{(\tau)}} \right)_{T,P,y_{l \neq j,n+1}} \qquad (2.5).$$

The physical sense of the parameters

$\tilde{S}^{(\alpha\to\beta)} = [\tilde{S}^{(a)} - \tilde{S}^{(\beta)} + (\vec{Y}^{(\beta)} - \vec{Y}^{(\alpha)})\nabla\tilde{S}^{(a)}]$,

$\tilde{V}^{(\alpha\to\beta)} = [\tilde{V}^{(a)} - \tilde{V}^{(\beta)} + (\vec{Y}^{(\beta)} - \vec{Y}^{(\alpha)})\nabla\tilde{V}^{(a)}]$ and

$n_1^{(\alpha\to\beta)} = \left[n_1^{(\alpha)} - n_1^{(\beta)} + (\vec{Y}^{(\beta)} - \vec{Y}^{(\alpha)})\nabla n_1^{(\alpha)} \right]$ are entropy, volume, and number of moles of 1 component changes in the process of isotherm-isobaric formation of 1 mole of β phase from an infinitely large mass of α phase, moreover, taken into account masses of all *(n+1)* components without 1-st one.

These systems (2.1) (2.3) are really the systems of *(1-2-3…r)*-phase equilibrium shift in different potential metrics.

Let us unite all "resulting phases" into a heterogeneous complex of phases. Then we write van der Waals equations in the metric of complete [and incomplete] Gibbs potential in *n* [*(n+1)*]-component system in full [reduced concentration range (without 1 component)] for the equilibria of the producing phase *(p-ph$_1$* (give it number 1) and heterogeneous complex of resulting phases (note *het*) [2,9,13]:

$$(\vec{X}^{(het)} - \vec{X}^{(1)})\hat{G}^{(1)} d\vec{X}^{(1)} = S^{(1\to het)} dT - V^{(1\to het)} dP \qquad (2.6),$$

$$(\vec{X}^{(1)} - \vec{X}^{(het)})\hat{G}^{(het)} d\vec{X}^{(het)} = S^{(het\to 1)} dT - V^{(het\to 1)} dP \qquad (2.7),$$

$$(\vec{Y}^{(het)} - \vec{Y}^{(1)})\hat{G}_{[1]}^{(1)} d\vec{Y}^{(1)} = \tilde{S}^{(1\to het)} dT - \tilde{V}^{(1\to het)} dP + n_1^{(1\to het)} d\mu_1 \qquad (2.8),$$

$$(\vec{Y}^{(1)} - \vec{Y}^{(het)})\hat{G}_{[1]}^{(het)} d\vec{Y}^{(het)} = \tilde{S}^{(het\to 1)} dT - \tilde{V}^{(het\to 1)} dP + n_1^{(het\to 1)} d\mu_1 \qquad (2.9),$$

Where: equations (2.6), and (2.8) are written in the variables of producing phase number 1, and equations (2.7), and (2.9) in the variables of a heterogeneous complex of resulting phases noted – *het.* The physical sense of all phase effects in these equations is absolutely similar to those in the equations systems (2.1), and (2.3), but one of the equilibrium phases is represented by phases complex. Let us determine signs of the effects in different non-variant phase processes in Table 1.

A. *(crys), (melt), (evap), (solid-evap), (subl), (cond), (polym-trans),– crystallization, melting, evaporation, evaporation from solid, sublimation, condensation, polymorph transformation;*

B. *(liquid-delam), (liquid-homog), (solid-delam), (solid-homog) – delamination in liquid, homogenization of liquids, delamination in solid, homogenization of solids,*

C. *(condens, cryst), (melt, evap), (subl, polym-trans), (solid-evap, polym-trans), (cryst, polym-trans), (melt, polym-trans) – two parallel phase processes from (A);*

D. $(_{solvent}^{(cryst)}), (_{solvent}^{(dissol)})$, - *crystallization, dissolution with decrease or increase of solvent molecules when a solvent is introduced or removed;*

E . $(_{component}^{(liquid-delam)}), (_{component}^{(liquid-homog)}), (_{component}^{(solid-delam)}), (_{component}^{(solid-homog)})$ – *delamination or homogenization of liquids or solids when a component is introduced or removed.*

Signs of phase effects in Table 2 are the following:

- $S^{(cryst)} < 0, S^{(melt)} > 0$, because liquid and solid can not form a critical state in principle [2],

- $S^{(cond)} < 0, S^{(subl)} < 0, S^{(evap)} > 0, S^{(solid-evap)} > 0$,

$V^{(cond)} < 0, V^{(subl)} < 0, V^{(evap)} > 0 V^{(solid-evap)} > 0$ when we shall not consider states, closed to critical and supercritical states for equilibrium liquid-vapor,

- $n_{solvent}^{(cryst)} < 0, n_{solvent}^{(dissol)} > 0$ when the liquid phase is more solvent rich, then all equilibrium solid phases and their heterogeneous complex. There are some exotic cases, when it is not so, and signs are converted. In this case, so-called "forbidden types of solubility diagrams" are realized [14]. But this type is very rare (these cases usually are not investigated), so one can consider almost without loss of generality that signs of solvent phase effects are as mentioned above,

In single component system:

$S^{(condens,cryst)} < 0, V^{(condens,cryst)} < 0, S^{(melt,evap)} > 0, V^{(melt,evap)} > 0,$

$S^{(subl, polym\text{-}trans)} < 0, V^{(subl, polym\text{-}trans)} < 0,$

$S^{(solid\text{-}evap, polym\text{-}trans)} > 0, V^{(solid\text{-}evap, polym\text{-}trans)} > 0,$

$S^{(cryst, polym\text{-}trans)} < 0, S^{(melt, polym\text{-}trans)} > 0,$ solid and liquid and solid and vapor can not form a critical state.

One can consider the stability of mono-variant equilibria near non-variant points only, if he knows the sign of the corresponding phase effect of the process *p - ph$_1$* ↔ *het.* So, we should exclude from the consideration types of phase processes in Table 2: V, VI, VII, VIII, XII).

2.1 Linear independent phases compositions

Single component phase processes type IX, X, and XI in Table 2 we shall consider later. Let us consider *r*-phase non-variant phase process *(n=r-1)* in *n*-component system in full

Table 2: Signs of phase affect different types of non-variant phase processes (non-variant phase processes):

N	Phase process ↔ "↔ Producing phase" "± resulting phases" $p-ph_1 \leftrightarrow \pm ph_2 \pm ph_3 \pm ... \pm ph_r$ opened or closed system; components number (n); Phases number (r)	Diagram of phase equilibrium, Full or reduced	Phase effect of the direct process $p-ph_1 \leftrightarrow het$	Sign of the effect of the direct process	Phase effect of the reverse process $het \leftrightarrow p-ph_1$	Sign of the effect of the reverse process
I.	$l \leftrightarrow \pm s_i \pm s_k \pm s_n \pm ... \pm s_m$ closed, $r = n+1, n \geq 2$	Fusibility, P=const, full	$S^{(cryst)}$	<0	$S^{(melt)}$	>0
II.	$v \leftrightarrow \pm l_i \pm l_k \pm l_n \pm ... \pm l_m$ closed, $v \leftrightarrow \pm s_i \pm s_k \pm s_n \pm ... \pm s_m$ $r = n+1, n \geq 2$	liquid-vapor, solid-vapor P=const, full	$S^{(\mathrm{cond})}$ $S^{(\mathrm{subl})}$	<0 <0	$S^{(evap)}$ $S^{(solid-evap)}$	>0 >0
III.	$v \leftrightarrow \pm l_i \pm l_k \pm l_n \pm ... \pm l_m$ closed, $v \leftrightarrow \pm s_i \pm s_k \pm s_n \pm ... \pm s_m$ $v \leftrightarrow \pm l \pm s$	liquid-vapor, solid-vapor P=const, full	$V^{(\mathrm{cond})}$ $V^{(\mathrm{subl})}$	<0 <0	$V^{(solid-evap)}$ $V^{(solid-evap)}$	>0 >0
IV.	$l \leftrightarrow \pm s_i \pm s_k \pm s_n \pm ... \pm s_m$ opened, $r = n, n \geq 3$	solubility P=const; T=const, reduced	$n^{(cryst)}_{solvent}$	<0	$n^{(dissol)}_{solvent}$	>0
V.	$l \leftrightarrow \pm l_k \pm l_n \pm ... \pm l_m$ Closed, $r = n+1, n \geq 2$	delamina-tion, P=const, full	$S^{(liquid-delam)}$	n.d.	$S^{(liquid-\mathrm{hom}og)}$	n.d.
VI.	$s \leftrightarrow \pm s_k \pm s_n \pm ... \pm s_m$ Closed, $r = n+1, n \geq 2$	delamina-tion, P=const, full	$S^{(solid-delam)}$	n.d.	$S^{(solid-\mathrm{hom}og)}$	n.d.
VII.	$l \leftrightarrow \pm l_k \pm l_n \pm ... \pm l_m$ opened, $r = n, n \geq 3$	delamina-tion, P=const; T=const, reduced	$n^{(liquid-delam)}_{component}$	n.d.	$n^{(liquid-\mathrm{hom}og)}_{component}$	n.d.
VIII.	$s \leftrightarrow \pm s_k \pm s_n \pm ... \pm s_m$ opened, $r = n, n \geq 3$	delamina-tion, P=const; T=const, reduced	$n^{(solid-delam)}_{component}$	n.d.	$n^{(solid-\mathrm{hom}og)}_{component}$	n.d.
IX.	$v \leftrightarrow \pm l \pm s$ Indifferently,	single component, absence	$S^{(condens,cryst)}$ $V^{(condens,cryst)}$	<0 <0	$S^{(melt,evap)}$ $V^{(melt,evap)}$	>0 >0
X.	$v \leftrightarrow \pm s_i \pm s_k$ Indifferently, $r = 3, n = 1$	single component, absence	$S^{(\mathrm{subl,\ polym\text{-}trans})}$ $V^{(\mathrm{subl,\ polym\text{-}trans})}$	<0 <0	$S^{(\mathrm{solid\text{-}evap,\ polym\text{-}trans})}$ $V^{(\mathrm{solid\text{-}evap,\ polym\text{-}trans})}$	>0 >0
XI.	$l \leftrightarrow \pm s_i \pm s_k$ Indifferently, $r = 3, n = 1$	single component, absence	$S^{(\mathrm{cryst,\ polym\text{-}trans})}$ $V^{(\mathrm{cryst,\ polym\text{-}trans})}$	<0 n.d.	$S^{(\mathrm{melt,\ polym\text{-}trans})}$ $V^{(\mathrm{melt,\ polym\text{-}trans})}$	>0 n.d.
XII.	$s \leftrightarrow s_i \leftrightarrow s_k$ Indifferently, $r = 3, n = 1$	single component, absence	$S^{(\mathrm{polym\text{-}trans})}$ $V^{(\mathrm{polym\text{-}trans})}$	n.d. n.d.	$S^{(\mathrm{polym\text{-}trans})}$ $V^{(\mathrm{polym\text{-}trans})}$	n.d. n.d.

