DIFFERENT TYPES OF NON-VARIANT POINTS AND NON-VARIANT PHASE PROCESSES IN THE PHASE DIAGRAMS OF BINARY, TERNARY AND MULTICOMPONENT SYSTEMS (Review)

In the article the General classification of all nonvariant points in the arbitrary types diagrams of phase equilibrium with arbitrary number of components is carried out. The topological features of the arrangement of such nonvariant points relative to the figurative points of equilibrium phases are considered. Stability of monovariant equilibria (curves on phase diagrams) in the nearest neighborhood of nonvariant points is also considered. Recurrent equations are given for calculating the number of topological elements of phase diagrams (points, curves, surfaces, volumes, etc.) of phase coexistence from the data on the number of similar elements in less component subsystems. All the obtained regularities are confirmed by examples of specific phase diagrams of solubility, fusibility, liquid-vapor, delamination, etc.

Key words: Diagrams of phase equilibrium, metrics of complete and incomplete Gibbs potential, non-variant points, stability of mono-variant equilibrium, topological isomorphism.

In статье проведена общая классификация всех нонвариантных точек на диаграммах фазовых равновесий произвольного типа с произвольным числом компонентов. Рассмотрены топологические особенности расположения таких нонвариантных точек относительно фигуративных точек равновесных фаз. Рассмотрена устойчивость нонвариантных точек (кривых на фазовых диаграммах) в ближайшей окрестности нонвариантных точек. Приведены рекуррентные уравнения для расчета числа топологических элементов фазовых диаграмм (точек, кривых, поверхностей, объемов и т.п.) сосуществования фаз из данных по числу подобных элементов в менее компонентных подсистемах. Все полученные закономерности подтверждены примерами конкретных фазовых диаграмм растворимости, плавкости, жидкость-пар, расслаивания и т.д.

Ключевые слова: диаграммы фазового равновесия, метрики полного и неполного потенциала Гиббса, нонвариантные точки, устойчивость одновариантного равновесия, топологический изоморфизм.
Введение

Основная цель статьи состоит в том, чтобы классифицировать моновариантные точки на фазовых диаграммах различного типа независимо от чисел компонентов и типа рассматривающего равновесия; рассмотрении моновариантных равновесий в ближайшей окрестности моновариантных точек; и выводе правила расчета топологических элементов фазовых диаграмм различного типа (точек, линий, поверхностей, объемов и т.д.) из данных о числе компонентов и фаз в системе.

Гиббс фазы роли и характеристики различных типов невариантных фазовых процессов

Известно, что моновариантные точки на фазовых диаграммах равновесия находятся в точках, где производная равновесия по параметру равна нулю. В этом случае число компонентов и число фаз, которые могут изменяться независимо друг от друга, определяется условием

\[ f = n - k + 2 - l \]

где: \( n \) - число компонентов, \( k \) - число фаз, \( l \) - число независимых параметров системы. Для расчета моновариантных точек используются различные подходы, в том числе и использование правила Гиббса.

Таблица 1. Характеристики различных типов невариантных фазовых процессов (формальная система коэффициентов для равновесия).

<table>
<thead>
<tr>
<th>Number; &quot;Producing phase&quot;</th>
<th>Phase process</th>
<th>Diagram of phase equilibrium</th>
<th>Limiting conditions</th>
<th>Concentration space</th>
<th>Components number (n); Phases number (r)</th>
<th>Opened or closed system (N system)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. liquid (l)</td>
<td>( l \leftrightarrow \pm s_l \pm s_1 \pm s_n \pm s_m )</td>
<td>fusibility</td>
<td>( P=const )</td>
<td>full</td>
<td>( r = n + 1 ); ( n \geq 2 )</td>
<td>closed</td>
</tr>
<tr>
<td>II. vapor (v)</td>
<td>( v \leftrightarrow \pm l_v \pm l_1 \pm l_n \pm l_m )</td>
<td>liquid-vapor</td>
<td>( P=const )</td>
<td>( T=const )</td>
<td>( r=1 )</td>
<td>opened</td>
</tr>
<tr>
<td>III. (v)</td>
<td>( v \leftrightarrow \pm s_v \pm s_1 \pm s_n \pm s_m )</td>
<td>liquid-vapor (solid-vapor)</td>
<td>( T=const )</td>
<td>( r = n + 1 ); ( n \geq 2 )</td>
<td></td>
<td>opened</td>
</tr>
<tr>
<td>IV. (l)</td>
<td>( l \leftrightarrow \pm s_l \pm s_1 \pm s_n \pm s_m )</td>
<td>solubility</td>
<td>( P=const ); ( T=const )</td>
<td>reduced, without solvent (w)</td>
<td>( r = n ); ( n \geq 3 )</td>
<td>opened</td>
</tr>
<tr>
<td>V. (l)</td>
<td>( l \leftrightarrow \pm l_v \pm l_i \pm l_n \pm l_m )</td>
<td>delamination</td>
<td>( P=const )</td>
<td>full</td>
<td>( r = n + 1 ); ( n \geq 2 )</td>
<td>closed</td>
</tr>
<tr>
<td>VI. solid (s)</td>
<td>( s \leftrightarrow \pm s_k \pm s_1 \pm s_n \pm s_m )</td>
<td>( T=const )</td>
<td>( P=const ); ( T=const )</td>
<td>reduced, without one component</td>
<td>( r = n ); ( n \geq 3 )</td>
<td>opened</td>
</tr>
<tr>
<td>VII. (l)</td>
<td>( l \leftrightarrow \pm l_k \pm l_i \pm l_n \pm l_m )</td>
<td>( T=const )</td>
<td>( P=const ); ( T=const )</td>
<td>reduced, without one component</td>
<td>( r = n ); ( n \geq 3 )</td>
<td>opened</td>
</tr>
</tbody>
</table>
Driving forces in non-variant process may be different:
- External heat supply or removal at $P=\text{const}$; which consumed in non-variant phase process with phases masses change;
- External pressure supply or removal at $T=\text{const}$; which also consumed in heterogeneous system volume change in non-variant phase process;
- External component supply or removal at $T$, $P=\text{const}$; which also consumed in non-variant phase process (in these cases phase process becomes open).

Stability of mono-variant equilibrium in the nearest neighborhood of non-variant points was considered in the same articles [3, 5]. But common consideration, taking into account topological isomorphism of phase diagrams, was not conducted. In this part of articles we shall also use the criterions of the stability of heterogeneous phases complex relatively infinitely small state changes (or criterion of diffusional stability). Probably the first authors [2, 8] got these conditions, authors [8] demonstrated the principle difference between them and similar conditions for the individual phase on the example of hetero-azeotropes in ternary three-phase system. Authors [9] generalized these criterions on the systems with the arbitrary components numbers, arbitrary 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 [10]) in reduced concentration space.

