

Use of Graph Theory in Thermodynamics of Phase Equilibria

Jan Turulski[†] and Jan Niedzielski^{*,‡}

16-035 Czarna Wies Kościelna, ul.Cicha 18, Poland, Chemistry Institute, University at Białystok,
15-443 Białystok, al. Pilsudskiego 11/4, Poland, and Chemistry Department, Warsaw University,
02-089 Warsaw, Poland

Received July 3, 2001

A concept to use graph theory for the description of phase equilibria is developed. It is shown that a specific planar graph, called the graph of state, corresponds unequivocally to a specific state of phase equilibrium. Hence, the involved problem of enumeration of different states equilibria in complex systems is simplified to the problem of enumeration of graphs of the specified type. One-phase systems with three independent components can exist in two forms, normal and exotic; while the normal form is of course known also for systems with 1 and 2 components, the exotic form can only exist if the number of components is 3 or more. It can be speculated that stable quasicrystals represent such an exotic form. Assuming the occurrence of all of the thermodynamically allowed processes, the number of one-phase exotic states in systems that consist of tens of bioelements can, intuitively, be used as a measure of Earth's biodiversity.

1. INTRODUCTION

A condition for thermodynamic equilibrium in the system with C independent components and P phases is equality of chemical potentials, $\mu_i^{(j)}$, for the i th component ($i = 1, 2, \dots, C$) in the individual phases ($j = 1, 2, \dots, P$).

$$\mu_i^{(1)} = \mu_i^{(2)} = \dots = \mu_i^{(P)} \quad (1)$$

where $i = 1, 2, \dots, C$.

This set of equations leads to the well-known Gibbs phase rule¹

$$f = C - P + 2 \quad (2)$$

where f , C , and P denote respectively the number of phases, components of the system in equilibrium between phases, and degrees of freedom. Many authors have noticed a striking similarity between eq 2 and the famous Euler's formula,² giving a fundamental relationship between vertices (V), edges (E), and faces (F) of a simple polyhedron and generally of a planar graph on the surface topologically isomorphic with a two-dimensional sphere³ (henceforth called 2-sphere).

$$F = E - V + 2 \quad (3)$$

For at least half a century many scientists endeavored to use graph theory not only to clarify such special problems as enumeration of chemical compounds and quantitative structure–activity relationships (QSAR) but also to develop broad generalizations useful for quantum and physical chemistry as a whole.^{2,4} Many of them^{5–11} were intrigued by the consequences for physical chemistry of the correspondence $f \leftrightarrow F$, $C \leftrightarrow E$, and $P \leftrightarrow V$. Despite considerable ingenuity the problem has never been solved, and the exact connection between the Euler formula and the Gibbs phase

rule remains to be established. Some investigators even assert that any coincidence is purely accidental. For instance, Weinhold¹² has shown that particular relationships suggested by Mindel⁹ to prove the correspondence between variables in eqs 2 and 3 are unacceptable.

It is strange that most of the physicochemical interpretations of eq 3 put emphasis on the dependencies between the properties of simple polyhedra rather than the properties of graphs. Even though every simple polyhedron can be represented by a graph, it seems that interpretation of the Euler formula on the basis of graph theory, i.e., on the basis of relations between vertices, edges, and faces of a planar graph on the surface isomorphic with a 2-sphere, will be more fruitful.

Another feature of all reasonable attempts made so far to establish connection between eqs 2 and 3 is inherent assumption of the correspondence $f \leftrightarrow F$ and $P \leftrightarrow V$. Note that the similarity is also conserved under the assumption of the correspondence $f \leftrightarrow V$ and $P \leftrightarrow F$.

The aim of this work is to interpret the Gibbs phase rule using graph theory. Every state of thermodynamic equilibrium will be represented by a planar graph on the surface isomorphic with a 2-sphere. The vertices (V) are assumed to represent the thermodynamic degrees of freedom (f), the edges (E), the individual independent components ($i = 1, 2, \dots, C$), and the faces (F), the phases of the system ($j = 1, 2, \dots, P$). Only such state equilibria are considered that can be described by the simplest version of the phase rule. We exclude such states for which additional conditions are imposed on the thermodynamic equilibrium. For instance, azeotropy that involves equality of concentrations between the phases will not be considered.

