Novel type of thermodynamically stable phase in complex chemical systems[#]

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Abstract

Interpretation of thermodynamic equilibrium on the basis of graph theory predicts the existence of exotic phases in multicomponent systems with at least three independent components. The difference between normal and exotic states results from the difference in topology of the graph of state. We discuss under what conditions the transformation of the normal phase into the exotic phase can occur in the complex system. The knowledge of such conditions may be of importance for materials chemistry in search for the systems that form stable exotic phases.

Key words: graph theory, thermodynamic equilibrium, quasicrystals

Introduction

For many years different authors suggested the use of planar graphs in thermodynamic equilibria [1-10]. It seems, however, that most of the suggestions were curiosities without any practical consequences. In our recent work [9] we have shown that the use of graphs in description of thermodynamic equilibria can, in simple way, offer new insights, hardly

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[#] This work is to commemorate Professor Henryk Matyja from Warsaw Technical University.

available with the use of standard thermodynamic description. The details can be found in ref [9]; here we present only a brief summary.

0. We consider thermodynamic systems consisting of P phases and C independent constituents. We also assume that simple Gibbs phase rule is obeyed: $f = C - P + 2$, where f is the number of thermodynamic degrees of freedom. Thus we assume that the system is not subjected to any external fields, and the component concentrations are constrained only by the law of mass conservation. Consequently, as in our former work [9], we exclude the thermodynamic states that correspond to azeotropes and, generally, to any congruent transformations.

1. We introduce a two-dimensional surface, Σ, defined by two coordinates that are functions of thermodynamic parameters.

2. We select f points on this surface. Through the imposition of thermodynamic constrictions of the reference state, each of these points has only one degree of freedom.
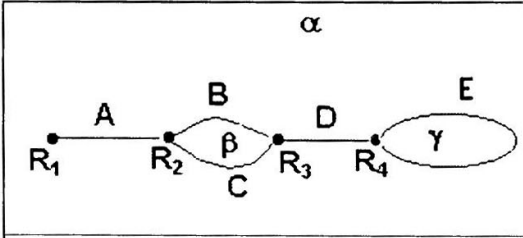

Figure 1: Examples of the graph of state for the three-phase (α, β, γ), five-component (A, B, C, D, E) system. Graph $\mathcal{G}$ is associated with the following distribution of components between the phases: α = (A, B, C, D, E); β = (B, C); γ = (E). For the meaning of R, see text and Table A1.

3. The lines that link the selected points on the surface represent individual independent components of the system. In this way, the lines and points form a planar graph with f vertices and C edges. The sequence of edges enclosing an area on the surface forms the face that represents a phase of the system. The composition of such a phase corresponds to the sequence of edges. Phase transformations in the system can be described by gluing and separating of two graph vertices. It is evident from the above points that we are concerned with planar general graphs that may have multiple loops and edges [5].

An example of the graph of state for the selected system with 5 independent components (A, B, C, D, E) and three phases (α, β, γ) is shown in Fig. 1. We have shown [9] that the graph representation can unequivocally ascribe a planar graph to the state of thermodynamic
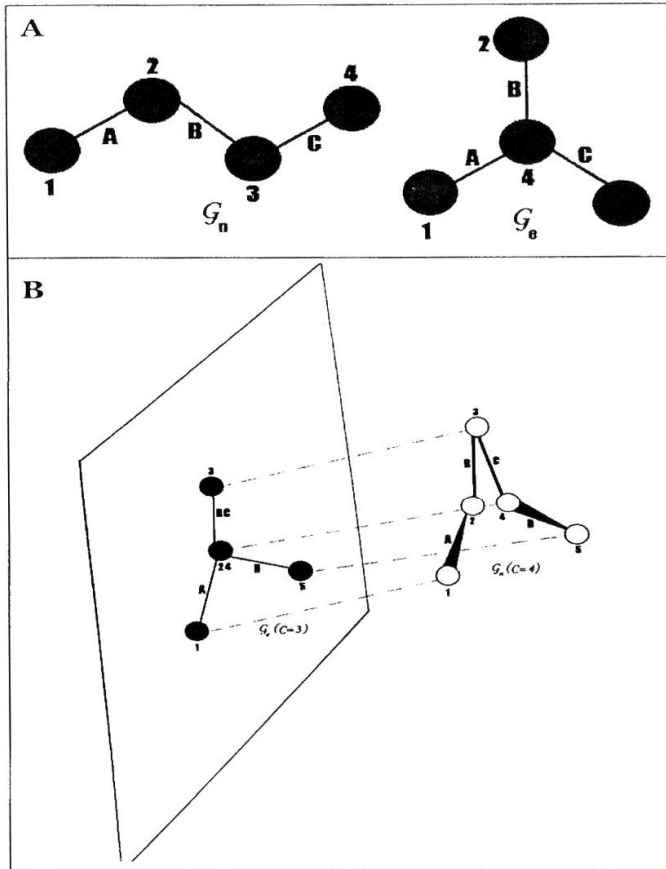
Figure 2: Graphs of state of the one-phase three-component (A, B, C) system. Fig.2A: $\mathcal{G}_n$ graph represents the normal one-phase state of the system; $\mathcal{G}_e$ graph represents the exotic state of the system. Fig. 2B:Projection of the graph for the normal state of four-components system, $\mathcal{G}_n$ (C=4), on the selected two-dimensional surface gives the graph for the exotic state of three-component system, $\mathcal{G}_e$ (C=3).