"n.d." – not determined.

concentration space at *T=const* or *P=const* (equation (2.10), types in Table 2: I, II, III, XIII) or in *(n+1)*-component system *(n=r)* in reduced (without solvent) concentration space at *T,P=const* (equation (2.11), type IV in Table 2):

$$p-ph_1 \leftrightarrow \alpha_2 ph_2 + \alpha_3 ph_3 + ...\alpha_r ph_r \quad (2.10),$$

$$p-ph_1 \leftrightarrow \tilde{\alpha}_2 ph_2 + \tilde{\alpha}_3 ph_3 + ...\tilde{\alpha}_r ph_r \quad (2.11),$$

Where signs $\alpha_i[\tilde{\alpha}_i]$ are arbitrary. In non-variant point come or go *r-1* curves of mono-variant equilibrium, corresponds to coexisting of the phases p - $ph_1, ph_2 ... ph_{i-1}, ph_{i+1}, ph_{i+2}, ... ph_r$ (without one of the resulting phase – ph_i. Let us prove.

Rule II: If the figurative point of the resulting phase ph_i lies in *opposition=trans (conjunction=cis)* to the figurative point of producing phase relative to the hyper-plane of the rest *r-2* resulting phases, then the mono-variant curve comes to the non-variant point with the *decrease (increase)* of temperature at *P=const*; *increase (decrease)* of pressure at *T=const* in full concentration space; or with the *decrease (increase)* of solvent chemical potential at *P, T=const* in reduced concentration space (without solvent).

Let us distribute the set of the resulting phases $ph_{2,} ph_3 ... ph_r$ into two subsets: I - $ph_{2,} ph_3 ... ph_\mu$, for which $\alpha_i(\tilde{\alpha}_i) > 0$, and II - $ph_{\mu+1}$, $ph_{\mu+2}$, …… ph_r, for which $\alpha_i(\tilde{\alpha}_i) < 0$, herewith subset I can not be empty. Let us rewrite (2.10), and (2.11) through the modules $/\alpha_i/(/\tilde{\alpha}_i/)$ in full or reduced concentration spaces:

$$\begin{aligned} &p - ph_1 + /\alpha_2/\ ph_2 + /\alpha_3/\ ph_3 + \ldots /\ \alpha_u /\ ph_u \leftrightarrow \\ &/\alpha_{u+1}/\ ph_{u+1} + /\alpha_{u+2}/\ ph_{u+2} + \ldots /\ \alpha_r /\ ph_r \end{aligned} \quad (2.12),$$

$$\begin{aligned} &p - ph_1 + /\tilde{\alpha}_2/\ ph_2 + /\tilde{\alpha}_3/\ ph_3 + \ldots /\ \tilde{\alpha}_u /\ ph_u \leftrightarrow \\ &/\tilde{\alpha}_{u+1}/\ ph_{u+1} + /\tilde{\alpha}_{u+2}/\ ph_{u+2} + \ldots /\ \tilde{\alpha}_r /\ ph_r \end{aligned} \quad (2.13).$$

In the classical thermodynamic conditions [1,2] masses of equilibrium phases are ignored. Let us construct a non-variant equilibrium, where masses of all equilibrium phases are finite and the mass of one of the resulting phases - ph_i is infinitely small.

There are two principal cases:

A) ph_i belongs to the I subset.

There are three variants of the impact on non-variant equilibrium:

- Put to the system an infinitely small amount of heat or entropy ($+Q_P = +TS_P$), or
- Act on the system by infinitely small volume increase ($+V_T$), or
- Act on the system by adding of infinitely small solvent amount (component number 1) ($+n_{1(P,T)}$).

In this case process, (2.12), and (2.13) will pass from right to left; phase ph_i will disappear, and the system will pass on the mono-variant curve without this phase. On this curve in the comparison with a non-variant point:

$dT_p > 0,\ dP_T < 0,\ d\mu_{1(P,T)} > 0$ (2.14),

According to the stability criterion of heterogeneous phases complex relatively infinitely small state changes [2]:

$$(dT/dS)^{(het)}_{P,n_i} > 0; (dP/dV)^{(het)}_{T,n_i} < 0; (d\mu_1/dn_1)^{(het)}_{T,P,n_{i\neq 1}} > 0 \quad (2.15)$$

B) ph_i belongs to the II subset.

There are also three variants of the impact on non-variant equilibrium:

- Withdraw from the system an infinitely small amount of heat or entropy ($-Q_P = -TS_P$), or
- Act on the system by infinitely small volume decrease ($-V_T$), or
- Act on the system by the removal (for example, evaporation) of infinitely small solvent amount (component number 1) ($-n_{1(P,T)}$).

In this case process, (2.12), and (2.13) will pass from left to right; phase ph_i will also disappear, and the system will pass on a mono-variant curve without this phase. On this curve in the comparison with a non-variant point:

$dT_p < 0,\ dP_T > 0,\ d\mu_{1(P,T)} < 0$ (2.16),

Also according to the stability criterion of heterogeneous phases complex (2.15). Different types of the stability of mono-variant equilibrium at state parameters changes are represented in Figure 3.

2.2 Linear Dependent Phases Compositions

In these cases phase composition of two resulting phases (name them ph_2 and ph_3) have the same composition in full (Types I, II, III) or reduced (without solvent) (Type IV) concentration ranges. But, according to physical sense) one should recognize, that phases ph_2 and ph_3 should be only solid–polymorph modifications of a single substance (Type I – fusibility diagrams) or different crystal solvates of a single substance (Type IV – solubility diagrams). It was absolutely impossible to imagine two different liquid phases with the same composition (with the exception of the equilibrium of the liquid-crystal phase with the isotropic liquid phase). Exclude these exotic cases (Types II, III). Let us prove.

Rule III: If figurative points of two resulting phases ph_2 and ph_3 *coincide*, then all *(r-3)* mono-variant curves with their participation of both ph_2 and ph_3 phases, come to a non-variant point with the *constancy* of temperature at *P=const*; in full concentration space; or with solvent chemical potential at *P, T=const* in reduced concentration space (without solvent). Simultaneously, the *rest* 2 mono-variant *curves* with the participation of ph_2 separately from ph_3 come to a non-variant point: first – with the *increase*, second – with the *decrease* of temperature at *P=const*; in full concentration space; or with solvent chemical potential at *P, T=const* in reduced concentration space (without solvent).

For the proof of III Rule let us write the system van der Waals equations in the metric of complete [and incomplete] Gibbs potential in *n* [*(n+1)*]-component system in full [reduced concentration range (without 1 component)] for the equilibria of the producing phase *p-ph*$_1$ and both resulting phases ph_2 and ph_3 in the variables of *p-ph*$_1$ with variable composition at *T=const [T,P=const]*:

$$(\vec{X}^{(ph_2)} - \vec{X}^{(p-ph_1)})\hat{G}^{(1)} d\vec{X}^{(p-ph_1)} = S^{(p-ph_1 \rightarrow ph_2)} dT \quad (2.17),$$

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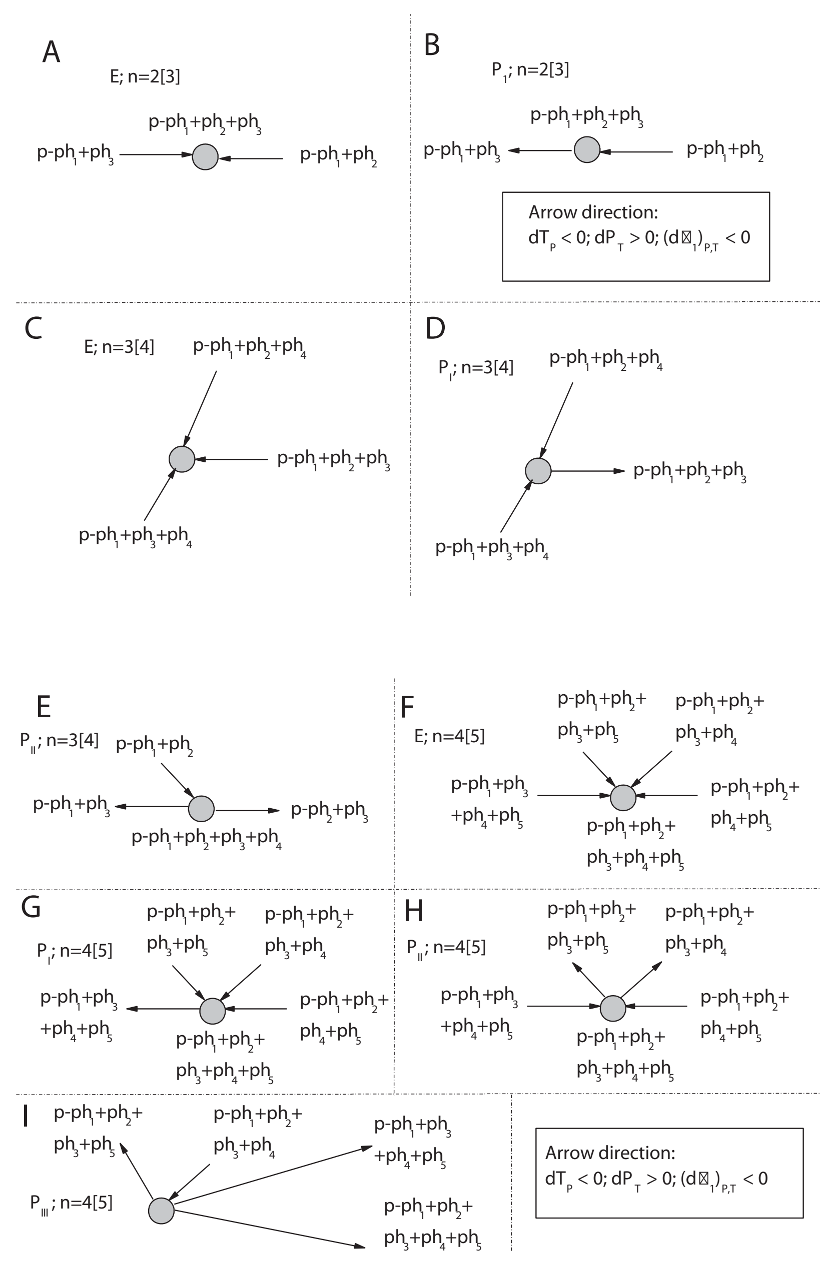