2. THEORY

(a) Assumptions. Assumption 1. p , T , c_1 , c_2 , ..., and c_n define the thermodynamic parameters (pressure, temperature, and concentrations of independent components) that char-

* Corresponding author phone:

[†] 16-035 Czarna Wies Kościelna and University at Białystok.

[‡] Warsaw University.

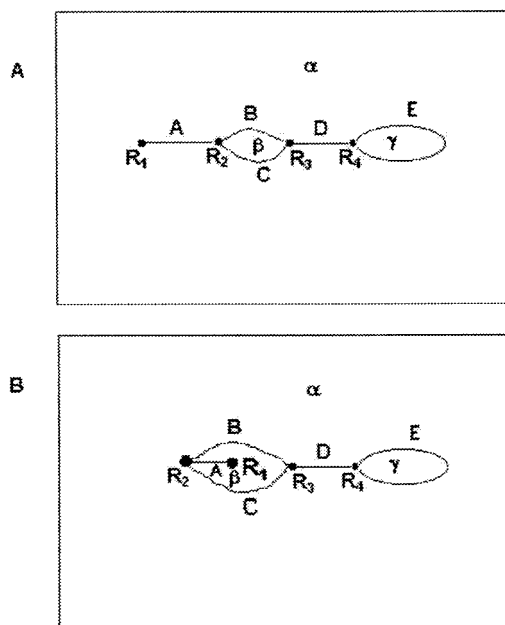


Figure 1. Examples of the graphs of state for the three-phase (α, β, γ) five-component ($A-E$) system. (A) Graph G is associated with the following distribution of components between the phases: $\alpha = (A, B, C, D, E)$; $\beta = (B, C)$; $\gamma = (E)$. (B) Graph G' is isomorphic with graph G : $\alpha = (B, C, D, E)$; $\beta = (A, B, C)$; $\gamma = (E)$.

acterize the equilibrium state of the system. The superscript “o” on the right side describes the values for these parameters in some reference state (i.e. standard state).

Assumption 2. The \hat{R} function defines the surface isomorphic with a 2-sphere:

$$\hat{R} = \left\{ \begin{array}{l} X = X(p, T, c_1, c_2, \dots, c_C) \\ Y = Y(p, T, c_1, c_2, \dots, c_C) \end{array} \right\} \quad (4)$$

Here (X, Y) are coordinates on this 2-sphere, similar to (Θ, φ) that define spherical coordinates on the usual sphere surface.

Assumption 3. R_1, R_2, \dots, R_f are the points on the R surface defined in the following way: R_k is formed by the replacement of all of the thermodynamic parameters, except for the k th parameter, by their values in the reference state:

$$R_1 = \left\{ \begin{array}{l} X = X(p, T^\circ, c_1^\circ, c_2^\circ, \dots, c_C^\circ) \\ Y = Y(p, T^\circ, c_1^\circ, c_2^\circ, \dots, c_C^\circ) \end{array} \right\}, \dots, \\ R_3 = \left\{ \begin{array}{l} X = X(p^\circ, T^\circ, c_1^\circ, c_2^\circ, \dots, c_C^\circ) \\ Y = Y(p^\circ, T^\circ, c_1^\circ, c_2^\circ, \dots, c_C^\circ) \end{array} \right\}, \dots \quad (5)$$

Assumption 4. G is the thermodynamic function defined on the 2-sphere. The values for G in the equilibrium state are described by the thermodynamic parameters through R_1, R_2, \dots, R_f :

$$G = G(R_1, R_2, \dots, R_f) \quad (6)$$

(b) Interpretation and Consequences. According to the phase rule (eq 2), G can be represented by a planar graph G on the surface (eq 4). Henceforth this graph will be called the graph of state. An example of the graph of state for the three-phase (phases α, β, γ) and the five-component system (independent components $A-E$) is shown in Figure 1. Graph vertices represent degrees of freedom. As a rule, the R_k vertices on the surface isomorphic with a 2-sphere should

