

Original Scientific Paper

On Selected Properties of the Gibbs Function Topological Manifold

JAN TURULSKI *

Third Age University, 16–035 Czarna Wies Koscielna, Poland, and
 Chemistry Institute, University at Bialystok, 15–443, Bialystok, Poland

ARTICLE INFO

Article History:

Received: 30 July 2022

Accepted: 8 August 2022

Published online: 30 December 2022

Academic Editor: Ali Reza Ashrafi

Keywords:

Thermodynamic equilibrium

Gibbs function

Topological manifold

Graph theory

ABSTRACT

Quantitatively, the equilibrium in classical thermodynamics in the C -component isobaric-isothermal system is determined by the minimum value of the Gibbs function. The topological manifold of this function is a 2-D dimensional, smooth piece, geometric creation. These pieces represent individual states of single-phase systems. Successive pieces of the manifold are glued along the line of phase transitions to form the manifold of the whole, en bloc, C -component system. Gluing smooth pieces together must guarantee the continuity of the glued whole. The study found the dependence of the number of ways of gluing single-phase pieces on the number of components of the system. It has also been shown that the distribution of components in individual phases of the system is represented by a planar graph with 4 faces, called a normal graph. Studies of the topological properties of the manifold fragments representing single-phase equilibrium states indicate that the value of the Gibbs potential in these states is encoded in the geometry of the topological manifold. In concrete terms, this value is equal to the length of the minimum path lying on the surface of the manifold, connecting the various degrees of freedom of the system (the vertices of the graph). In complex systems, with very large C , the number of paths connecting the degrees of freedom is monstrously large. Preliminary calculations show that in such systems the number of paths with a minimum length or not much different from it may be greater than one. This suggests that thermodynamic equilibrium states in complex systems may be degenerate.

This work also recalled the results of my previous research on the application of topology in the thermodynamics of equilibria.

© 2022 University of Kashan Press. All rights reserved

1. INTRODUCTION

Isobaric–isothermal equilibrium ($p, T = \text{const}$) in closed chemical systems with C components (mole fractions of the components: (x_1, x_2, \dots, x_c)) is described by the Gibbs potential $G(p, T, x_1, x_2, \dots, x_c)$. This paper addresses some of the many different problems related to this equilibrium. One such problem appeared in chemistry about a century ago [1] when scientists attempted to apply graph theory to equilibrium thermodynamics. Over the subsequent 100 years, various research groups [2–9] strived to find a solution. The problem concerned a similarity a form of the Gibbs phase rule:

$$f = C - p + 2, \quad (1)$$

where f –number of degrees of freedom in a thermodynamic system, C –number of independent components; and p –number of phases; with a form of the Euler equation connecting the individual constituents of a planar graph located on a surface that is isomorphic with the 2-D surface of a sphere:

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

where F –number of faces of a planar graph; E –number of edges of that graph; and V – number of vertices of that graph. The aforementioned problem is to determine whether this similarity between equations from the vastly different fields of thermodynamics, topology, and graph theory results from some deeper principle unknown to classical thermodynamics [2, 7, 9] or is simply a coincidence [8], a frivolous act of God. Unfortunately, all of the studies invoked above that investigated, or even attempted to explain, the similarity between Equations (1) and (2) only revolved around the similarity between the parameters in both equations. Simply speaking, researchers so far have focused on finding out why the similarity between Equations (1) and (2) results from one of two possible forms of correspondence between the parameters of both equations, rather than the other one, i.e., $f \leftrightarrow F, p \leftrightarrow V, C \leftrightarrow E$ or $f \leftrightarrow V, p \leftrightarrow F, C \leftrightarrow E$. However, as Trinajscic writes [10], such an approach does not explain the cause of the strange correspondence between the two equations. The author of this paper agrees that the approach is misguided because the similarity between the equations cannot be explained by looking for correspondence between their parameters. In my opinion, which I introduced in Study number [11], the explanation lies in a constituent that usually does not explicitly appear in either equation. This constituent is the 2-D surface isomorphic with the sphere on which the planar graph (2) is presented. While in topology this type of graph can be located on any abstract 2-D surface, including an ordinary plane, sphere, or any 2-D surface with no holes, it is unclear what thermodynamic surface could house a graph described by the Gibbs equation (1). Studies number [11, 12] suggested that the Gibbs function topological manifold could be such a surface. A graph representing equilibrium in a thermodynamic system located on that surface was called a state graph. Many properties of state graphs are presented in the aforementioned study [11]. This paper explains the factors that cause the Gibbs function topological manifold of the studied systems to be two-dimensional, rather than $C + 1$ –dimensional. The paper also investigates how many different