Figure 3: Different types of the stability of mono-variant equilibrium at state parameters changes (case of independence of the composition of all phases in full or reduced concentration space): gray circles – producing phases points; arrow directs show the direction of temperature and solvent chemical potentials increase, pressure increase. Component numbers *n*: 3.A, 3B *(n=2[3])*, 3.C, 3.E, 3D *(n=3[4])*, 3.E, 3.F, 3G, 3.H, 3I *(n=4[5])*. The location of figurative points corresponds to the following figure pairs: *3.A-1.B; 3.B-1C; 3.C-1.D; 3.D-1.E; 3.E-1.F; 3.F-1.G; 3.G-1.H; 3.H-1.I; 3.I-1.J.*

$$(\vec{X}^{(ph_3)} - \vec{X}^{(p-ph_1)})\hat{G}^{(1)}d\vec{X}^{(p-ph_1)} = S^{(p-ph_1 \to ph_3)}dT \qquad (2.18),$$

$$(\vec{Y}^{(ph_2)} - \vec{Y}^{(p-ph_1)})\hat{G}_{[1]}^{(1)}d\vec{Y}^{(1)} = n_1^{(p-ph_1 \to ph_2)}d\mu_1 \qquad (2.19),$$

$$(\vec{Y}^{(ph_3)} - \vec{Y}^{(p-ph_1)})\hat{G}_{[1]}^{(1)}d\vec{Y}^{(1)} = n_1^{(p-ph_1 \to ph_3)}d\mu_1 \qquad (2.20).$$

Subtract from eq. (2.17) eq.(2.18) and form eq.(2.19) eq.(2.20) and get

$$\begin{aligned}(\vec{X}^{(ph_2)} - \vec{X}^{(ph_3)})\hat{G}^{(1)}d\vec{X}^{(p-ph_1)} &= \\ [S^{(p-ph_1 \to ph_2)} - S^{(p-ph_1 \to ph_3)}]dT &= 0\end{aligned} \qquad (2.21),$$

$$\begin{aligned}(\vec{Y}^{(ph_2)} - \vec{Y}^{(p-ph_3)})\hat{G}_{[1]}^{(1)}d\vec{Y}^{(1)} &= \\ [n_1^{(p-ph_1 \to ph_2)} - n_1^{(p-ph_1 \to ph_3)}]d\mu_1 &= 0\end{aligned} \qquad (2.22).$$

The last equations are valid, because, according to the conditions of consideration:

$$\vec{X}^{(ph_2)} - \vec{X}^{(ph_3)} = \vec{0}, \vec{Y}^{(ph_2)} - \vec{Y}^{(p-ph_3)} = \vec{0} \qquad (2.23),$$

$$dT_P = 0, d\mu_{1(T,P)} = 0 \qquad (2.24).$$

Naturally, if ph_2 is a more high-temperature modification in comparison with ph_3, then mono-variant curve *p-ph$_1$ – ph$_2$ –*

ph_4... ph_r comes to non-variant point with *decrease* and mono-variant curve p-ph_1 – ph_3 – ph_4... ph_r comes to non-variant point with *increase* of temperature at *P=const* [solvent chemical potential at *P, T=const*] in full [reduced] concentration space.

2.3 Single-component systems

In this case, the composition of all 3 phases is equal. So, both state parameters – *T, P* on mono-variant curves can change, according to the consequence of van der Waals equations:

$$[dP/dT]_{p-ph_1+ph_2} = S^{p-ph_1\to ph_2}/V^{p-ph_1\to ph_2} \quad (2.25),$$

$$[dP/dT]_{p-ph_1+ph_3} = S^{p-ph_1\to ph_3}/V^{p-ph_1\to ph_3} \quad (2.26),$$

$$[dP/dT]_{ph_2+ph_2} = S^{ph_2\to ph_3}/V^{ph_2\to ph_3} \quad (2.27).$$

Signs of different effects are represented in Table 2 for Types IX, X, XI, and XII. Directions of *T* and *P* changing while moving into non-variant points are represented in (Figure 4D-4F*).* Sometimes, one can not determine signs of phase effects - $S^{p-ph_1\to phi}$ and especially $V^{p-ph_1\to ph_i}$, so can not also determine *dT* and especially *dP.*

3. Thermodynamics of Heterogeneous Systems Rules, Concerning Topology of Phase Equilibrium Diagrams

Let us make some remarks, concerning objects of our consideration.

A) We shall consider fusibility diagrams at *P=const* in full concentration space in *n*-component systems in variables T- X_i and solubility diagrams at *P,T=const* in reduced concentration in *(n+1)*-component systems in variables Y_i – Y_j (Types I, IV). So, the producing phase is liquid, and the resulting phases are solids. In these cases, concrete resulting phases have constant composition or variable composition with preservation of the crystal structure – solid solutions in the narrow regions of composition changes). Close liquid-vapor diagrams at *P=const or T=const* (and delamination diagrams) in the common case do not contain phases with constant composition and can not be considered by a used method.

B) Let us exclude all sub-solidus transformations completely or delamination in the liquid phase.

C) Also let us exclude systems, where the transformation from solid to liquid – dissolution in the solution or melt is not accompanied by irreversible chemical reactions, for example, solvolysis (hydrolysis).

D) We shall also consider diagrams of usual systems such as M,N...P//X(-Solvent) or M//X,Y...Z(-Solvent) and mutual systems M,N...P// X,Y...Z(-Solvent), where: M,N...P are cations, or elements of the k-th group of Periodic law - A^k, or alcohol groups etc; X, Y...Z are anions, or elements of (8-k)-th group of Periodic law – A^{8-k}, or acid groups etc. Let us exclude unstable cuts of the mutual diagrams, such as MX-NY...-PZ (-Solvent) [15].

Let us consider the simplest phase diagram stable relative to both the infinitely small and finite state changes "old diagram" with the crystallization of old resulting solid phases "s-old". Let us consider the formation of new resulting solid phase "s-new" and "new diagram". This diagram will be absolutely stable, but the "old diagram" will lose the stability relatively finite state change (namely "s-new" formation). Let us prove two auxiliary Lemmas.

Lemma I: In solubility [fusibility] diagram of *(n+1)[n]*-component systems *can not exist* 2 or more non-variant points – eutonics-peritonics [eutectics-peritectics] type with the *same set of solid phases*.

Let's get proof from the nasty one. If in the solubility diagram, there are 2 different liquid phase compositions – l_1 and l_2, which are in equilibrium with the set of solid phases: s_1, s_2...s_n. Let us unite liquid+solid phases into 2 heterogeneous complexes: het_1 and het_2. Let us change the masses of equilibrium phases in het_1 in such a way, that the composition of het_1 and het_2 in the reduced concentration space will be the same: $\vec{Y}^{(het_1)} = \vec{Y}^{(het_2)}$. One can always do it because phase compositions are independent. States of het_1 and het_2 correspond to different solvent content $n_1^{(het_1)} \neq n_1^{(het_2)}$. Then, let us remove (evaporate) solvent from a more rich complex - het_1, and make it equal to het_2. In this process, all solutions should transfer into the complex of solid phases (eutonics) or should lose *k* solid phases (k-type peritonics). As a result, one will get two finitely different states of a heterogeneous system, corresponding to the same pressure, temperature, and component masses. This contradicts the stability criterion of the heterogeneous system relative to the finite state changes (binodal criterion) [1,2]. This criterion imposes on the system more stringent restrictions than the stability criterion for relatively infinitely small state changes (spinodal or diffusional stability criterion). In particular, in the ternary system impossibility of the intersection of two nodes liquid-solid (cuts, connecting figurative points of equilibrium phases) for one solid phase at *T,P=const* follows from both criteria, the impossibility of this intersection for two different solid phases liquid-solid$_1$ and liquid-solid$_2$ follows only from binodal criterion.

The case of the fusibility diagram is absolutely similar. If two melts – l_1 and l_2, are in equilibrium with the set of solid phases: s_1, s_2...s_n, and temperatures of non-variant equilibria are different $T_1 \neq T_2$ (case $T_1 = T_2$ is similar to solubility diagrams). Changing masses of s_1, s_2...s_n, for the first – more high-temperature heterogeneous phase complex – het_1, align the brutto-compositions of both complexes – het_1, and het_2, in full concentration space will be the same: $\vec{X}^{(het_1)} = \vec{X}^{(het_2)}$.