The goal to predict recurrently the number of phase diagrams 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, well-known “azeotrope rule” [11], for phase equilibrium diagrams liquid-vapor allows to calculate the number of special diagram points – knots, saddles, focus-es (in the role of which are points of individual components, binary azeotrope, ternary azeotropes, etc).

**Classification of Non-variant Points and Non-variant Phase Processes in the Different Types 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 $f=0$ (non-variant process is closed). Renumber phases: 1 phase $p$-$p_{h_{1}}$ is “producing phase”; 2, 3... $p_{h_{2}}, p_{h_{3}}, ... p_{h_{r}}$ are “resulting phases”. The main requirements, applicable to $p$-$p_{h_{1}}$ is, that it is the phase with variable composition. This phase, as a rule, should differ according to aggregation state from $p_{h_{2}}, p_{h_{3}}, ... p_{h_{r}}$ (this requirement is not valid only for delamination phase equilibrium diagrams types V, VI, VII, VIII in Table 1). So, we consider I, II, III, V, VI non-variant phase processes at $T=\text{const}$ or $P=\text{const}$. Without loss of generality will assume that the mass of $p$-$p_{h_{1}}$ phase is equal to 1 mole:

$$p - p_{h_{1}} \leftrightarrow \alpha_{2} p_{h_{2}} + \alpha_{3} p_{h_{3}} + ... \alpha_{r} p_{h_{r}}$$

(1.1)

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

$$\alpha_{2} X_{1}^{(2)} + \alpha_{3} X_{1}^{(3)} + ... \alpha_{r} X_{1}^{(r)} = X_{1}^{(1)}$$

(1.2)

$$\alpha_{2} X_{2}^{(2)} + \alpha_{3} X_{2}^{(3)} + ... \alpha_{r} X_{2}^{(r)} = X_{2}^{(1)}$$

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

$$\sum_{i=2}^{r} \alpha_{i} = 1$$

(1.3)

Solve system (1.2):

$$\alpha_{i} = \frac{\Delta_{i}^{(r)}}{\Delta^{(r)}} = 1 - \sum_{i=2}^{r} \frac{\Delta_{i}^{(r)}}{\Delta^{(r)}}$$

(1.4)

where:

$$\Delta^{(1)} = \begin{bmatrix} X_{1}^{(1)} X_{1}^{(1)} \ldots X_{1}^{(1)} \\ X_{2}^{(1)} X_{2}^{(2)} \ldots X_{2}^{(1)} \\ \vdots \vdots \vdots \end{bmatrix}$$

$$\Delta^{(r)} = \begin{bmatrix} X_{1}^{(r)} X_{1}^{(r)} \ldots X_{1}^{(r)} \\ X_{2}^{(r)} X_{2}^{(r)} \ldots X_{2}^{(r)} \\ \vdots \vdots \vdots \end{bmatrix}$$

(1.5)

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

$$\Delta^{(r-2)} * p - p_{h_{1}} \leftrightarrow \sum_{i=2}^{r} \alpha_{i}^{(r-2)} * p_{h_{i}}$$

(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 $p$-$p_{h_{1}}$ is “producing phase”; 2, 3... $p_{h_{2}}, p_{h_{3}}, ... p_{h_{r}}$ are “resulting phases”. The requirement that $-p$-$p_{h_{1}}$ is the phase with variable composition is valid. This phase, as a rule, should differ according to aggregation state from $p_{h_{2}}, p_{h_{3}}, ... p_{h_{r}}$ (this requirement is not valid only for delamination phase equilibrium diagrams types V, VI, VII, VIII in Table 1). We consider IV, VII, VIII, non-variant phase processes at $T,P=\text{const}$ in Table 1. Without loss of generality will assume that the mass of $p$-$p_{h_{1}}$ phase is equal to 1 mole (without taking into account one of the components with number 1):
\[ p - ph_i \leftrightarrow \tilde{\alpha}_i ph_i + \tilde{\alpha}_i ph_i + \ldots \tilde{\alpha}_i ph_i \] (1.7).

Let us rewrite phase process (1.7) through molar fraction of \( i \)-th components in \( j \)-th phase in reduced concentration space without 1-component (such molar fractions, as a rule, are named indexes Jaenecke - \( Y_{ji} \)):

\[ Y_{ji} = \frac{n_i}{n_j} \sum_{i=1}^{k} Y_{ji}^{(i)} = 1 \] (1.8),

where: \( n_i \) - mole number of \( i \)-th components in \( j \)-th phase.

\[ \tilde{\alpha}_i Y_{ji}^{(1)} + \tilde{\alpha}_i Y_{ji}^{(2)} + \ldots + \tilde{\alpha}_i Y_{ji}^{(r)} = Y_{ji} \]

(1.9).

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

\[ \sum_{j=1}^{r} \tilde{\alpha}_i = 1 \] (1.10).

Solve system (1.9):

\[ \tilde{\alpha}_i = \frac{Y_{ji}^{(1)}}{\sum_{j=1}^{r} Y_{ji}^{(1)}} = \sum_{j=1}^{r} \frac{Y_{ji}^{(i)}}{Y_{ji}^{(1)}} \] (1.11),

where:

\[ \tilde{Y}_{ji}^{(1)} = \frac{Y_{ji}^{(1)}}{\sum_{j=1}^{r} Y_{ji}^{(1)}} \]

(1.12).

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

\[ \tilde{Y}_{ji}^{(1)} \cdot p - ph_i \leftrightarrow \sum_{i=1}^{k} \tilde{Y}_{ji}^{(2)} \cdot ph_i \] (1.13).

Let us classify non-variant points.

**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. Number of components in this case \( n=2 \) in full [reduced] concentration space for different types of diagrams from the Table 1 I, II, III, V, VI (IV, VII, VIII). So, determinants \( \Delta^{(r-1)} \neq 0 \) or \( \tilde{\Delta}^{(r-1)} \neq 0 \). According to [12] determinants:

\[ \Delta^{(r-1)}; \tilde{\Delta}^{(r-1)}; \tilde{\Delta}^{(r-1)} \] with the dimension (r-1) and (r-2) matching columns have one (different) sign, if figurative points of \( p-ph_i \) - phase and \( ph_i \) - phase lie cis (trans) of hyper-plane, passing through the figurative points of all other resulting phases: \( ph_2, ph_3, \ldots, ph_{r-1}, ph_r \). Sometimes in multidimensional geometry one says, that points \( p-ph_i \) - 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 \( \alpha_i \) 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 \( \alpha_i \) there is possible the realization the following types of non-variant points:

A) All \( \alpha_i \) > 0. In this case one says, that \( p-ph_i \) forms congruently, and non-variant point is named eutectic (Type I in Table 1.), eutonic (Type IV), congruent aze trope (Type II, III), congruent liquid delamination (Type V, VII) or solid delamination (Type VI, VIII) points.