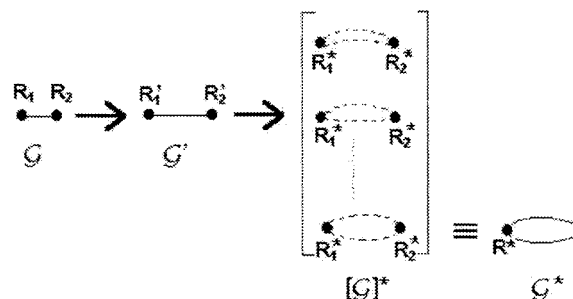


Figure 2. Transformation of graph G into graph G^* describing phase transformation of a one-component system into two-phases system.

feature two degrees of freedom. However, under our formalism, restrictions of the standard state are imposed on every vertex, which decreases the number of degrees of freedom to one per every vertex. Note that rigid determination of all the thermodynamic parameters for R_k results in vertices that have zero degrees of freedom. Two vertices joined by an edge, R_k and R_l , represent an independent component of the system. For instance, according to Figure 1, $A = (R_1, R_2)$, $B = (R_2, R_3)$, etc. A face of the graph limited by the sequence of A, B, C, \dots edges is interpreted as a phase formed by the A, B, C, \dots components. In Figure 1A all of the components form the α phase, B and C form the β phase, and only E forms the γ phase. In other words, a Φ phase is formed by the components whose edges are immersed in the Φ face. Note that two isomorphic graphs can represent different division of components between phases. For instance, the G graph in Figure 1A is isomorphic with another graph obtained by immersion of the A edge in the B phase (Figure 1B). The individual phases of such a system are formed by the following components: $\alpha = (B, C, D, E)$, $\beta = (A, B, C)$, $\gamma = (E)$. Using graph representation of thermodynamic equilibrium described above, it can be asserted that modification of thermodynamic parameters that does not result in the formation of new phases can be interpreted as the transformation of the G graph into the G' graph, isomorphic with G . Any difference between the two graphs resolves itself into the difference between the lengths of edges. Consequently, the $G \Rightarrow G'$ transformation can be realized using two different ways:

- (i) The distances between the R_1, R_2, \dots, R_f vertices joined by the edges are all minimized.
- (ii) At least two vertices are joined by the edge whose length on the surface (eq 4) is not minimal.

Intuitively, the first case corresponds to the equilibrium transformation and the second to the nonequilibrium one. In this work we are concerned with transformations involving equilibrium. Thus we assume that all of the G graph edges on the surface (eq 4) are at a minimum; i.e., the lines are the geodesic lines.

Let us consider an example of the transformation that occurs in the one-phase, one-component system shown in Figure 2. It is seen that, under the condition of equilibrium transformation, the length of geodesic line that links R_1 and R_2 increases until both the vertices attain the locations R_1^* and R_2^* . Under such condition there are at least two geodesic lines of the same length that link the vertices; see the $[G]^*$ graph in Figure 2. A one-component system will be represented by such a graph belonging to the set of $[G]^*$

graphs, which is characterized by smooth transition of one edge into another at one of the vertices. This graph consists of one loop and one vertex, for example R^* , and represents a two-phase state of the system. Therefore, the phase transformation in the system is interpreted by the gluing of vertices in the graph of state.

The location of R^* on the surface (eq 4) deserves some attention. Note that $G(R_1, R_2)$ in the point of phase transformation is in fact a function of only one variable $G = G(R^*)$. According to the definition of R we obtain

$$G(R^*) = G_a(X^*, Y^*) + iG_b(X^*, Y^*) \quad (7)$$

The differential for $G(R^*)$ can be given in the form

$$dG(R^*) = \left(\frac{\partial G_a}{\partial X^*}\right)dX^* + i\left(\frac{\partial G_b}{\partial X^*}\right)dX^* - i\left(\frac{\partial G_a}{\partial Y^*}\right)dY^* + \left(\frac{\partial G_b}{\partial Y^*}\right)dY^* \quad (8)$$

The following relationships ensue:

$$\begin{cases} \frac{dX^*}{dY^*} = \omega \\ \frac{dX^*}{dY^*} = -\omega' \end{cases} \quad (9)$$