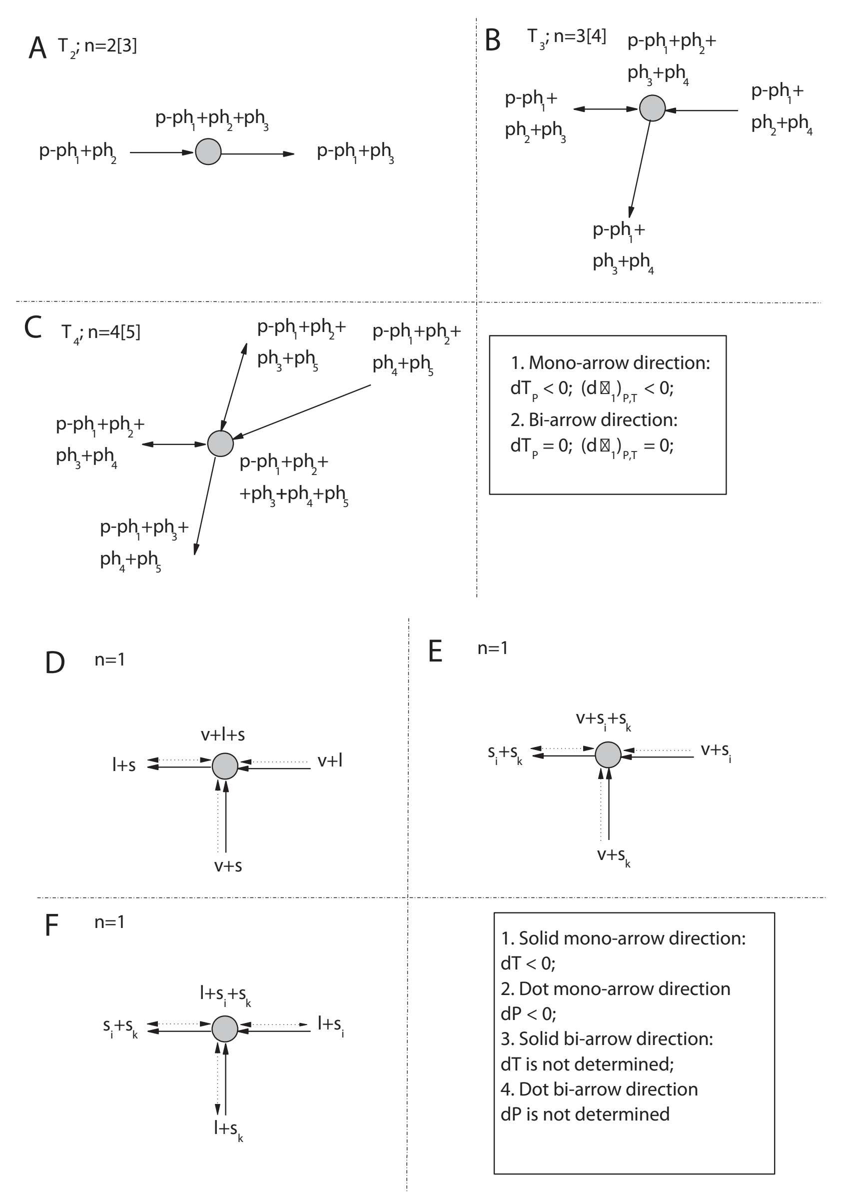

Figure 4: Different types of the stability of mono-variant equilibrium at state parameters changes (case of the dependence of the composition of two phases in full or reduced concentration space): gray circles – producing phases points; arrow directs show the direction of temperature and solvent chemical potentials increase. Component numbers *n*: 4.A *(n=2[3])*, 4B *(n=3[4])*, 4C *(n=4[5])* 4.D, 4.E, 4.F *(n=1)*. The location of figurative points corresponds to the following figure pairs: *4.A-2.B; 4.B-2C; 4.C-2.D; 4.D, 4.E, 4.F – 1.A.*

Then downgrade temperature from T_1 to T_2. In this process, het_1 should transfer into a mixture of solid phases (eutectics) or should lose *k* solid phases (k-type peritectics). This also contradicts the stability criterion of heterogeneous systems relative to the finite state changes.

Lemma II: In solubility [fusibility] diagram of *(n+1)[n]*-component systems *can not exist* 2 or more non-variant transition points type with the *same set of solid phases* (excluding the very rare case of transition points of *congruent desolvation [congruent polymorph transformation]*).

Let us explain the terminology. Transition points of congruent desolvation [congruent polymorph transformation]) is a non-variant point, with the following properties:

A) At evaporation [temperature decrease] in these points occurs a non-variant process without the participation of the liquid phase, one of the solid phases – s_1 (high-temperature polymorph modification [crystal solvate with higher solvent content]) transfers into other solid phases – s_2 (low-temperature polymorph modification [crystal solvate with lower solvent content]).

B) Phases s_1 and s_2 have the same composition in reduced [full] concentration space. They are the congruently soluble [melting] compounds. The simplest cases are represented in Figure 5. One should note, that this type of non-variant point meets very rare. In binary fusibility diagrams, they meet in some first percent. In ternary solubility diagrams, we can not find any one case (although ternary compounds with different solvent content sometimes meet, all of them somehow are soluble incongruently). In the ternary or more component fusibility (quaternary or more component solubility) diagrams such points are not just rare, but almost unbelievable (we do not know any examples). Let us neglect these cases in our consideration, but draw graphically the schemes of its realization (Figure 5C, 5D).

The proof of Lemma II is similar to Lemma I. If in the solubility diagram, there are two liquid non-variant solutions l_1 and l_2, which are in the equilibrium with solid phases: $s_1, s_2 \ldots s_n$, and composition in a reduced concentration of two crystal-solvates coincides: $\vec{Y}^{(s_1)} = \vec{Y}^{(s_2)}$. If in the reduced concentration space points l_1 and l_2 lie in the conjunction (cis) hyperplane, they pass through solid phase points. Let us form two heterogeneous complexes – het_1 (from phases: l_1, s_1, s_2, $s_3 \ldots s_n$) and het_2 (from phases: l_2, s_1, s_2, $s_3 \ldots s_n$), mixing in different proportions equilibrium phases. The composition of het_1 and het_2 will be the same, according to all components, except solvent. Let us transfer in het_1 part of s_1 into s_2 by removing (evaporating) the solvent (if s_1 is more reach than s_2), l_1 and l_2 will have constant composition. As a result, one can get two complexes with different equilibrium liquids and the same state parameters. This also contradicts the stability criterion of heterogeneous systems relative to the finite state changes.

In the case of fusibility diagrams proof is easy. Transition non-variant points should have the same equilibrium temperatures – the temperature of polymorph transformation phase s_1 into phase s_2. So, the formation of het_1 and het_2 by mixing in the different proportions phases: l_1, s_1, s_2, $s_3 \ldots s_n$) and l_2, s_1, s_2, $s_3 \ldots s_n$, immediately contradicts to stability criterion of the heterogeneous system relative to the finitely state changes.

One can understand, that such consideration can not be applied in the case if the reduced concentration space points l_1 and l_2 lie in the opposition (trans) hyperplane, and pass through solid phase points. In this case, it is impossible to equalize compositions of heterogeneous complexes, which lie in the different hyper-surfaces, relatively mentioned hyper-plane. This situation may be realized in cases of the formation of the phases of congruent polymorph transformation [desolvatation] (points T_i^c in Figure 5).

Lemma I and II have obvious consequences:

Consequence I: Passing through a non-variant point in solubility [fusibility] diagram of ternary [binary] system jump of solid phase composition in reduced [full] concentration space occurs in the same direction as solution [melt] composition change.

Consequence II: In solubility [fusibility] diagram of *(n+1)[n]*-component system can not coexist separated elements of phase diagrams, corresponding to the crystallization of the same set of solid phases. In the simple case of solubility in ternary system [fusibility in binary system] can not realize several branches of crystallization of the same solid phase with constant composition. Despite the obvious statement, for example in the system, Na_2CO_3-K_2CO_3-H_2O *at 30°C* authors [17] determined the following order of solid phases crystallization: $Na_2CO_3{*}10H_2O$; $Na_2CO_3{*}7H_2O$; Na_2CO_3; $Na_2CO_3{*}\ K_2CO_3{*}6H_2O$; Na_2CO_3; $Na_2CO_3{*}\ K_2CO_3$; $2K_2CO_3{*}3H_2O$. This order directly contradicts both consequences I, and II simultaneously.

Consequence III: So, in solubility [fusibility] diagram in *(n+1)[n]*-component system geometrical element of the crystallization of "new phase" – S_i^{new} (branch, or surface, or volume, or hyper-volume) may locate in phase diagram by the only one way – replacing specific metastable non-variant point (eutectic-eutonic, peritectic-peritonic, transition points – E,P,T_i^{old}) inside concentration *(n+1)[n]*-component simplex, or metastable non-variant point inside less variant *(n+1)[n]*-component sub-system, …or tops of *(n+1)[n]*-component simplex, corresponds to melting point or solubility of components in *(2)[1]*-component sub-systems. This does not apply, of course, to phases of congruent polymorph transformation [desolvatation] formation T_i^c. Possible and impossible types of "new phases" appearance are represented in Figures 6-8.

4. Number of Topological Elements in Phase Diagrams of Binary, Ternary, and Quaternary Systems

Let us calculate the number of topological elements: non-variant points, mono-variant curves, surfaces, bi-variant surfaces, maybe tri-variant volumes, etc in the diagrams of solubility [fusibility] diagram in *(n+1)[n]*-component systems in the in variables $Y_i - Y_j$ or T-X_i in reduced [full] concentration space, correspondingly (Types I, IV).

4.1 Solubility [fusibility] diagram in 3*[2]*-component systems.

Let us denote: R^3 full number of solid phases, crystallizing in the system; R_D^3 – number of solid phases with different compositions in reduced [full] concentration space; $R_T^3 = R^3 - R_D^3$ – number of solid phases with the composition, matching with one of the phases from R_D^3. First of all, suppose, that in the system there is no congruent desolvation [polymorph transformation] solid phases: $R_C^3 = 0$. Denote N^3 – full number of non-variant points; N_{EP}^3 – sum number of eutonics-eutectics and peritonics-peritectics; $N_T^3 = N^3 - N_{EP}^3$ – sum number of transition points; L^3 – sum number of mono-variant curves. From lemma I, II, consequences I-III and Figure 6. follows, that each new solid phase generates 1 new mono-variant curve and 1 additional non-variant point – Figure 6A, and 6C. If a new solid phase eliminates 1 old solid phase no additional points and curves are generated – Figure 6D. If a new solid phase eliminates 2 old solid phases 1 old point curve is eliminated. In the common case, if the formation of the S^{new} solid phase eliminates *Z* old non-variant points – E,P,T^{old}, then it also eliminates *Z-1* mono-variant curves and generates 2 new non-variant points – E,P,T^{new} and *1* mono-variant curves.