B) For some \( \alpha_j \) < 0. \( p-ph_i \) forms incongruently, and non-variant point is named k-type peritectic (Type I in Table 1.), k-type aperitectic (Type IV), k-type incongruent aze trope (Type II, III), k-type incongruent liquid delamination (Type V, VII) or solid delamination (Type VI, VIII) points.

C) One more type of non-variant point corresponds to 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 location of non-variant points and \( p-ph_i \) equilibrium figurative points in the systems with the different components numbers are represented in Fig.1.

- In single-component system \( n=1 \) in full concentration space without limiting conditions (\( l=0 \)) the variant of linear independence the 3 equilibrium phases composition is impossible, because 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. So, for example, the solubility diagram in the binary system at \( T, P=\text{const} \) is non-variant point. In the both cases concentration spaces are non-dimensional (geometric points). So, Fig.1.A can not generate specific non-variant points, considered earlier. Phase diagram types IX, X, XI in this case can not be realized.

- In the systems \( n=2 \) (types I, II, III, V, VI) at \( T, P=\text{const} \) \( n=3 \) (IV, VII, VIII) at \( T, P=\text{const} \) – Fig.1.B. 1.C concentration space is mono-dimensional (cut in strict line). It is possible to realize only two types of non-variant points – E and P;

- In the systems \( n=3 \) (types I, II, III, V, VI) at \( T, P=\text{const} \) \( n=4 \) (IV, VII, VIII) at \( T, P=\text{const} \) – Fig.1.D. 1.E, 1.F concentration space is bi-dimensional (triangle plane). It is possible to realize three types of non-variant points – E, P, P_0;

- In the systems \( n=4 \) (types I, II, III, V, VI) at \( T, P=\text{const} \) \( n=5 \) (IV, VII, VIII) at \( T, P=\text{const} \) – Fig.1.F. 1.G, 1.H, 1.I, 1.J concentration space is three-dimensional (tetrahedron volume). It is possible to realize four types of non-variant points – E, P_0, P_\infty, P_\infty;
**const** concentration space is multidimensional (simplex hyper-volume). It is possible to realize \( N \) types of non-variant points – \( E, P_1\ldots P_{N-1} \).

![Diagram showing different types 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, peritontics, 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-1.F \( (n=3[4]) \), 1.G-1.J \( (n=4[5]) \).]

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 non-variant points classification are equivalent. Only one 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 triangle, but the square, in the systems with \( n=4(5) \) it is not tetrahedron, but cube, etc.

**Linear Dependent Phases Compositions**

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

The only real case of the realization of such linear dependence is in 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 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 \( p-ph_1, ph_i \) 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) are represented in Fig.2.

- **In 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 Fig.2.A. 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 driving force of non-variant process is external pressure the same pro-
cesses occurs: at the efforts of pressure increase will start non-variant processes, decreasing sum phases volume. In the cases of reverse driving forces reverse phase processes will start.

Topologically similarly 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). And in the process of solvent removing crystal-solvate with larger number of solvent molecules will transfer to crystal-solvate with smaller number of solvent molecules.

- In the systems $n=2$ (types I, II, III, V, VI) at $T$ or $P=\text{const}$, $n=3$ (IV, VII, VIII) at $T,P=\text{const}$ - Fig.2.B, concentration space is mono-dimensional (cut in strict line). It is possible to realize only one type of non-variant transition points $T_0$;

- In the systems $n=3$ (types I, II, III, V, VI) at $T$ or $P=\text{const}$, $n=4$ (IV, VII, VIII) at $T,P=\text{const}$ - Fig.1.C concentration space is bi-dimensional (triangle plane). It is possible to realize only one type of non-variant transition points $T_0$;

- In the systems $n=4$ (types I, II, III, V, VI) at $T$ or $P=\text{const}$, $n=5$ (IV, VII, VIII) at $T,P=\text{const}$ - Fig.1.D concentration space is three-dimensional (tetrahedron volume). It is possible to realize only one type of non-variant transition points $T_{10}$;

- In the multicomponent systems $n=N$ (types I, II, III, V, VI) at $T$ or $P=\text{const}$, $n=N+1$ (IV, VII, VIII) at $T,P=\text{const}$ concentration space is multidimensional (simplex hyper-volume). It is also possible to realize one type of non-variant transition points $T_{N+1}$.

**Stability of Mono-variant Equilibrium in the Nearest Neighborhood of Non-variant Points**

Now we shall consider the questions, concerning with 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 geometrical image, as mono-variant curves, comes into non-variant points). Authors [3] solved this problem for fusibility diagrams in time consuming manner, using some additional relations in particular from [6]. We shall try to solve this problem considerably easily, using criterions of the stability of heterogeneous phases complex relatively infinitely small state changes [2].

Then we write differential van der Waals equation for the equilibria of the phases pairs $(p-\text{ph})$ (give it number 1), $p_{\text{ph}_3}, p_{\text{ph}_3}...p_{\text{ph}}$ (give them numbers 2, $3,...\lambda$) in $n$-component system in the variables of 1 phase in the metric of Gibbs potential in full concentration range [3, 5-7]:

$$
(\vec{X}^{(i)} - \vec{X}^{(i)})d\vec{X}^{(i)} = S^{(i-2)}>dT - V^{(i-2)}>dP
$$

$$
(\vec{X}^{(i)} - \vec{X}^{(i)})d\vec{X}^{(i)} = S^{(i-3)}>dT - V^{(i-3)}>dP
$$

(2.1).

$$
(\vec{X}^{(i)} - \vec{X}^{(i)})d\vec{X}^{(i)} = S^{(i-4)}>dT - V^{(i-4)}>dP
$$

Here: $V^{(i)}$ and $S^{(i)}$ – molar phase volumes and entropies of phase $i$; $\nabla V^{(i)}$ and $\nabla S^{(i)}$ – concentration gradients of $V^{(i)}$ and $S^{(i)}$ with the elements $(\partial V^{(i)}/\partial X^{(i)}), (\partial S^{(i)}/\partial X^{(i)})$ correspondingly; $\vec{X}^{(i)}$ – vector of the state of figurative point of $i$ phase in concentration space with elements $X^{(i)}$; $d\vec{X}^{(i)}$ – vector $\vec{X}^{(i)}$ shift at $(\alpha - \beta)$ equilibrium shift with elements $dX^{(i)}$; $G^{(i)}$ – operator, corresponding to the matrix of second derivatives $G^{(i)}$:

$$
G^{(i)} = \left(\frac{\partial^2 G^{(i)}}{\partial X^{(i)}}\right),
$$

(2.2),

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

Physical sense of the parameters $S^{(i-2)} = [S^{(i)} - S^{(i)} + (\vec{X}^{(i)} - \vec{X}^{(i)})\nabla V^{(i)}]$ and $V^{(i-2)} = [V^{(i)} - V^{(i)} + (\vec{X}^{(i)} - \vec{X}^{(i)})\nabla V^{(i)}]$ are entropy and volume changes in the process of isothermynozoric formation of 1 mole of $i$ phase from infinitely large mass of $\alpha$ phase.