Here

$$\begin{cases} \omega = \left(\frac{\partial G_b}{\partial Y^*}\right) / \left(\frac{\partial G_a}{\partial X^*}\right) \\ \omega' = \left(\frac{\partial G_a}{\partial Y^*}\right) / \left(\frac{\partial G_b}{\partial X^*}\right) \end{cases} \quad (10)$$

Note that dX^* and dY^* can also be written in the form

$$\begin{cases} dX^* = X_p^* dp + X_T^* dT \\ dY^* = Y_p^* dp + Y_T^* dT \end{cases} \quad (11)$$

where the symbols with the subscripts stand for the derivatives; i.e., $X_T^* = (\partial X^* / \partial T)$. Substitution from eq 11 into eq 9 gives the following dependence of pressure on temperature in the point of gluing the graph vertices, i.e., in the point of phase transformation in a one-component system:

$$\frac{dp}{dT} = -\frac{X_T^* - \omega Y_T^*}{X_p^* - \omega Y_p^*} \quad (12)$$

A comparison with the Clausius–Clapeyron equation^{13,14} indicates that $\omega = 1$ ($\omega' = -1$) in equilibrium transformations. Moreover, the X and Y functions are proportional to the Gibbs potentials, g_α and g_β , of the corresponding phases

$$\begin{cases} X = ag_\alpha + b \\ Y = ag_\beta + b \end{cases} \quad (13)$$

where a and b are constants. Obviously, eq 13 defines the 2-sphere for the one-component systems. The form of equations for such surface for the systems with $C > 1$ is the subject of investigations.

We can now summarize the conclusions that can be derived upon examination of eqs 9–14.

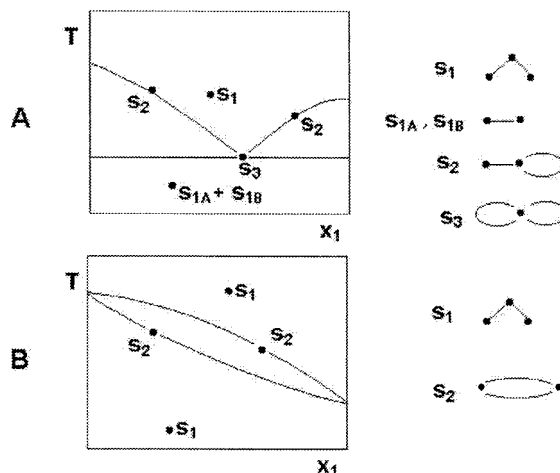


Figure 3. Phase diagram temperature (T) vs concentration (x_1) for two-component systems and the corresponding graphs of state on the right side: (A) nonmiscible components in one of the phases; (B) perfect miscibility of components in both phases.

Gluing the vertices of the graph of state that corresponds to the formation of a new phase in the system occurs in the point R^* falling on the $Y = X$ line. Such a conclusion is based on eq 9 under condition $\omega = 1$. This conclusion is tantamount to the equality of the Gibbs potentials for both phases (see eq 13). In thermodynamics such equality is a well-known condition for equilibrium in one-component system with two phases.

It is easily seen that conditions $\omega = 1$ and $\omega' = -1$ lead to the following differential equations fulfilled by the real and imaginary parts of $G(R^*)$:

$$\left(\frac{\partial^2}{\partial X^{*2}} + \frac{\partial^2}{\partial Y^{*2}}\right)G_z = 0 \quad (14)$$

$$z = a, b$$

The solutions of eq 14 are G_v and G_w functions shown as

$$\begin{cases} G_v = (a_1 e^{\beta X^*} + a_2 e^{-\beta X^*}) \cos(\beta Y^*) \\ G_w = (a_1 e^{\beta Y^*} + a_2 e^{-\beta Y^*}) \cos(\beta X^*) \end{cases} \quad (15)$$

$$v = a, b$$

$$w = b, a$$

where a_1 , a_2 , and β are constants.