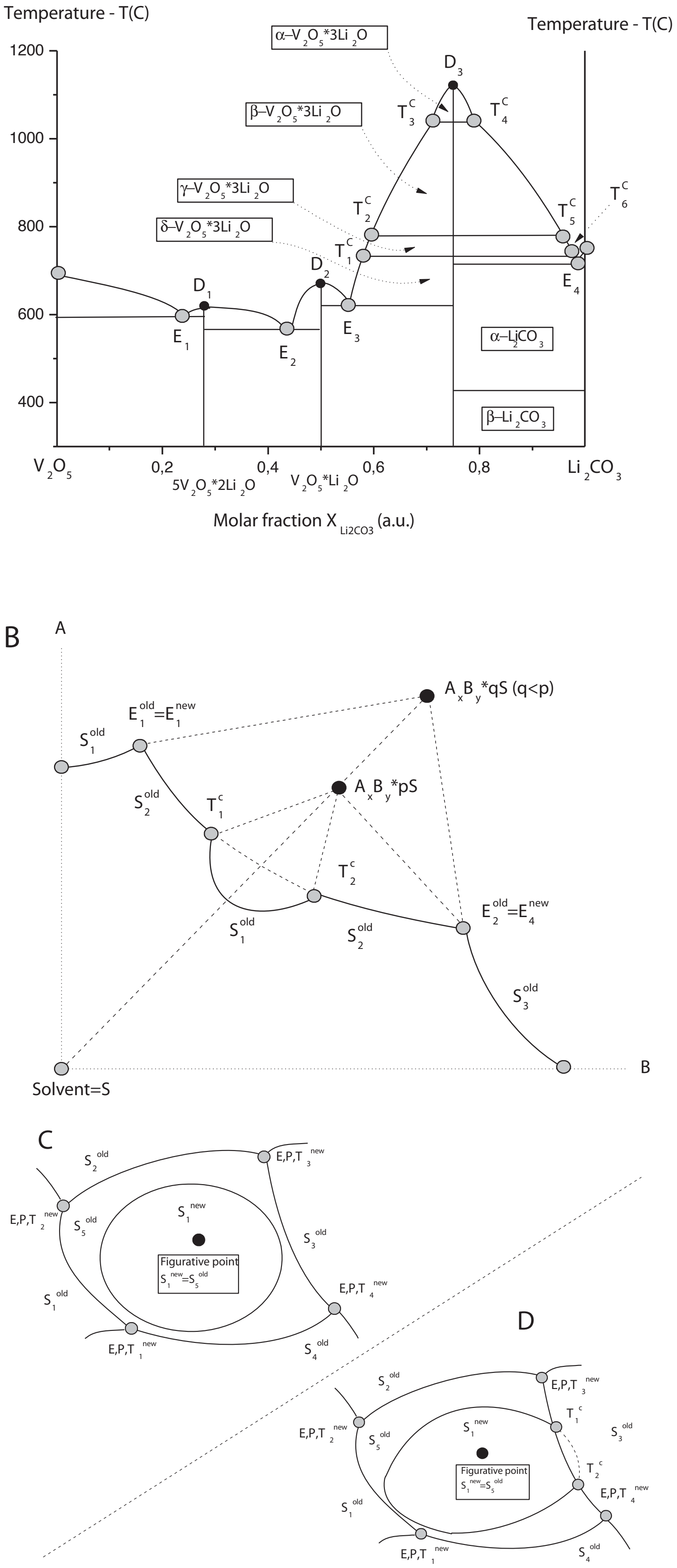

Figure 5: Diagram of fusibility of binary system V_2O_5-Li_2CO_3 (5.A), solubility in abstract ternary system (5.B), fusibility [solubility] in ternary [quaternary] system with congruent polymorph transformation [desolvatation] phases (5.C, 5.D): gray circles - nonvariant points – eurectics-eutonics - E_i, all types of non-variant points – E,P,T_i, transition points of congruent desolvation [congruent polymorph transformation] - T_i^c, black circles – distectics (5.A), figutaive points of the compound crystal solvates (5.B, 5.C, 5.D). Dot lined – limiting nodes liquid-solid and direction solvent-solid, metastable mono-variant curves (5.D). The term “old” corresponds to metastable diagrams without “new” solid phase formation.

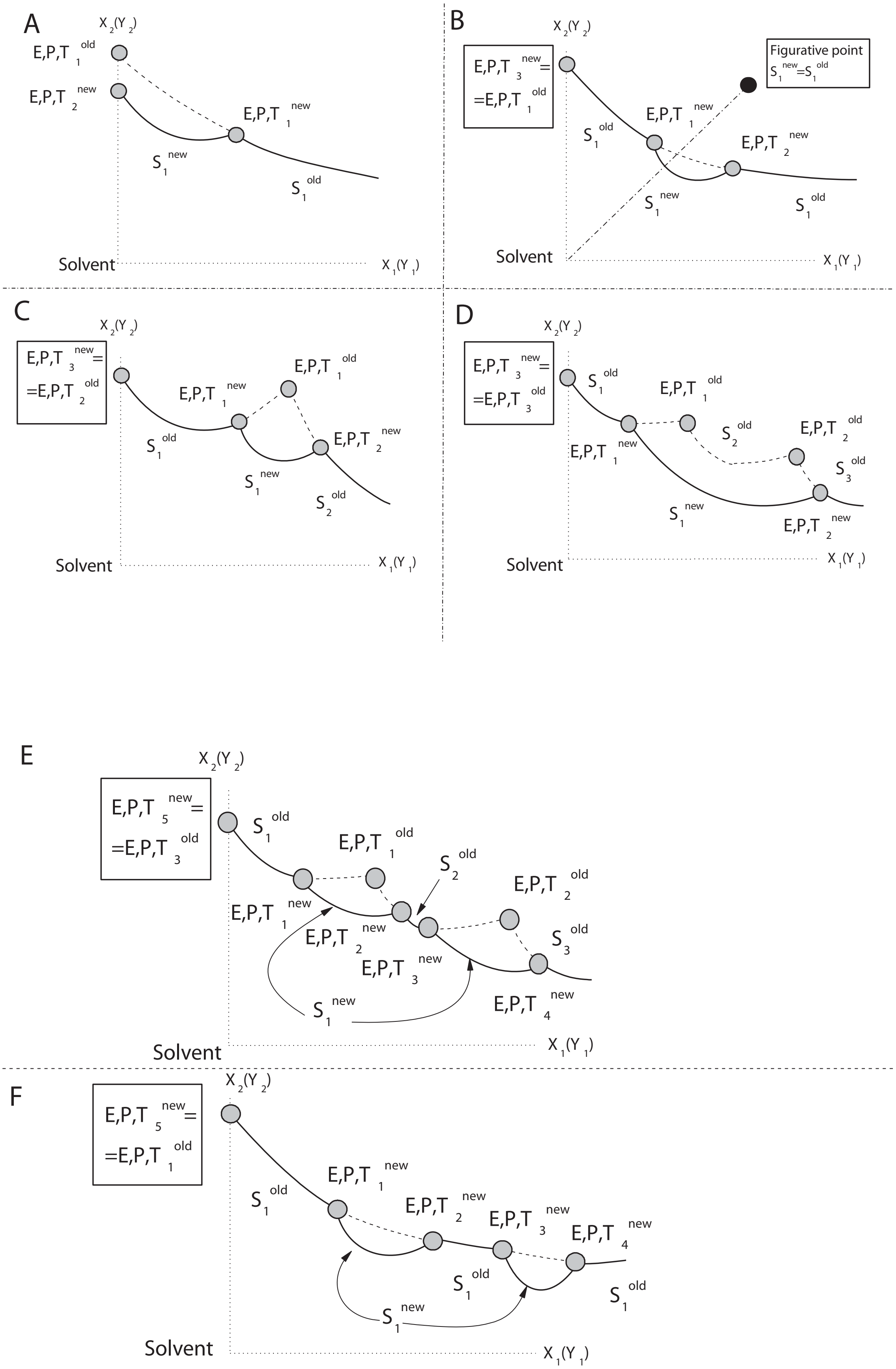

Figure 6: Some possible (6.A, 6.B. 6.C, 6.D) and impossible (6.E, 6.F) types of "new phases" appear in fusibility [solubility] diagrams of ternary [binary] systems. Fig. 6.B. corresponds to the phase of congruent polymorph transformation [desolvatation] formation (its point is a black circle). Dot lines correspond to metastable mono-variant curves and gray circles – to non-variant old and new points.