equilibrium of the system. Individual thermodynamic equilibria can now be enumerated, and allowed types of equilibria can be predicted. Note, that the degree of complexity of the system

does not affect critically the determination of the number and type of equilibria in the system. All one-phase state equilibria in the system with C independent components can be represented by a C-edge tree. At $C = 1$ or $C = 2$ such a tree will, of necessity, be a nonbranched tree. The state represented by such graphs can be called normal. Starting from C = 3, exotic states, represented by the branched trees and unavailable in simpler systems, may appear in the system. Examples of the graph of state for all the types of one-phase equilibria in a three-component system are shown in Fig. 2A.

Note that from geometrical point of view the graph for exotic state can be treated as a projection on the two-dimensional surface of a certain graph for the normal state of the four-component system. Consequently, two edges (B, C) and two vertices (2,4) of the graph degenerate into one edge (BC) and one vertex (24), as can be seen in Fig. 2B. Generally, the graphs for exotic states are formed by projection of the graphs for normal states in a multidimensional space. It can be argued that the thermodynamically stable quasicrystals [11-14] are the exotic states consistent with our representation. Quasicrystals were discovered in 1984 by Shechtman and his coworkers [11]. A 5-fold symmetry such a quasicrystal is forming in Al-Mn alloy is forbidden for crystal lattices in the three-dimensional space. However, it is allowed for crystal lattices in the n-dimensional space $(n > 3)$ [12]. A projection of such crystals onto the usual three-dimensional space gives a structure that has no three-dimensional translation periodicity, characteristic for normal crystals, but has other symmetry elements forbidden for normal crystals, eg. 5-fold axis. Quasicrystals obtained by Shechtman et al. by rapid cooling of the Al-Mn alloy were found to be thermodynamically meta-stable [12]. Since this pioneering work many other stable and meta-stable quasicrystals were found. While two-component quasicrystals such as Al-TM (TM = Ir, Pt, Os, Ru, Rh, Mn, Fe, Co, Ni, Cr); Mn-Si; Cr-Ni; V-Ni obtained in different laboratories are meta-stable [14], addition of the third and consecutive components usually results in thermodynamic stabilization of the system, yielding stable quasicrystals such as Al-Ni-Co; Al–Cu-Co; Al-Cu-Co-Si; Al-Mn-Pd; Al-Li-Cu; Al-Pd-Mn; Zn-Mg-RE (RE = La, Ce, Nd, Sm, Gd, Dy, Y) [14]. Up to 2000 all known stable quasicrystals contained at least 3 components. In this year Tsai et al. [16,17] reported the formation of stable quasicrystals in binary alloys: $Cd_{5.7}Yb$ and $Cd_{17}Ca_3$. These quasicrystals were obtained by congruent solidification, while most ternary and quaternary quasicrystals were obtained in non-congruent transformations. Lograsso [18] obtained $Cd_{5.7}Yb$ quasicrystal in macroscopic amounts, ~0.75 cm^3, using very pure components (Cd –
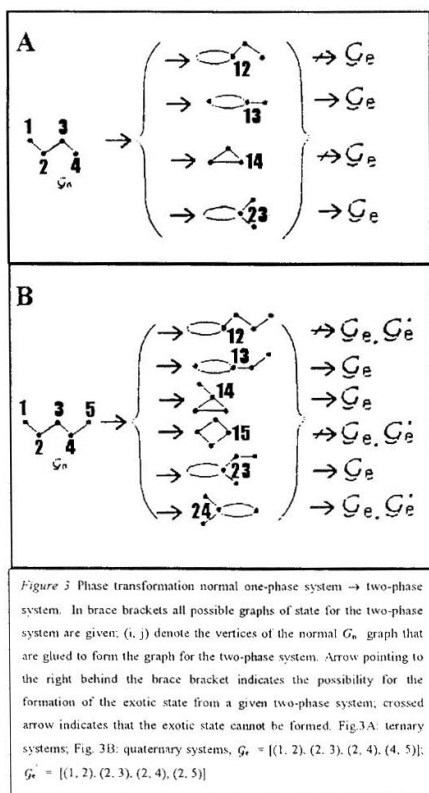
99.99%, Yb – 99.9%). Trace contaminants were inevitably present, however. The role of such contaminants in stabilization is unknown. Since 2000, no other stable binary quasicrystals were obtained. It looks as though the Tsai's discovery invalidates a paradigm on the role of three components in the stabilization of quasicrystals. We still believe that only at least three-component systems are capable of forming stable quasicrystals. Exceptional are only such two-component systems that feature equilibrium points for congruent transformations on the phase diagram. Equilibrium for such points cannot be represented by a planar graph on the Σ surface [9]. Instead, the Gibbs phase rule in a more general form has to be used: $f = C - P + 2 - q$, where q is the number of relations between the component concentrations in individual phases (for a simple congruent equilibrium $q = 1$). The problem of graph representation for such states is not solved so far.