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

$$
(\vec{Y} - \vec{Y}^{(i)})d\vec{Y} = S^{(i-2)}>dT - V^{(i-2)}>dP + n^{(i-2)}>\mu_i
$$

$$
(\vec{Y} - \vec{Y}^{(i)})d\vec{Y} = S^{(i-3)}>dT - V^{(i-3)}>dP + n^{(i-3)} \mu_i
$$

$$
(\vec{Y} - \vec{Y}^{(i)})d\vec{Y} = S^{(i-4)}>dT - V^{(i-4)}>dP + n^{(i-4)} \mu_i
$$

(2.3).

![Diagram](image-url)
Designations here are similar to the equations (2.1), but functions: $G_{11} = G - n_i \mu_i = \sum_{i=2}^{n+1} n_i \mu_i$ (where $\mu_i$ are chemical potentials of the solvent and dissolved components), $\tilde{S}$ and $\tilde{V}$ are calculated relative to one mole of $n$ components without 1 component-solvent, and vectors $Y^{(r^*)}$ characterize position of figurative point of $r$ phase in reduced $(n)$-dimensional concentration space:

$$Y^{(r^*)} = n_i^{(r^*)} \sum_{i=1}^{n+1} n_i^{(r^*)} \left( \sum_{i=2}^{n+1} n_i^{(r^*)} \right) = 1 \right) \text{(2.4).}$$

In this case matrices $C_{11}^{(r^*)}$ are also nondegenerate and corresponding quadratic bilinear forms are determined positively, according Sylvester’s criterion [6, 7].

$$G_{11}^{(r^*)} = \left( \frac{\partial^2 G_{11}^{(r^*)}}{\partial Y^{(r^*)}} \right)_{F, P, \alpha, \beta, \gamma, \delta, \varepsilon, \zeta, \eta, \theta, \varphi, \psi, \omega} \left( \frac{\partial Y^{(r^*)}}{\partial Y^{(r^*)}} \right) = 0 \right) \text{(2.5).}$$

Physical sense of the parameters $\tilde{S}^{(a \rightarrow b)} = \left[ \tilde{S}^{(a)} - \tilde{S}^{(b)} \left( \tilde{V}^{(a)} - \tilde{V}^{(b)} \right) \left( \tilde{V}^{(a)} - \tilde{V}^{(b)} \right) \right]$, $\tilde{V}^{(a \rightarrow b)} = \left[ \tilde{V}^{(a)} - \tilde{V}^{(b)} \left( \tilde{V}^{(a)} - \tilde{V}^{(b)} \right) \left( \tilde{V}^{(a)} - \tilde{V}^{(b)} \right) \right]$ and $n_i^{(a \rightarrow b)} = n_i^{(a)} - n_i^{(b)} \left( \tilde{V}^{(a)} - \tilde{V}^{(b)} \right) \left( \tilde{V}^{(a)} - \tilde{V}^{(b)} \right)$ are entropy, volume and number of moles of 1 component changes in the process of isotherm-isobaric formation of 1 mole of $r$ phase from infinitely large mass of $a$ 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 heterogeneous complex of phases. Then we write van der Waals equations in the metric of complete (and incomplete) Gibbs potential in $n \cdot (n+1)$-component system in full [reduced concentration range (without 1 component)] for the equilibria of the producing phase $(p, ph_1, \ldots, ph_n)$ (give it number 1) and heterogeneous complex of resulting phases (note $het$) [2, 9, 13]:

$$\left( \tilde{X}^{(het)} \right) - \tilde{X}^{(1)} \right) \left( \tilde{G}^{(het)} \right) \left( \tilde{d} \tilde{X}^{(1)} \right) = S^{(1-het)} \left( \tilde{d}T - \tilde{V}^{(1-het)} \right) \left( \tilde{d}P \right) \text{(2.6),}$$

$$\left( \tilde{X}^{(het)} \right) - \tilde{X}^{(het-1)} \right) \left( \tilde{G}^{(het)} \right) \left( \tilde{d} \tilde{X}^{(het-1)} \right) = S^{(het-1)} \left( \tilde{d}T - \tilde{V}^{(het-1)} \right) \left( \tilde{d}P \right) \text{(2.7),}$$

$$\left( \tilde{V}^{(het)} \right) - \tilde{V}^{(1)} \right) \left( \tilde{G}^{(het)} \right) \left( \tilde{d} \tilde{V}^{(1)} \right) = S^{(1)} \left( \tilde{d}T - \tilde{V}^{(1)} \right) \left( \tilde{d}P + n_i^{(het-het)} \right) \mu_i \text{(2.8),}$$

$$\left( \tilde{V}^{(het)} \right) - \tilde{V}^{(het-1)} \right) \left( \tilde{G}^{(het)} \right) \left( \tilde{d} \tilde{V}^{(het-1)} \right) = S^{(het-1)} \left( \tilde{d}T - \tilde{V}^{(het-1)} \right) \left( \tilde{d}P + n_i^{(het-het)} \right) \mu_i \text{(2.9),}$$

where: equations (2.6), (2.8) are written in the variables of producing phase number 1, and equations (2.7), (2.9) in the variables of heterogeneous complex of resulting phases noted – $het$. Physical sense of all phase effects in these equations is absolutely similar these in the equations systems (2.1), (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.