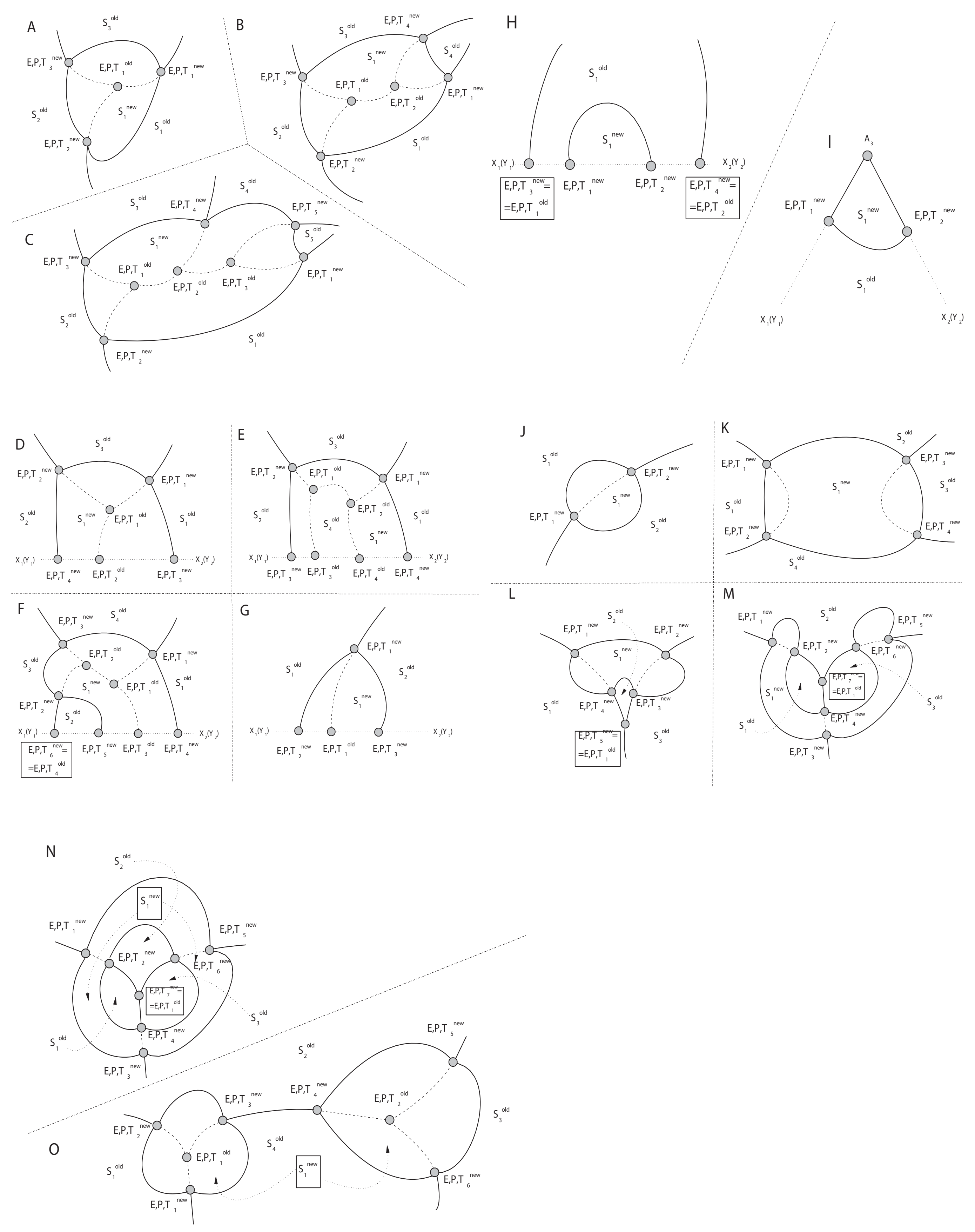

Figure 7: Some possible (7.A, 7.B. 7.C, 7.D, 7.F, 7.G, 7.I) and impossible (7.E, 7.H - congruent desolvation [polymorph transformation], 7.J, 7.K, 7.L, 7.M, 7.N, 7.O) types of “new phases” appearance in fusibility [solubility] diagrams of quaternary [ternary] systems. Dot lines correspond to metastable mono-variant curves, gray circles – to non-variant old and new points, and A_3 – the figurative point of the component.

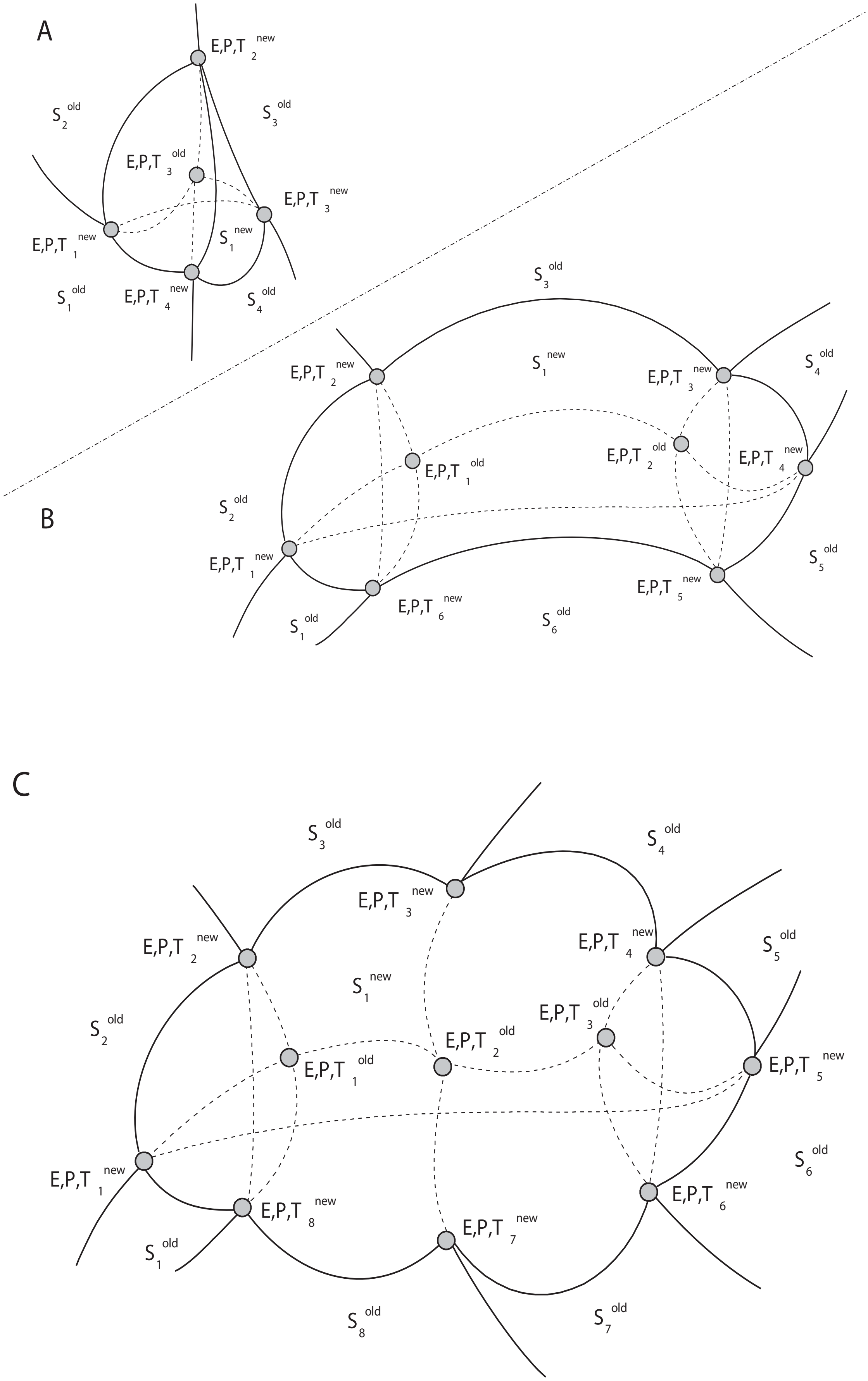

Figure 8: Some possible types of “new phases” appearance in fusibility [solubility] diagrams of five-component [quaternary] systems. Dot lines correspond to metastable mono-variant curves and gray circles – to non-variant old and new points.

So the total number of generated elements is *2-Z* non-variant points and also *2-Z* mono-variant curves. Such construction in elementary graph theory is named an *L*-chain [18] with tops in non-variant points and edges are mono-variant curves. So:

$L^3 = R^3$ (4.1),

$N^3 = R^3 - 1$ (4.2),

$N_{EP}^3 = R_D^3 - 1$ (4.3),

$N_T^3 = R^3 - 1 - (R_D^3 - 1) = R_T^3$ (4.4).

If in the considered type of the systems there are congruent desolvation [polymorph transformation] solid phases: $R_C^3 \neq 0$, one should divide the diagram into the parts between component and compound or compound$_1$ – compound$_2$ (such reception is often named "diagrams triangulation"). In this case, the congruent desolvation [polymorph transformation] solid phase transfers into usual component crystal solvates [component polymorph modification] phases, and one can use formulas (4.1-4.4). Let us show the application of these formulas on the concrete examples – Figure 9.

4.2 Solubility [fusibility] diagram in *4[3]*-component systems

Let us denote: R^4 full number of solid phases, crystallizing in the system; R_D^4 – number of solid phases with different compositions in reduced [full] concentration space; $R_T^4 = R^4 - R_D^4$ – number of solid phases with the composition, matching with one of the phases from R_D^4. Also suppose, that in the system there are no congruent desolvation [polymorph transformation] solid phases: $R_C^4 = 0$ (remind, that we have not found any one example of diagrams with such phase formation). Denote N_{sur}^4 – number of surfaces (fields) of single phase crystallization; N^4 – full number of non-variant points; N_{EP}^4 – sum number of eutonics-eutectics and peritonics-peritectics; $N_T^4 = N^4 - N_{EP}^4$ – sum number of transition points; L^4_{tr} – sum number of mono-variant curves in concentration simplex in in-mutual systems (Roseboom triangle), L^4_{sq} – sum number of mono-variant curves in concentration simplex in mutual systems (Jaenecke square); $\sum N^{(3)}, \sum N_{EP}^{(3)}, \sum N_T^{(3)}$ - sum number of all non-variant points, eutectics-peritectics [eutonics-peritonics], transition points in all 3 (in-mutual) or 4 (mutual) sub-systems; $\sum L^{(3)}$ - sum number of all mono-variant curves in all 3 (in-mutual) or 4 (mutual) sub-systems Table 3.

From lemma I, II, consequences I-III and Figure 7. follows, that:

Such construction is also a usual graph [18] with the tops in non-variant points and edges in mono-variant curves. Direct calculation gives us:

So:

$N_{sur}^4 = R^4$ (4.5),

$$N^4 = 2R^4 - \sum N^{(3)} - 2 \quad (4.6),$$

$$N_{EP}^4 = 2R_D^4 - \sum N_{EP}^{(3)} - 2 \quad (4.7),$$

$$N_T^4 = R^4 - 1 - \left(R_D^4 - 1\right) = R_T^4 - \sum N_T^{(3)} \quad (4.8),$$

$$L^4_{tr} = 3R^4 - \sum L^{(3)} \quad (4.9),$$

$$L^4_{sq} = 3R^4 - \sum L^{(3)} + 1 \quad (4.10).$$

Let us show the application of these formulas on the concrete examples – Figure 10.

4.3 Solubility [fusibility] diagram in *5[4]*-component systems

The number of geometrical elements in such systems is not invariant with the number of equilibrium phases and number of geometrical elements in the sub-systems. These numbers depend on the topology structure of concrete phase diagrams. This fact can be illustrated by Figure 8, where one can see some possible variants of the new solid phase appearance, which generates a different and undefined number of elements. This fact is not absolutely unexpected. For example from the graphs theory, it is known, that [21]:

A) There is a minimal number of colors for coloring L-chain to boundary links should have different colors. This minimal color number is equal to 2.

B) There is a minimal number of colors for coloring a plan geographic map (without enclaves, loops, etc) to boundary countries should have different colors. This minimal color number is equal to 3.

Table 3: The number of geometrical elements changes in the case of "new solid phase" formation.