This way quasicrystalline state of matter can be placed in usual phenomenological equilibrium thermodynamics. In such thermodynamics equilibrium for the system is described as an extreme for certain thermodynamic function $G(\chi_1, \chi_2, \chi_3, ..., \chi_f)$, where χ_i are the thermodynamic parameters. On the basis of the Gibbs phase rule this function can be given in the form: $G(a_1(R_i, R_j), a_2(R_k, R_l), ..., a_C(R_m, R_n))$, where R_i is the point on the two-dimensional surface isomorphic with the surface of a sphere, described by $\Sigma = R_i(\chi_1, \chi_2, \chi_3, ..., \chi_f)$, $i=1,2$ [9]. Each of the state functions defined this way can be represented by a graph. For instance, the graph shown in Fig. 1 corresponds to the state function given in **Appendix**. The number of non-isomorphic graphs of state for a given thermodynamic state corresponds to the number of topologically different equilibrium states in the system. A state for the one-phase system with one or two independent components can be represented by only one tree, with one or two edges, respectively. As the number of independent components increases to three, two topologically different equilibrium states become available: the first state is represented on the Σ surface by a non-branched tree, while the second one by a branched tree. It seems natural to assume that the first tree represents the typical state characteristic for one- or two-component systems, i.e. the crystalline state. However, the branched tree can only appear for at least three-component systems and represents the quasicrystalline state. Such an assignment is consistent with the fact that the branched tree on the two-dimensional surface can be obtained by a projection of the non-branched graph from the three- or higher dimensional space. In a similar way crystals from the n-dimensional space (n > 3) can be projected to give quasicrystals in the three-dimensional space [12].

It seems that only graph representation of equilibria states can rationalize the existence of stable quasicrystals, and to find for them a proper location within the frame of phenomenological thermodynamics. A question now arises, which complex thermodynamic normal states can be transformed into exotic states. The answer is of obvious interest for materials chemistry searching for new stable quasicrystals.

Phenomenological thermodynamics of the transformation:

"normal state" → "exotic state"

Figure 3 Phase transformation normal one-phase system → two-phase system. In brace brackets all possible graphs of state for the two-phase system are given; (i, j) denote the vertices of the normal G_n graph that are glued to form the graph for the two-phase system. Arrow pointing to the right behind the brace bracket indicates the possibility for the formation of the exotic state from a given two-phase system; crossed arrow indicates that the exotic state cannot be formed. Fig.3A: ternary systems; Fig. 3B: quaternary systems, $G_e = [(1, 2), (2, 3), (2, 4), (4, 5)]$; $G_e^* = [(1, 2), (2, 3), (2, 4), (2, 5)]$

Since phenomenological approach is on the macroscopic level, we cannot establish at what values of temperature, pressure, composition, rate of cooling etc. the transformation of a normal state into exotic state occurs. However, we can pinpoint the general features of the system that indicate the possibility of such transformation.

In agreement with graph representation of equilibria, the state phase transformations are described either by gluing of two or more vertices of the graph of state or by separating the glued vertices. Transformations of interest in this work must involve at least three independent components because branched graphs can exist only for such systems.

Thus, we can formulate the first intrinsic feature of the systems that can exist as exotic states.

1. All thermodynamic states whose normal stable phase can be transformed into exotic stable phase possess at least three independent components.