Since an arbitrarily small area of the 2-spheric surface behaves as a Euclid surface, $|G(R^*)| = (G_a^2 + G_b^2)^{1/2}$ at $R^* \rightarrow 0$ should be proportional to $|R^*|$, because the length of the closed line on the Euclid surface is proportional to the radius. Hence, $a_1 = -a_2$. Taking into account that at R^* the equality $X^* = Y^*$ is obeyed, we obtain the following expression for the function that describes a graph for the two-phase system:

$$G(R^*) = a \sinh(\beta X^*) \cos(\beta X^*) (1 + i) \quad (16)$$

So far only one-component systems were considered. We now turn to two-component model systems (A and B components are quantized by x_1 and x_2 , respectively). Figure 3 shows two kinds of model phase diagrams $T = f(x_1)$. S_1 (S_{1A} , S_{1B}), S_2 , and S_3 correspond to one- (with the components

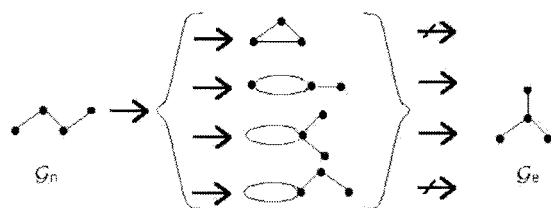


Figure 4. Transformation of graph G_n into graph G_e describing thermodynamic phase transformation (one-phase \rightleftharpoons two-phase) in the normal (n) and exotic (e) state. Crossed arrows indicate the processes do not occur.

AB, A, or B), two-, and three-phase systems, respectively. The pertinent graphs of state are shown on the right side of the corresponding diagram. While only one graph of state exists for the one-phase system, two nonisomorphic graphs of states exist for the two-phase system. The first one corresponds to equilibrium in the system, which involves components perfectly miscible in both phases; the second one involves nonmiscible components. It means that graphs of state can differentiate between fundamentally different states of the systems. It is a very valuable property that can be used for enumeration of the states that are fundamentally different in involved systems. By fundamental difference we mean a difference that is not caused by geometry of the system, as investigated by crystallography. Fundamental difference is caused by differences in topology of the graph of state and, consequently, by differences in the form of dependence of $G(R_1, R_2, \dots, R_f)$ on variables. At first sight it may look as though the graph theory cannot contribute much to physical chemistry or, strictly, to thermodynamic equilibria in two-phase two-component systems. Indeed, it has been established by thermodynamics for a very long time that two different types of states occur in such systems. However, at a larger number of independent components insurmountable difficulties emerge. Thermodynamics can tackle, although with considerable difficulty, three- or even four-component systems. The task becomes too involved if the number of components exceeds 4. The graph theory, as developed in this work to describe states in equilibrium, can manage such a task fairly easily. A construction of flat nonisomorphic graphs with f vertices is not difficult unless the number of vertices becomes too large. Hence, existence of the specific types of state equilibria can be predicted for the systems with many components.

The use of graph representation of equilibrium states to enumerate topologically different equilibrium states in the multicomponent systems with $C \leq 4$ is shown in Figure 4. As said before, enumeration of different types of state equilibria in multicomponent systems is a serious problem in phenomenological thermodynamics. The application of graph representation makes the task easier. The problem resolves itself into enumeration of the nonisomorphic graphs of certain type. For some graphs a solution is known. If not, practical construction of graphs can offer a partial solution. We adopted this method preparing Figure 4. It is seen that for two-phase systems at $C = 2$ there are two different graphs; this number increases to 4 at $C = 3$ and to 9 at $C = 4$. For three-phase systems, while there are no topologically different graphs at $C = 2$, there are 4 at $C = 3$ and as many as 12 at $C = 4$. Strangely enough, one-phase systems with at least three independent components should exist in two topologically different forms. For simple systems ($C \leq 2$),

$C \backslash P$	1	2	3	4	5
1					
2					
3					
4	3	9	12	6	1

Figure 5. Examples of graphs of state for C -component, P -phase systems. For $C = 4$ only the number of graphs is given.