<table>
<thead>
<tr>
<th>$N$</th>
<th>Phase process</th>
<th>Diagram of phase equilibrium, Full or reduced</th>
<th>Phase effect of the direct process $p - ph_i \leftrightarrow$ het</th>
<th>Sign of the effect of the direct process</th>
<th>Phase effect of the reverse process $het \leftrightarrow p - ph_i$</th>
<th>Sign of the effect of the reverse process</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>$l \leftrightarrow \pm s_i \pm s_x \pm s_n \pm s_m$</td>
<td>Fusibility, $P = \text{const}$, full</td>
<td>$S^{(cryst)}$</td>
<td>$&lt; 0$</td>
<td>$S^{(melt)}$</td>
<td>$&gt; 0$</td>
</tr>
<tr>
<td></td>
<td>$l \leftrightarrow \pm s_i \pm s_x \pm s_n \pm s_m$</td>
<td>closed, $r = n + 1, n \geq 2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II.</td>
<td>$v \leftrightarrow \pm l_i \pm l_x \pm l_n \pm l_m$</td>
<td>liquid-vapor, $P = \text{const}$, full</td>
<td>$S^{(cond)}$</td>
<td>$&lt; 0$</td>
<td>$S^{(evap)}$</td>
<td>$&gt; 0$</td>
</tr>
<tr>
<td></td>
<td>$v \leftrightarrow \pm s_i \pm s_x \pm s_n \pm s_m$</td>
<td>liquid-vapor, $P = \text{const}$, full</td>
<td>$S^{(subb)}$</td>
<td>$&lt; 0$</td>
<td>$S^{(solid-evap)}$</td>
<td>$&gt; 0$</td>
</tr>
<tr>
<td></td>
<td>$v \leftrightarrow \pm l_i \pm l_x \pm l_n \pm l_m$</td>
<td>closed, $r = n + 1, n \geq 2$</td>
<td>$V^{(cond)}$</td>
<td>$&lt; 0$</td>
<td>$V^{(solid-evap)}$</td>
<td>$&gt; 0$</td>
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<tr>
<td></td>
<td>$v \leftrightarrow \pm s_i \pm s_x \pm s_n \pm s_m$</td>
<td>closed, $r = n + 1, n \geq 2$</td>
<td>$V^{(subb)}$</td>
<td>$&lt; 0$</td>
<td>$V^{(solid-evap)}$</td>
<td>$&gt; 0$</td>
</tr>
<tr>
<td>В.</td>
<td>( l \leftrightarrow \pm l_k \pm l_n \pm \ldots \pm l_m )</td>
<td>открыто, ( r = n, n \geq 3 )</td>
<td>( S^{(\text{liquido-delamin})} )</td>
<td>n.d.</td>
<td>( S^{(\text{liquid} \rightarrow \text{bio-lg})} )</td>
<td>n.d.</td>
</tr>
<tr>
<td>---</td>
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</tr>
</tbody>
</table>

| ВІ. | \( s \leftrightarrow \pm s_k \pm s_n \pm \ldots \pm s_m \) | открыто, \( r = n, n \geq 3 \) | \( S^{(\text{solid} \rightarrow \text{delamin})} \) | n.d. | \( S^{(\text{solid} \rightarrow \text{bio-lg})} \) | n.d. |

| ВІІ. | \( l \leftrightarrow \pm l_k \pm l_n \pm \ldots \pm l_m \) | открыто, \( r = n, n \geq 3 \) | \( n^{(\text{cryst})} \) | <0 | \( n^{(\text{dissol})} \) | >0 |

| IX. | \( v \leftrightarrow \pm v \pm s \) | Относительно, одно компонент | \( S^{(\text{trans}, \text{cryst})} \) | <0 | \( S^{(\text{mel}, \text{evap})} \) | >0 |
| X. | \( v \leftrightarrow \pm v \pm s \) | Относительно, \( r = 3, n = 1 \) | одно компонент, отсутствие | \( S^{(\text{subl}, \text{polym}, \text{trans})} \) | <0 | \( S^{(\text{polym}, \text{trans})} \) | >0 |

| XI. | \( l \leftrightarrow \pm s \pm s_k \) | Относительно, \( r = 3, n = 1 \) | одно компонент, отсутствие | \( S^{(\text{crys}, \text{polym}, \text{trans})} \) | <0 | \( S^{(\text{polym}, \text{trans})} \) | >0 |

| XII. | \( s \leftrightarrow s \leftrightarrow s \) | Относительно, \( r = 3, n = 1 \) | одно компонент, отсутствие | \( S^{(\text{polym}, \text{trans})} \) | n.d. | \( S^{(\text{polym}, \text{trans})} \) | n.d. |

"n.d." — not determined.

Signs of phases effects in Table 2 is the following:

- \( S^{(\text{cryst})} < 0 \), \( S^{(\text{mel})} > 0 \), because liquid and solid can not form critical state in principle [2].
- \( S^{(\text{cond})} < 0 \), \( S^{(\text{subl})} < 0 \), \( S^{(\text{evap})} > 0 \), \( V^{(\text{cond})} < 0 \), \( V^{(\text{subl})} < 0 \), \( V^{(\text{evap})} > 0 \), when we shall not consider states, closed to critical and supercritical states for equilibrium liquid-vapor.
- \( n^{(\text{cryst})} > 0 \), \( n^{(\text{dissol})} > 0 \), when liquid phase more solvent rich, then all equilibrium solid phases and their heterogeneous complex. If fact there are some exotic cases, when it is not so, and signs are converted. In this case, so named "forbidden types of solubility diagrams" are realized [14]. But this types meet very-very rare (these cases usually are not investigated), so one can consider almost without loss of generality that signs of solvent phases effects are as mentioned above.

In single component system:

- \( S^{(\text{cond}, \text{cryst})} < 0 \), \( V^{(\text{cond}, \text{cryst})} < 0 \),
- \( S^{(\text{mel}, \text{evap})} > 0 \), \( V^{(\text{mel}, \text{evap})} > 0 \), \( S^{(\text{subl}, \text{polym}, \text{trans})} < 0 \), \( V^{(\text{subl}, \text{polym}, \text{trans})} < 0 \),
- \( S^{(\text{solv}, \text{polym}, \text{trans})} < 0 \), \( V^{(\text{solv}, \text{polym}, \text{trans})} < 0 \),
- \( S^{(\text{crys}, \text{polym}, \text{trans})} < 0 \), \( S^{(\text{mel}, \text{polym}, \text{trans})} > 0 \), because solid and liquid and solid and vapor can not form critical state.

One can consider stability of mono-variate equilibrium nearby non-variant points only, if he know sign of corresponding phase effect of the process

\[ p - ph_1 \leftrightarrow \alpha_1 ph_1 + \alpha_2 ph_2 + \ldots \alpha_r ph_r \] (2.10),

\[ p - ph_1 \leftrightarrow \alpha_1 ph_1 + \alpha_2 ph_2 + \ldots \alpha_r ph_r \] (2.11),

Where signs \( \alpha [\alpha_r] \) are arbitary. In non-variant point come or go \( r \)-1 curves of mono-variate equilibrium, corresponds to coexisting of the phases

\[ p - ph_1, ph_2, \ldots ph_{r-1}, ph_{r+1}, ph_{r+2}, \ldots ph_r \] (without one of the resulting phase \( ph_r \)). Let us prove

**Rule II:** If figurative point of the resulting phase \( ph_r \) lies in opposition-trans (conjunction-cis) to figurative point of producing phase relatively to hyper-plane of the rest \( r-2 \) resulting phases, then mono-variate curve comes to non-variant point with the **increase in decrease** (increase in decrease) of pressure at \( T=\text{const} \) in full concentration space; or with the **decrease in increase** of solvent chem-
Let us distribute the set of the resulting phases $p_{h_1}, p_{h_2}, p_{h_3}$ into two subsets: I - $p_{h_1}, p_{h_2}, p_{h_3}$, for which $\alpha_i(\vec{a}) > 0$ and II - $p_{h_{u+1}}, p_{h_{u+2}}, \ldots, p_{h_n}$, for which $\alpha_i(\vec{a}) < 0$.