Number of old non-variant points elimination	Number of old mono-variant curves elimination	Number of new non-variant points formation	Number of new mono-variant curves formation	Number of non-variant points change	Number of mono-variant curves change	Figure
-1	0	+3	+3	+2	+3	7.A
-2	-1	+4	+4	+2	+3	7.B, 7.D
-3	-2	+5	+5	+2	+3	7.C
-1	0	+3	+3	+2	+3	7.G
-3	-2	+5	+5	+2	+3	7.F
0	1	+2	+3	+2	+3	7.I
-Z	-Z+1	Z+2	Z+3	+2	+3	All possible variants in Fig.7

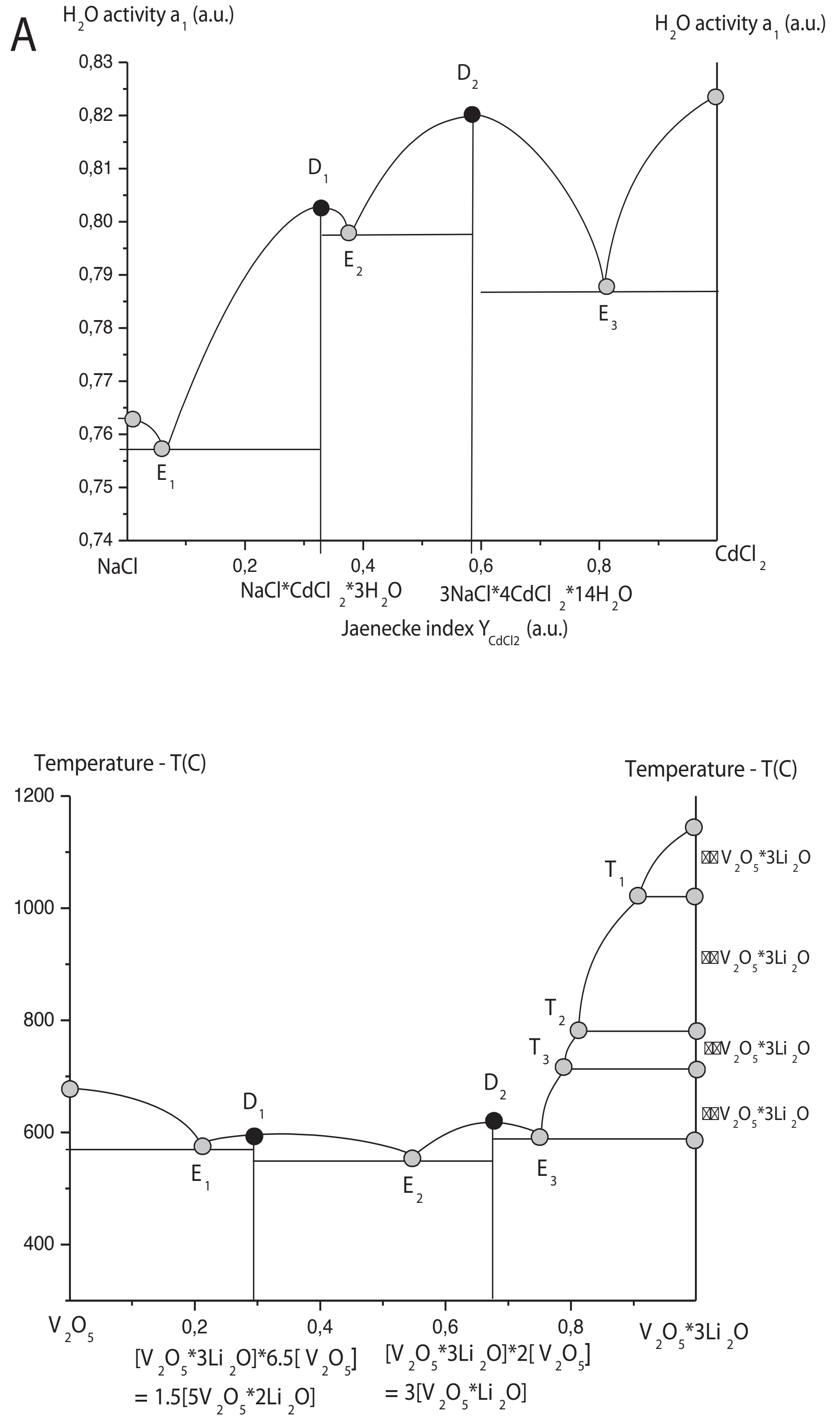

Figure 9: Solubility diagram in ternary system NaCl-$CdCl_2$-H_2O at 25C (9.A) and fusibility diagram in binary system V_2O_5-V_2O_5*$3Li_2O$ (9.B) after triangulation of fusibility diagram in binary system V_2O_5-Li_2CO_3 (5.A): gray circles – non-variant points – eurectics-eutonics - E_i, transition points - T_i, black circles – distectics-distonics. Initial data – from [5,19], correspondingly.

Let us check formulas (4.1)-(4.4) in these examples:

System NaCl-$CdCl_2$-H_2O at 25C:

$L^3 = R^3 = 4$; $N^3 = R^3 – 1 = 4 - 1 = 3$ (E_i); $N_{EP}^3 = R_D^3 - 1 = 4 – 1 = 3$($E_i$); $N_T^3 = R^3 – 1 – (R_D^3 - 1) = 3 – 3 = 0$;

System V_2O_5-V_2O_5*$3Li_2O$:

$L^3 = R^3 = 7$; $N^3 = R^3 – 1 = 7 - 1 = 6$ (E_i, T_i); $N_{EP}^3 = R_D^3 - 1 = 4 – 1 = 3$($E_i$); $N_T^3 = R^3 – 1 – (R_D^3 - 1) = 6 – 3 = 3$ (T_i).

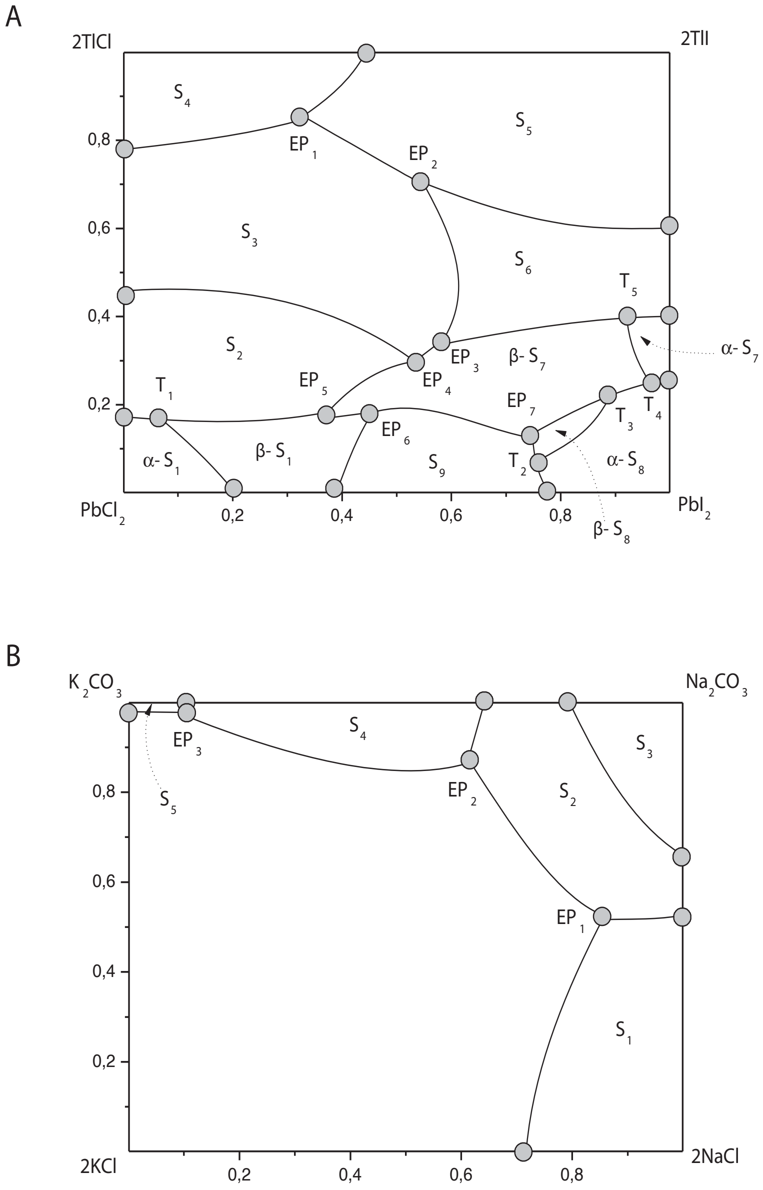

Figure 10: Fusibility diagram in ternary mutual system Tl^+, $Pb^{2+}//Cl^-$, I^- (9.A) and solubility diagram in quaternary mutual system Na^+, $K^+//Cl^-$, CO_3^{2-} -H_2O at 25C (9.B) and: gray circles – non-variant points – eurectics-eutonics (peritectics-peritonics - EP_i, transition points - T_i. Solid phases (Na^+, $K^+//Cl^-$, CO_3^{2-} -H_2O): $S_1 = NaCl$; $S_2 = Na_2CO_3{*}7H_2O$; $S_3 = Na_2CO_3{*}10H_2O$; $S_4 = Na_2CO_3{*}\ K_2CO_3{*}6H_2O$; $S_5 = K_2CO_3{*}1.5H_2O$. Solid phases (Tl^+, $Pb^{2+}//Cl^-$, I^-): $S_1 = PbCl_2$; $S_2 = TlCl{*}2PbCl_2$; $S_3 = 3TlCl{*}PbCl_2$; $S_4 = TlCl$; $S_5 = TlI$; $S_6 = 3TlI{*}PbI_2$; $S_7 = TlI{*}PbI_2$; $S_8 = PbI_2$; $S_9 = PbCl_2{*}PbI_2$; Initial data – from [20, 5], correspondingly.

Let us check formulas (4.5)-(4.10) in these examples:

System Tl^+, $Pb^{2+}//Cl^-$, I^-

$R^4 = N_{sur}^4 = 12$ (all phases); $R_D^4 = 9$ (phases with differ composition), $R_T^4 = 3$ (S_1, S_7, S_8 have the pairs with the same composition). In the binary sub-systems $\sum N_{EP}^{(3)} = 3+1+3+2 = 9, \sum N_T^{(3)} = 1, \sum N^{(3)} = 10, \ \sum L^{(3)} = 4+2+4+4 = 14$. According to our formulas, one can expect $N_T^4 = 2{*}3{-}1 = 5$ (T_1-T_5 in Fig.10.A); $N_{EP}^4 = 2{*}9{-}9{-}2{=}7$ eutectics-peritectics (EP_1-EP_7 in Fig.10.A); $N^4 = 2{*}12{-}10{-}2{=}12$ non-variant points (see Fig.10.A). Also one should expect $L_{sq}^4 = 3{*}12{-}14{+}1{=}24$ mono-variant curves (during calculations the "short curves" are not to be missed, for example from the point T_4 to the side TlI-PbI_2").