such a phenomenon cannot occur. At $C = 3$ the system can exist in a state that is represented by a nonbranched tree with 4 vertices or in a completely different state represented by a branched tree also with 4 vertices. Since the graph of the first type seems to be the usual generalization of the graphs characteristic for one- or two-component systems, it is natural to call such graphs normal, reserving the name exotic for the other graphs. It should be emphasized once more that the difference between normal and exotic graphs does not stem from different geometry; these graphs do not represent different crystallographic forms (i.e. different allotropic or polymorphic forms). Note that some systems in the normal state can be transformed into the exotic state, as is visualized in Figure 5. The normal one-phase system (for instance, a crystal), represented by the G_n graph, can be transformed into a two-phase system (crystal-liquid) under some conditions. Some of such two-phase systems can, under suitable conditions, be transformed into the exotic one-phase systems. However, not every normal system can be transformed into an exotic one. As shown in Figure 5, such transformation is not possible if all three components are perfectly miscible in both phases (such a two-component system is represented by the cyclic, triangular graph with three vertices). Similarly, a two-phase system whose one phase consists exclusively of one component (this state is represented by the last of two-phase graphs in Figure 5) is also nontransformable. To sum up, the normal systems that feature $\alpha = (A,B,C)$ and $\beta = (A,B,C)$ as well as some of the normal states that feature $\alpha = (A,B,C)$ and $\beta = (A)$ cannot undergo transformations into exotic systems.

A question of the reality of exotic thermodynamic systems remains to be answered. It may be argued, however, that quasicrystals, discovered in 1984 by Shechtman and his group,^{15,16} belong to this class. First, quasicrystals can only be formed in multicomponent systems. Even though many two-component quasicrystals have been obtained, they are all unstable.^{17,18} So far, only three- and multicomponent quasicrystals exhibit stability, in agreement with the appearance of exotic states only if the number of components exceeds 2. Second, addition of the third component leads frequently to the quasicrystal stabilization.¹⁸ Third, stable quasicrystals can be formed only in some multicomponent systems which agrees with the conclusion deduced from







C	1	2	3	4	5	6	9	17	30	50
\mathcal{G}										
η	1	1	2	3	6	11	106	123867	$5.27 \cdot 10^8$	$3.68 \cdot 10^{19}$

Figure 6. Graphs of state for one-phase C -component systems. η indicates the number of nonisomorphic graphs for given C .

Figure 5 that exotic states cannot be formed from all of the normal states. Component miscibility seems to be a decisive factor in the formation of exotic states postulated in this work. Unfortunately, as far as we know, laboratories engaged in quasicrystal synthesis have not studied the effects of mutual miscibility of components in both phases on the formation of quasicrystals. Further investigations are needed to settle the question that quasicrystals can be represented by the branched tree graphs of state called the exotic systems in this work. The results of such investigations notwithstanding, note that the number of states for one-phase systems increases dramatically with the number of independent components, C . The number of graphs is shown in Figure 6 for some selected C ; for C not too large the forms of the graphs are also given. The number of trees up to $C = 79$ can be found in a monograph by Knop et al.²⁰ It can be shown¹⁹ that the number of graphs, η , asymptotically obeys the following relationship:

$$\eta \approx 0.5349485 \frac{d^{-(C-1)}}{(C-1)^{5/2}} \quad (17)$$

where $d = 0.338\,321\,9$. Exponential increase in the number of exotic states with the number of components suggests that in systems with tens of components, exotic states may in fact predominate over the normal states. There the difference between the normality and exoticity becomes blurred. The exotic states should become normal for the multicomponent systems, representing the normal, widespread state of existence. If so, where can such exotic forms be found? To find an answer we turn our attention to biological systems.

Note that the number of independent components can usually be estimated from²¹

$$C = N - r - Z \quad (18)$$

where N is the number of chemical species (or components), r is the number of independent reactions in the system, and Z is the number of constrained conditions other than Σ (mole fraction of the component) = 1. In our approach Z is always zero; we do not account for equilibria in the systems with additional conditions imposed, for instance, on concentra-

tions. As shown by Brinkley,²² C can be expressed by the number of elements in the system, M .