Let us rewrite (2.10), (2.11) through the modules of $t_i, l_i(\vec{a})$ in full or reduced concentration spaces:

\[ p - p_{h_1} + \alpha_1 l_1(\vec{a}) + \alpha_2 l_2(\vec{a}) + \ldots + \alpha_i l_i(\vec{a}) + \ldots + \alpha_n l_n(\vec{a}) \leftrightarrow \alpha_{u+1} l_{u+1}(\vec{a}) + \alpha_{u+2} l_{u+2}(\vec{a}) + \ldots + \alpha_n l_n(\vec{a}) \quad (2.12) \]

\[ p - p_{h_1} + \alpha_1 l_1(\vec{a}) + \alpha_2 l_2(\vec{a}) + \ldots + \alpha_i l_i(\vec{a}) + \ldots + \alpha_{u-1} l_{u-1}(\vec{a}) + \alpha_u l_u(\vec{a}) + \alpha_{u+1} l_{u+1}(\vec{a}) + \alpha_{u+2} l_{u+2}(\vec{a}) + \ldots + \alpha_n l_n(\vec{a}) \leftrightarrow \alpha_{u+1} l_{u+1}(\vec{a}) + \alpha_{u+2} l_{u+2}(\vec{a}) + \ldots + \alpha_n l_n(\vec{a}) \quad (2.13) \]

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

There are two principle cases:
- A) $h_n$ belongs to I subset.
- B) $p_k$ belongs to II subset.

There are three variants of the impact on non-equilibrium:
- To put to the system infinitely small amount of heat or entropy ($+Q_0 = +\Delta S_{00}$) or
- Act on the system by infinitely small volume change ($+V_{00}$) or
- Act on the system by add of infinitely small solvent amount (component number $1$) ($+n_{1(P,T)}$).

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

\[ dT_p > 0, \quad dP_1 > 0, \quad d(\mu_{1(P,T)}) > 0 \quad (2.14) \]

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

**Linear Dependent Phases Compositions**

In these cases phase composition of two resulting phases (name them $p_{h_1}$ and $p_{h_2}$) 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 $p_{h_1}$ and $p_{h_2}$ should be only solid - polymorph modifications of single substance (Type I - fusibility diagrams) or different crystal solvates of single substance (Type IV - solubility diagrams). It absolutely impossible to imagine two different liquid phases with the same composition (with the exception of equilibrium of liquid-crystal phase with isotropic liquid phase). Exclude these exotic cases (Types II, III). Let us prove

**Rule III:** If figurative points of two resulting phase $p_{h_1}$ and $p_{h_2}$ coincides, then all ($r$-3) mono-variant curves with their participation of both $p_{h_1}$ and $p_{h_2}$ phases, come to non-variant point with the constancy of temperature at $P=\text{const}$, in full concentration space; or with sol-
vent chemical potential at \( P, T=\text{const} \) in reduced concentration space (without solvent). Simultaneously rest 2 mono-variant curves with the participation of \( p_{h_3} \) separately from \( p_{h_2} \) come to non-variant point: first – with the increase, second – with the decrease of temperature at \( P=\text{const} \); in full concentration space; or with solvent chemical potential at \( P, T=\text{const} \) 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 \( p_{h_2} \) and both resulting phases \( p_{h_2} \) and \( p_{h_3} \) in the variables of \( p_{h_2} \) with variable composition at \( T=\text{const} \) \((T,P=\text{const})\):

\[
(X^{(p_{h_2})} - X^{(p_{h_3})}) \hat{G}_i^{(1)} dX^{(p_{h_2})} = S^{(p_{h_2} \rightarrow p_{h_3})} dT
\]

(2.17),

\[
(Y^{(p_{h_2})} - Y^{(p_{h_3})}) \hat{G}_i^{(1)} dY^{(p_{h_2})} = S^{(p_{h_2} \rightarrow p_{h_3})} dT
\]

(2.18),

\[
(n_{i}^{(p_{h_2} \rightarrow p_{h_3})}) \hat{G}_i^{(1)} dY^{(p_{h_2})} = d\mu_i
\]

(2.19),

\[
((\hat{Y}^{(p_{h_2})} - \hat{Y}^{(p_{h_3})})) \hat{G}_i^{(1)} dY^{(p_{h_2})} = n_{i}^{(p_{h_2} \rightarrow p_{h_3})} d\mu_i
\]

(2.20).

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

\[
(X^{(p_{h_2})} - X^{(p_{h_3})}) \hat{G}_i^{(1)} dX^{(p_{h_2})} = [S^{(p_{h_2} \rightarrow p_{h_3})} - S^{(p_{h_2} \rightarrow p_{h_3})}] dT = 0
\]

(2.21),

\[
(Y^{(p_{h_2})} - Y^{(p_{h_3})}) \hat{G}_i^{(1)} dY^{(p_{h_2})} = [n_{i}^{(p_{h_2} \rightarrow p_{h_3})} - n_{i}^{(p_{h_2} \rightarrow p_{h_3})}] d\mu_i = 0
\]

(2.22).

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

\[
(X^{(p_{h_2})} - X^{(p_{h_3})}) = 0, \quad (Y^{(p_{h_2})} - Y^{(p_{h_3})}) = 0
\]

(2.23),

\[
dT = 0, \quad d\mu_i (T,P) = 0 \quad (2.24).
\]

Naturally, if \( p_{h_3} \) is more high temperature modification in the comparison with \( p_{h_2} \), then mono-variant curve \( p_{h_2} - p_{h_3} - p_{h_3} \) comes to non-variant point with decrease and mono-variant curve \( p_{h_2} - p_{h_3} \) comes to non-variant point with increase of temperature at \( P=\text{const} \) [solvent chemical potential at \( P, T=\text{const} \)] in full [reduced] concentration space.

![Fig.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: 4A \( (n=2[2]) \), 4B \( (n=3[4]) \), 4C \( (n=4[5]) \). 4D, 4E, 4F \( (n=1) \). Location of figurative points corresponds to the following figures pairs: 4A:2.B; 4B:2C; 4C:2.D; 4.D, 4.E, 4.F:1.A.](image)

### Thermodynamic 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 \( P=\text{const} \) in full concentration space in \( n \)-component systems in variables \( T, X \) and solubility diagrams at \( P,T=\text{const} \) in reduced concentration in \( (n+1) \)-component systems in variables \( Y_i \). So, producing phase is liquid and 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 \( P=\text{const} \) or \( T=\text{const} \) (and delamination diagrams) in common case does not contain phases with constant composition and can not be considered by used method.