System Na^+, $K^+//Cl^-$, CO_3^{2-} -H_2O.

One can see, that: $R^4 = N_{sur}^4 = 6$ (all phases); $R_D^4 = 5$ (phases with different composition), and $R_T^4 = 1$ (S_3 have the pairs with the same composition). In the ternary sub-systems $\sum N_{EP}^{(3)} = 2+1+1+1 = 5, \sum N_T^{(3)} = 2, \sum N^{(3)} = 7, \ \sum L^{(3)} = 4+3+2+2 = 11$. According to our formulas, one can expect $N_T^4 = 2{*}1{-}2 = 0$ (absence in Fig.10.B); $N_{EP}^4 = 2{*}5{-}5{-}2{=}3$ eutonics-peritonics (EP_1-EP_3 in Fig.10.B); $N^4 = 2{*}6{-}7{-}2{=}3$ non-variant points (see Fig.10.B). Also one should expect $L_{sq}^4 = 3{*}6{-}11{+}1{=}8$ mono-variant curves. All calculations are absolutely correct.

C) There is no minimal number of colors for coloring volume cellular structure, because this parameter is not invariant, and depends on the topology of the volume structure.

4.4 Phase equilibrium diagrams with solid solutions and liquid-vapor equilibrium

It is interesting to note, that formulas (4.1)-(4.9) may applied successfully with the systems with solid solutions crystallization if we use van der Waals phase determination. So one should distinguish two phases with the same quantitative composition (for example $Co_xNi_{1-x}SO_4{*}7H_2O$ (monoclinic) and $Co_xNi_{1-x}SO_4{*}7H_2O$ (rhombus), because they fundamentally are described by different state equations. An essential condition of the belonging of the set of solid solutions to one phase is the conservation of crystal structure (syngony).

Calculation of phase elements in the diagrams of phase equilibrium liquid-vapor (with delamination in liquid phases) is absolutely trivial.

5. A new type of non-invariant points and phase processes in the solubility diagrams of multicomponent systems

Specific, never met before, types of non-variant points in the solubility diagrams of multicomponent systems, are realized when in the diagram appears the curve (field, surface, volume, hyper-volume) of crystallization of solid solvent. In the future, we will refer to such non-invariant points as solvent crystallization points – *SC* points. Such points have very special topological and physicochemical features on isothermal-isobaric solubility diagrams. And their topological analogues on fusibility diagrams or liquid-vapor equilibrium diagrams simply do not exist. Earlier, authors, who elaborated classification of non-variant equilibria in solubility diagrams missed this special type of non-variant points [5,13,22-26]. For this fact, there is a simple explanation. Diagram elements for solid solvent crystallization are realized, as a rule, at low temperatures. For such solvent as water, for example, at $T \leq 0$ °C, and such data in water-salt systems even more or less accessible (see, for example, solubility references [27,28]). But for the solvents - low molecular weight alcohols, alkanes, aromatic compounds, etc. temperature of the appearance of *SC*-points even lower $T \leq -n{\cdot}10C$, and such data in the literature are practically absent. Let us assign for the solid phase, which is pure solvent, symbol S_1. For the diagrams figurative point of the solid phase S_1, can not be described in the reduced solvent-free concentration space, because, according to eq. (1.8), when calculating the Jaenecke index in this phase uncertainty generates non-settlement:

$$Y_i^{(s_1)} = n_i^{(s_1)} \Big/ \sum_{k=2}^{n+1} n_k^{(s_1)} = 0/0; \sum_{i=2}^{n+1} Y_i^{(s_1)} \neq 1 \qquad (5.1),$$

As summation in (5.1) is carried out for all dissolved components or without solvent, and the solid phase does not contain such components, only solvent.

So, one can not also determine the parameters of the non-variant process of isotherm solvent evaporation from non-variant liquid solution $-\tilde{\alpha}_{s_1}$ in eq. (1.11). Such a non-variant process of solvent evaporation will cause simultaneous dissolution of the solid solvent phase - S_1, until whole S_1 phase dissolves. All this process should be realized at the condition of the constancy of solvent activity. When whole S_1 phase dissolves system becomes mono-variant, heterogeneous system will come out from *SC*-point to a mono-variant curve without S_1 phase, and solvent activity with further evaporation of water, will begin to decrease.

Into non-variant *SC*-point in *n*-component system coexist *n* phases: saturated solution, *n-1* solid phases ($s_1, s_2 \dots s_{n-1}$), one of which is pure solid solvent - $s_{1.}$ Into *SC*-point come *(n-1)* mono-variant curves - without one of the solid phases from the set ($s_1, s_2 \dots s_{n-1}$). All *(n-2)* mono-variant curves, containing S_1 come to *SC*-point at constant water activity, and only *1* mono-variant curve, without s_1, containing ($s_{2\ \dots\ \mathrm{of}}\, s_{n-1}$) come to *SC*-point when increasing water activity. None of the mono-variant curves is coming to the *SC*-point when decreasing water activity. This behavior is absolutely unique among other non-invariant points on solubility diagrams.

It is quite clear, that the authors, classifying earlier diagrams of fusibility or liquid-vapor phase equilibria, did not note such non-invariant points, they are absent here [6,29,30]. Really, these diagrams (which should be full topological analogs of describing solubility diagram) exist in full concentration space of variables ($\vec{x}$). And it is impossible to imagine the existence of an equilibrium solid phase, which consists of the component, missing in the system.

In order to demonstrate the realization of *SC*-point in real systems, we selected two ternary and mutual quaternary water-salt systems: $Na^+, Ni^{2+} // SO_4^{2-} - H_2O$ at -3 ^{0}C and $Na^+, Ni^{2+} // Cl^-, SO_4^{2-} - H_2O$ at -5 ^{0}C, which are represented below in Figures 11, 12. The calculation is based on the equations of the classical K.Pitzer model [31-33]. The algorithm of phase equilibrium calculation in such systems (which is not the subject of the present article) is also in detail represented in [5,34,35]. It is very clear from Figures 11,12, that *SC*-points in both systems possess all the characteristics, described above in section 5.

The authors hope that the results obtained in the work will be further extended and extended to invariant points and processes not currently considered (for example, associated with the nematic-isotropic phase or transformations of the second kind), as well as with special types of phase equilibria, which are carried out only in systems involving unusual phases - delaminated vapor, supercritical fluids, liquid crystals, plasma, etc.

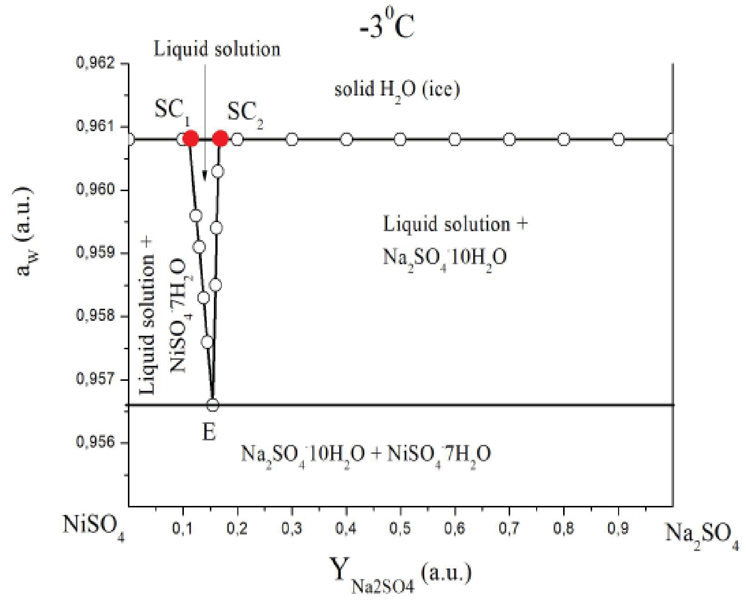

Figure 11: Solubility diagram in ternary system $Na^+,Ni^{2+}//SO_4^{2-}-H_2O$ at -3 ^{0}C in the variables water activity – Yaenecke indexes; points – calculation by K.Pitzer equations, *E* – eutonics, *SC$_i$* red circles – solution crystallization points.

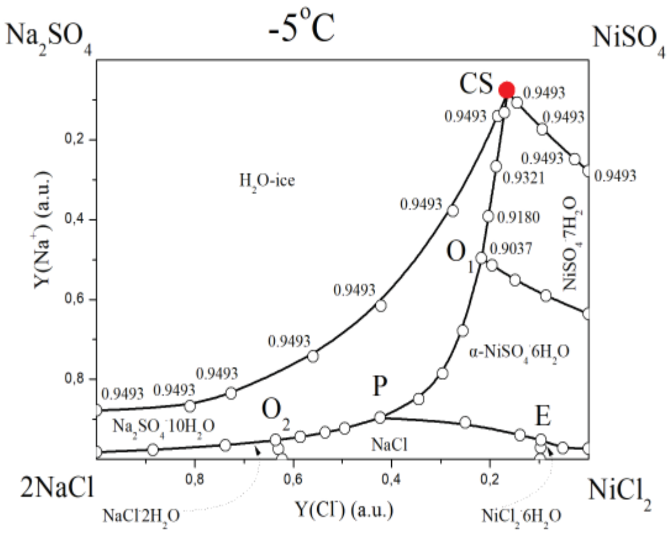

Figure 12: Solubility diagram in quaternary mutual system $Na^+,Ni^{2+}//Cl^-,SO_4^{2-}-H_2O$ at -5^{0}C in ions Yaenecke indexes square; open circles – calculation by K.Pitzer equations, *E* – eutonics, *SC* red circles - solution crystallization points, *P* – peritonics, *O$_i$* – points of crystal-hydrate coexisting. Water activity values are represented near calculated points in the crystallization curves.

Conclusion

General classification of non-invariant points in phase equilibrium diagrams of all possible types in the systems with an arbitrary number of components and equilibrium phases. The complete topological isomorphism of the diagrams of fusibility, solubility, and liquid-vapor equilibria in various sets of variables is demonstrated. A previously undescribed type of non-invariant points and phase processes in the solubility diagrams is described and characterized.

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