$$C = M + r' - Z \quad (19)$$

where r' is the number of independent reactions that do not occur due to kinetic restrictions. In very involved multicomponent systems, in which all the reactions allowed kinetically ($r' = 0$) occur under equilibrium conditions, C is determined by the number of elements that form the system.²¹ Thus, the number of different equilibrium states depends on M . Specifically, if the number of elements is large, the number of available one-phase systems is given by (17). According to Emsley,²³ there are at least 26 but probably 29 elements that are important biochemically (the role of such element as Al is dubious). We can round this number up to 30, including the electron, on the assumption that redox reactions occur in living organisms. As shown by Knop et al.,²⁰ in systems composed of 30 elements, no matter what is the number of different molecules, there are 4.03×10^{10} different one-phase systems, irrespective of the number of components (the number of different molecules). It is tempting to speculate that this number has something to do with biological diversity of the biosphere, determined by the number of biological species, extinct and extant. There are different estimations of this number. It is currently accepted that the number of organisms actually living on Earth does not exceed tens of millions, up to about 8×10^7 .^{24,25} Mass extinctions of much of the life on Earth have occurred a number of times during the Paleozoic and Mesozoic eras and subsequently. These events are probably related to either bolide impacts or volcanic eruptions or both. Some involved losses of 50% or more of the observed families. Thus, the full number of species that ever lived on Earth may be reasonably estimated on the order of billions in fairly good agreement with the number of states in 30-element systems in which all the allowed reactions are assumed to occur.

We are of course aware that the living organism, a heterogeneous and nonequilibrated space-time-ordered open system,²⁶ bears little resemblance to the state of thermodynamic equilibrium in a multicomponent system. However, graphs have been remarkably successful in enumerations in

very disparate fields. Perhaps also the enumeration suggested in this work is more than playing with numbers. Nonequilibrium systems in living species evolve under thermodynamic forces in sensu largo. New species formed as a result of evolution can indeed be represented by suitable types of the graph of state (obviously, the edges of this graph are no longer the geodesic lines). If such a graph of a nonequilibrium state is isomorphic with some graph of exotic equilibria in complex systems, the problem of biological diversity is resolved easily by estimation of the number of thermodynamic equilibria in systems containing about 30 biochemical elements, assuming the occurrence of all kinetically allowed reactions.

While the correspondence between nonequilibrium and equilibrium graphs for the systems not far distant from equilibrium seems to be well justified, it is not so for the living organisms which are certainly very far from equilibrium. The application of the Gibbs phase rule in the form of eq 2 may be put in doubt. If only for this reason, our considerations on the links between biodiversity of life on Earth and the number of exotic equilibrium states are only speculative. However, the search for the links between biology, as measured by the number of living organisms, and chemistry, as measured by the number of thermodynamic states in complex systems, seems to be a worthwhile task. Until hypotheses put on more firm ground are devised, speculation offered in this work is hoped to be of some interest.

3. CONCLUSIONS

The systems with independent components, C , determined by the number of components, N , and the number of independent reactions, r , are considered. The equilibrium in such systems can be represented by a graph of state, G , a planar graph on the surface isomorphic with 2-sphere in which the number of vertices, R_i , is the number of degrees of freedom, f , the number of edges (including loops), is the number of independent components, and the number of faces is the number of phases. The lengths of graph edges are the geodesic lines on the R surface. Equilibrium thermodynamic transformation that does not involve the formation of new phases is described by the transformation of isomorphic graphs, G into G' , involving only the changes in graph edges lengths.

Phase transformation in the system is described by the gluing of graph vertices. Since specific graphs of state represent strictly specific states of thermodynamic equilibria, graphs can be used to enumerate the types of equilibria possible in complex thermodynamic systems. In one-phase three-component systems ($C = 3$) the graphs indicate the presence of exotic equilibria states, described by a branched tree, that exist apart from the normal states. The exotic states cannot be formed in one- and two-component systems. It is suggested that the exotic state equilibria may correspond to recently discovered stable quasicrystals that also can only be formed in multicomponent systems.

The number of exotic states increases sharply with the number of components. It is suggested that the number of such states in systems consisting of about 30 bioelements, in which all the kinetically allowed reactions are assumed to occur, have something to do with a diversity of biological species on the Earth.