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

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

D) We shall also consider diagrams usual system s such as M,N,P//X(Y-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 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\(^{8k}\), or acid groups etc. Let us exclude instable cuts of the mutual diagrams, such as: MX-NY...PZ(Solvent) [15].

Let us consider simplest phase diagram stable relative both infinite 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 "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-peritetics [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 – \(l\) and \(l\) in the equilibrium with the set of solid phases: \(s\), \(s\),...\(s\). Let us unite liquid + solid phases into 2 heterogeneous complexes: \(het\) and \(het\). Let us change the masses of equilibrium phases in \(het\) in such way, that the composition of \(het\) and \(het\) in the reduced concentration space will be the same: \(Y(\text{het}) = Y(\text{het})\). One can always do it, because phase compositions are independent. States of \(het\) and \(het\) correspond to different solvent content \(n_1(\text{het}) \neq n_1(\text{het})\). Then, let us remove (evaporate) solvent from more rich complex - \(het\) and make it equal to \(het\). In this process all solution should transfer into the complex of solid phases (eutonics), or should lose \(k\) solid phases (k-type peritotics). As the result, one will get two finitely different states of heterogeneous system, correspond to the same pressure, temperature and components masses. This contradicts to the stability criterion of heterogeneous system relative to the finitely state changes (binodal criterion) [1, 2]. This criterion imposes on the system more stringent restrictions then stability criterion relatively infinitely small state changes (spinodal or diffusional stability criterion). In particular, in the ternary system impossibility of intersection of two nodes liquid-solid (cuts, connecting figurative points of equilibrium phases) for one solid phase at \(T,P=\text{const}\) 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 – \(l\) and \(l\) which are in the equilibrium with the set of solid phases: \(s\), \(s\),...\(s\) 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 \(s\), \(s\),...\(s\) for the first – more high temperature heterogeneous phase complex – \(het\) align the brutto-compositions of both complexes – \(het\) and \(het\) in full concentration space will be the same: \(X(\text{het}) = X(\text{het})\). Then downgrade temperature from \(T_1\) to \(T_2\). In this process \(het\) should transfer into mixture of solid phases (eutectics) or should lose \(k\) solid phases (k-type peritectics).

This also contradicts to the stability criterion of heterogeneous system relative to the finitely state changes.

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 very rare case of transition points of congruent desolvation [congruent polymorph transformation]).

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

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

B) Phases \(s\) and \(s\) have the same composition in reduced [full] concentration space. They are the congruently soluble [melting] compounds. Simplest cases are represented in Fig.5. One should note, that this type of non-variant points 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 the 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 it’s realization (Fig. 5.C, 5.D).
The proof of Lemma II is similar to Lemma I. If in solubility diagram there are two liquid non-variant solutions $I_1$ and $I_2$ which are in the equilibrium with solid phases: $s_1, s_2, ..., s_n$ and composition in reduced concentration of two crystal-solvates coincides: $Y_{1(s_1)} = Y_{1(s_2)}$. If in the reduced concentration space points $I_1$ and $I_2$ lies in the conjunction (cis) hyperplane, passes through solid phases points. Let us form two heterogeneous complexes – het$_1$ (from phases: $I_1, s_1, s_2, ..., s_n$) and het$_2$ (from phases: $I_2, s_1, s_2, ..., s_n$) mixing in different proportions equilibrium phases. 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) of the solvent (if $s_1$ is more reach then $s_2$,) $I_1$ and $I_2$ will have constant composition. As the result, one can get two complexes with the different equilibrium liquids and same state parameters. This also contradicts to the stability criterion of heterogeneous system relative to the finitely state changes.

In the case of solubility diagrams proof is easily. Transition non-variant points should have the same equilibrium temperatures – temperature of polymorph transformation phase $s_1$ into phase $s_2$. So, formation of het$_1$ and het$_2$ by mixing in the different proportions phases: $I_1, s_1, s_2, ..., s_n$ and $I_2, s_1, s_2, ..., s_n$ immediately contradicts to stability criterion of heterogeneous system relative to the finitely state changes.

One can understand, that such consideration can not be applied in the case, if in the reduced concentration space points $I_1$ and $I_2$ lies in the opposition (trans) hyperplane, passes through solid phases points. In this case it is impossible to equilize compositions of heterogeneous complexes, which are 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 [desolvation] (points $T_i^*$ in Fig.5).

Lemma I, II have obvious consequences:

**Consequence I:** Passing through 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 solubility [melt] composition change.

**Consequence II:** In solubility [fusibility] diagram of $(n+1)/n$-component system can not coexist separated elements of phase diagrams, correspond 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 of the obvious this statement, for example in the system $Na_2CO_3-K_2CO_3-H_2O$ at $30^\circ$C authors [17] determined following order of solid phases crystallization: $Na_2CO_3\cdot10H_2O; Na_2CO_3\cdot7H_2O; Na_2CO_3\cdot6H_2O; Na_2CO_3\cdotNa_2CO_3\cdotK_2CO_3; 2K_2CO_3\cdot3H_2O$. This order directly contradict to the both consequences I, II simultaneously.

**Consequence III:** So, in solubility [fusibility] diagram in $(n+1)/n$-component system geometrical element of the crystallization of "new phase" – $S_{new}$ (branch, or surface, or volume, or hyper-volume) may locate in phase diagram by the only one way – replacing specific metastable non-variant point (eutectics-eutonics, peritectics-peritonic), transition points – EPT,$T^{id}$ 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 not applies, of course, to phases of congruent polymorph transformation [desolvation] formation $T_i^*$. Possible and impossible types of "new phases" appearance are represented in Figures 6, 7, 8.
Fig. 6. Some possible (6.A, 6.B, 6.C, 6.D) and impossible (6.E, 6.F) types of "new phases" appearance in fusibility [solubility] diagrams of ternary [binary] systems. Fig. 6.B. corresponds to phase of congruent polymorph transformation [desolvatation] formation (its point is black circle). Dot lines correspond to metastable mono-variant curves, gray circles – to non-variant old and new points.
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).