A phase transformation „one-phase x system" → „one-phase y system" must involve the two-phase system as an intermediáte. All possible channels for the transformation of the one-phase system in the normal state (G_n graph of state) into the two-phase system are shown in Fig. 3 for $C = 3$ (Fig. 3A) and $C = 4$ (Fig. 3B). It is seen that, topologically, the one-phase normal state at $C = 3$ can be transformed into four different types of the two-phase system, while at $C = 4$ the number of such transformátions increases to six. The change in thermodynamic parameters can either transform the two-phase system back into the normal one-phase system or transform it into ·the one-phase exotic system, represented by the respective branched tree (G_e or $G_e^{'}$). It can be seen in Fig. 3 that, at both $C = 3$ and $C = 4$, there are only two types of two-phase equilibria that cannot be transformed into the one-phase exotic states. In the first system both phases contain all components (we will henceforth denote as [n]+[m] a system containing „n" components in one phase and „m" components in another). Another non-transformable type belongs, according to our notation, to [C]+[1] series – while one phase contains all components, the second one contains only one component. Inspection of the topology of the graph of state leads to the following conclusion.

2. One-phase exotic states can exist in the system for the following types of two-phase equilibria: [C]+[1], [C]+[2], [C]+[3], ..., [C]+[C-1], where C≥3. The two-phase equilibria [C]+[C] and some types of [C]+[1] equilibria preclude the existence of exotic states. The latter statement requires some comments. We will use the four-component system as an example. If a crystal of such a system (i.e. a normal state) melts, and a liquid contains all four components, the two-phase system that is being formed belongs to the [4]+[4] type, and the transformation into the exotic state is excluded (see Fig. 3B). The situation of the two-phase system [4]+[1] is less clear. Such an equilibrium is represented by the first and fifth graphs in brace brackets in Fig. 3B. While the first graph cannot be transformed into a graph of exotic state by taking apart glued vertices, the fifth graph can. A number of two-phase [C]+[1] equilibria transformable into exotic states increases as C increases. While at $C≤5$ there is only one such equilibrium, there are two at $C=6$, and three at $C=7$. Thus, only in [C]+[C] equilibrium is the existence of exotic phases rigorously forbidden. In other systems, representing probably a sizable majority of all available systems, exotic states are likely to be

formed under suitable thermodynamic conditions. However, little can be said about such conditions on the grounds of phenomenological thermodynamics.

Conclusions

Complex thermodynamic systems, containing at least three independent components and described by the two-phase equilibrium of the type [C]+[C-k], where k = 1, 2....C-1, can exist as exotic states (i.e. quasicrystals) that differ by the topology of the graph of state from the normal states (i.e. crystals).

Appendix

Table A1. Explanation of symbols and definitions

	Symbols used in phenomenological thermodynamics	Symbols for thermodynamics using graph theory
Degree of freedom	f	f
Pressure, temperature	p,T	p,T
Concentration of the ith component	c_i	c_i
Number of independent components	C	C
i^{th} thermodynamic parameter	$\chi_i \in (p,T,c_1, c_2,...,c_C)$	$\chi_i \in (p,T,c_1, c_2,...,c_C)$
Magnitude for the ith parameter in the reference state	$\chi_i^{\circ} \in (p^{\circ},T^{\circ},c_1^{\circ}, c_2^{\circ},...,c_C^{\circ})$	$\chi_i^{\circ} \in (p^{\circ},T^{\circ},c_1^{\circ}, c_2^{\circ},...,c_C^{\circ})$
Two-dimensional surface in the space of thermodynamic parameters	-	$\Sigma = R_i(\chi_1, \chi_2, \chi_3, ..., \chi_f)$, i=1,2
k^{th} point on the Σ surface (vertix for the graph of state)	-	$R_k = (\chi_1^{\circ}, \chi_2^{\circ},..., \chi_{k-1}^{\circ}, \chi_k, \chi_{k+1}^{\circ}, ..., \chi_f^{\circ})$
Arguments for the state function	$\chi_1, \chi_2, \chi_3, ..., \chi_f$	$R_1, R_2, ..., R_f$
State function, G	$G(\chi_1, \chi_2, \chi_3, ..., \chi_f)$	$G (a_1(R_i,R_j), a_2(R_k, R_l), ..., a_C(R_m,R_n))$
Example of the state function for the graph of state from Fig.1	$G(A(R_1, R_2), B(R_2,R_3), C(R_2,R_3), D(R_3,R_4), E(R_4,R_4))$	
Graph of state from Fig.1 at $R_2 \rightarrow R_3$ (gluing of vertices in R_{23} as a result of change in thermodynamic parameters)	$G(A(R_1, R_{23}), B(R_{23},R_{23}), C(R_{23},R_{23}), D(R_{23},R_4), E(R_4,R_4))$	

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