ACKNOWLEDGMENT

We thank Professor Nenad Trinajstić, Rudjer Bosković Institute, Zagreb, Croatia, for reading the manuscript of this paper and useful comments. We also thank him for making available to us a copy of his book.²⁰

REFERENCES AND NOTES

- (1) Hillert, M. *Phase Equilibria, Phase Diagrams and Phase Transformations*; Cambridge University Press: Cambridge, U.K., 1998.
- (2) Trinajstić, N. *Chemical Graph Theory*; CRC Press: Boca Raton, FL, 1992; pp 14–18.
- (3) Busacker, R. G.; Saaty, T. L. *Finite Graphs and Networks*; McGraw-Hill Book Co.: New York, 1965; pp127–133.
- (4) Balaban, A. T., Ed. *Chemical Applications of Graph Theory*; Academic Press: New York, 1976; Chapter 7 (by D. R. Rouvray) and Chapter 8 (by J. Brocas).
- (5) Rudel, O. Z. *Electrochem.* **1929**, 35, 54 (cited in ref 4).
- (6) Seifer, A. L.; Stein, V. S. Topology composition-property of diagram phase. *Zh. Neorg. Khim.* **1961**, 6, 2711.
- (7) Levin, I. The phase rule and topology. *J. Chem. Educ.* **1946**, 23, 1983.
- (8) Klochko, M. A. *Izv. Sek. Fiz.-Khim. Anal., Inst. Obshch. Neorg. Khim., Akad. Nauk SSSR* **1949**, 19, 82.
- (9) Mindel, J. Gibbs' phase rule and Euler formula. *J. Chem. Educ.* **1962**, 39, 512.
- (10) Rouvray, D. H. Uses of graph theory. *Chem. Br.* **1974**, 10, 11.
- (11) Radhakrishnan, T. P. Euler's formula and phase rule. *J. Math. Chem.* **1990**, 5, 381.
- (12) Weinhold, F. A. In *Theoretical Chemistry, Advances and Perspectives*; Eyring, H., Henderson, D., Eds.; Academic Press: New York, 1978; Vol.3, p 15.
- (13) Klotz, I. M.; Rosenberg, R. M. *Chemical Thermodynamics*; J. Wiley & Sons: New York, 1994.
- (14) Moore, W. J. *Physical Chemistry*, 5th ed.; Longman: London, 1972.
- (15) Shechtman, D.; Blech, I.; Gratias, D.; Cahn, J. W. Metallic phase with long-range orientation order and no translational symmetry. *Phys. Rev. Lett.* **1984**, 53, 1951.
- (16) Senechal, M. *Quasicrystal and Geometry*; Cambridge University Press: Cambridge, U.K., 1995 (preface).
- (17) Shechtman, D.; Lang, C. I. Quasiperiodic Materials: Discovery and Recent Developments. *MRS Bull.* 1997, 22 (11), 40.
- (18) Tsai, A. P. Metallurgy of Quasicrystals: Alloys and Preparation. *MRS Bull.* 1997, 22 (11), 43. Also see: Weber, S. URL address <http://www.Nirim.go.jp/~weber/index.html>.
- (19) Harary, F.; Palmer, E. M. *Graphical Enumeration*; Academic Press: New York, 1973 (Asymptotics chapter).
- (20) Knop, J. W.; Müller, W. R.; Szymanski, K.; Trinajstić, N. *Computer Generation of Certain Classes of Molecules*; SKTH/Kemia: Zagreb, 1985; pp 28–34.
- (21) Zhao, M.; Wang, Z.; Xiao, L. Determining the number of independent components by Brinkley's methods. *J. Chem. Educ.* **1992**, 69, 539.
- (22) Brinkley, S. R. Calculation of equilibrium composition of systems of many constituents. *J. Chem. Phys.* **1947**, 15, 107.
- (23) Emsley, J. *Oxford Chemistry Guides: The Elements*; Clarendon Press: Oxford, U.K., 1991.
- (24) Weiner, J. *Life and Biosphere Evolution*; PWN: Warsaw, 1999; pp 283–302 (in Polish).
- (25) Bryant, P. J. *Biodiversity and Conservation* (A Hypertext Book at URL address: <http://darwin.bio.uci.edu/~sustain/bio65/>), 2000; Chapter 6.
- (26) Glansdorff, P.; Prigogine, I. *Thermodynamic Theory of Structure, Stability and Fluctuations*; Wiley: London, 1971.

CI010260F