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

Let us denote: \(R^2\) full number of solid phases, crystallizing in the system; \(R_0^3\) – number of solid phases with different composition in reduced [full] concentration space; \(R_0^3 = R^2 + R_{01}^3\) – number of solid phases with the composition, matching with one of the phases from \(R_{01}^3\). First of all, suppose, that in the system there are no congruent desolvation [polymorph transformation] solid phases: \(R_{01}^3 = 0\). Denote: \(N^0\) – full number of non-variant points; \(N_{01}^3\) – sum number of eutonics-eutectics and peritonic-peritectics; \(N_{01}^3 = N^0 - N_{02}^3\) – sum number of transition points; \(L^3\) – sum number of mono-variant curves. From lemma I, II, consequences I-III and Fig.6. follows, that each new solid phase generates 1 new mono-variant curve and 1 additional non-variant point – Fig.6.A, 6.C. If new solid phase eliminates 1 old solid phase no additional points and curves are generated – Fig.6.D. If new solid phase eliminates 2 old solid phases, 1 old point curve curves is eliminated. In the common case, if formation of \(S_{mon}^3\) solid phase eliminates 2 old non-variant points – \(E,P,T_{01}^2\), then it also eliminates 2-1 mono-variant curves and generates 2 new non-variant points – \(E,P,T_{01}^2\) and 1 mono-variant curves. So total number of generated elements is: \(2^2\) non-variant points and also \(2^2\) mono-variant curves. Such construction is elementary graph theory is named as L-chain [18] with tops are in non-variant points and edges are mono-variant curves. So:

\[
L^3 = R^3 \quad \text{(4.1)},
\]

\[
N^0 = R^3 - 1 \quad \text{(4.2)},
\]

\[
N_{01}^3 = R_0^3 - 1 \quad \text{(4.3)},
\]

\[
N_{11}^3 = R^3 - 1 - (R_{01}^3 - 1) = R^3 \quad \text{(4.4)}.
\]

If in the considered type of the systems there are congruent desolvation [polymorph transformation] solid phases: \(R_{01}^3 \neq 0\), one should divide the diagram into the parts between component and compound or compound1 – compound2 (such reception is often named “diagrams triangulation”). In this case 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 formula on the concrete examples – Fig.9.

**Fig.9. Solubility diagram in ternary system NaCl-CdCl₂-H₂O at 25°C (9.A) and fusibility diagram in binary system V₂O₅-V₂O₅+3Li₂O (9.B) after triangulation of fusibility diagram in binary system V₂O₅-Li₂CO₃ (5.A): gray circles – non-variant points – eutectics-eutonics; E₁ transition points – T₁, black circles – disteectics-distonics. Initial data – from [19, 5], correspondingly.**

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

**System NaCl-CdCl₂-H₂O at 25°C:**

\[ L₁ = R₁ = 4; N₁ = R₁² - 1 = 4 - 1 = 3 (E₁); N₉₂ = R₂ - 1 = 4 - 1 = 3 (E₁); N₁ = R₁² - 1 - (R₁² - 1) = 3 \]

**System V₂O₅-V₂O₅+3Li₂O:**

\[ L₁ = R₁ = 7; N₁ = R₁² - 1 = 7 - 1 = 6 (E₁); N₇₂ = R₂ - 1 = 4 - 1 = 3 (T₁); N₁ = R₁² - 1 - (R₁² - 1) = 6 - 3 = 3 \]

Everything is correct.

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

Let us denote: \( R^f \) – full number of solid phases, crystallizing in the system; \( R^p \) – number of solid phases with different composition in reduced [full] concentration space; \( R^f - R^p \) – number of solid phases with the composition, matching with one of the phases from \( R^p \). Also suppose, that in the system there are no congruent desolvatisation [polymorph transformation] solid phases: \( R^f = 0 \) (remind, that we have not find any one example of diagrams with such phase formation). Denote: \( N_{sar}^d \) – number of surfaces (fields) of single phase crystallization; \( N^d \) – full number of non-variant points; \( N_{ep}^p \) – sum number of eutectics-eutectics and peritontics-peritontics; \( N^d = N^d - N_{ep}^p \) – sum number of transition points; \( L^e \) – sum number of mono-variant curves in concentration simplex in in-mutual systems (Roseboom triangle), \( L^e = 3R^f - 3 \sum N^d \).

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

**Table 3. Number of geometrical elements changes in the case of “new solid phase” formation.**

<table>
<thead>
<tr>
<th>Number of old non-variant points elimination</th>
<th>Number of old mono-variant curves elimination</th>
<th>Number of new non-variant points formation</th>
<th>Number of new mono-variant curves formation</th>
<th>Number of non-variant point change</th>
<th>Number of mono-variant curves change</th>
<th>Figure</th>
</tr>
</thead>
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<tr>
<td>-1</td>
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<td>+3</td>
<td>+3</td>
<td>+2</td>
<td>+3</td>
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</tr>
<tr>
<td>-2</td>
<td>-1</td>
<td>+4</td>
<td>+4</td>
<td>+2</td>
<td>+3</td>
<td>7.B</td>
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<td>+5</td>
<td>+2</td>
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<td>+3</td>
<td>+2</td>
<td>+3</td>
<td>7.F</td>
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<tr>
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<td>+2</td>
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<tr>
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<td>Z+2</td>
<td>Z+3</td>
<td>+2</td>
<td>+3</td>
<td>All possible variants in Fig.7</td>
</tr>
</tbody>
</table>

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

\[ N_{sar}^d = R^f \]

\[ N^d = 2R^f - \sum N^d - 2 \]

\[ N_{ep}^p = 2R^p - \sum N^d - 2 \]

\[ N^d = R^f - 1 - (R^f - 1) = R^f - \sum N^d \]

\[ L^e = 3R^f - 3 \sum N^d \]

Let us show the application of these formula on the concrete examples – Fig.10.
There is minimal number of colors for coloring L-chain to boundary links should have different color. This minimal colors number is equal 2.

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

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 volume structure.

1.1. Phase equilibrium diagrams with solid solutions and liquid-vapor equilibrium

In is interesting to note, that formulas (4.1)-(4.9) may applied successfully also with the systems with solid solutions crystallization, if we shall use van der Waals phase determination. So one should distinguish two phases with the same quantitative composition (for example CoNi\textsubscript{3}SO\textsubscript{4}\textsubscript{2}H\textsubscript{2}O (monoclinic) and CoNi\textsubscript{3}SO\textsubscript{4}\textsubscript{2}H\textsubscript{2}O (rhombic)), because they fundamentally are described by different state equations. Essential condition of the belonging of the set of solid solutions to one phase is 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.

Conclusion

Thus, the authors carried out the most General classification of nonvariant and monovariant equilibria regardless of the components number and the type of phase diagrams.

Заключение

Таким образом, авторами проведена наиболее общая классификация нонвариантных и моновариантных равновесий независимо от компонентности и типа рассматриваемых фазовых диаграмм.

Acknowledges

This work was supported by Russian Foundation for Basic Research – RFBR (Projects №18-08-00143 A, 19-015-00469 A, 19-016-00003 A). Research was performed with using the equipment of the Resource Centers 'GeoModel', Center for Chemical Analysis and Materials Research of Research park of St. Petersburg State University.

Благодарности


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