forms a 2-D Gibbs function topological manifold can take for chemical systems with C components. The number of these forms is equal to the number of types of invariant states within these systems. Lastly, the paper demonstrates that for isothermal-isobaric closed systems, the function $G(p, T, x_1, x_2, \dots, x_c)$ has an extraordinary property: its value, for equilibrium states in single-phase systems, is contained within the geometry of its topological manifold; specifically, it is equal to the minimal path connecting the vertices of the state graph. Consequently, searching for the equilibrium state graph in such systems is related to a generalized traveling salesman problem, known from graph theory. The fact that systems with many components may also contain many minimal paths (or paths approaching minimal) suggests that the classical definition of the equilibrium state should be adjusted to better fit such systems.

2. THEORY

Under isobaric-isothermal conditions, the states of thermodynamic equilibrium are described by the minimal value of the Gibbs function, $G(p, T, x_1, x_2, \dots, x_c)$ [13]. Consequently, the change, dG , of the value of the Gibbs function is given by the following equation:

$$dG = \mu_1 * dx_1 + \mu_2 * dx_2 + \mu_3 * dx_3 + \dots + \mu_c * dx_c, \quad (3)$$

where μ_i is the chemical potential of the i -th component:

$$\mu_i = \left(\frac{\partial G}{\partial x_i} \right)_{x_j \neq x_i}, \quad i = 1, 2, \dots, C. \quad (4)$$

Thus, one may think that the Gibbs function for such systems depends on C variables. However, because each chemical potential is parametrically dependent on pressure and temperature, and furthermore, the sum of mole fractions in closed systems equals 1 (i.e., the value of one of the fractions is determined by the sum of the others), then in actuality, the Gibbs potential depends on $C + 1$ arguments. Thus, it would seem that the topological manifold of this thermodynamic potential is a $C + 1$ -dimensional geometric construct.

Let us interrupt this line of thought to briefly explain what the topological manifold of a function is. A function of n variables can be imagined to occupy an $n + 1$ -dimensional space spanning n axes of that function's arguments and one axis of that function's values as an n -dimensional hypersurface created by the points corresponding to the values of the function. Such a hypersurface is called the *topological manifold* of the function. The topological manifold is smooth and continuous as long as for all values of the arguments, the function and its first derivatives are continuous. In turn, it is piecewise smooth as long as the first derivatives of the function are only discontinuous for selected values of arguments, e.g., along certain lines or planes. There is a slight inaccuracy in the statement above that the dimension of the topological manifold of a function of n arguments is equal to n . That is indeed the case but only as long as no external limitations or constraints are imposed upon the function, as some constraints may significantly decrease the dimension of the topological manifold. Let us use $G(p, T, x_1, x_2, \dots, x_c)$ as an example. The number of arguments suggests

that the topological manifold should have $C + 1$ dimensions. However, the function is first-order homogenous in relation to x_i , i.e.:

$$G(p, T, k * x_1, k * x_2, \dots, k * x_c) = k * G(p, T, x_1, x_2, \dots, x_c), \quad (5)$$

where k is any real number. Thus, the derivative with respect to the k -th argument of this function leads to the following equality:

$$\mu_1 * x_1 + \mu_2 * x_2 + \mu_3 * x_3 + \dots + \mu_c * x_c = G, \quad (6)$$

Therefore, the change in the value of the function with the property (6) is given by:

$$dG = (\mu_1 * dx_1 + \mu_2 * dx_2 + \mu_3 * dx_3 + \dots + \mu_c * dx_c), \\ + (x_1 * d\mu_1 + x_2 * d\mu_2 + x_3 * d\mu_3 + \dots + x_c * d\mu_c). \quad (7)$$

A comparison between Equations (3) and (7) leads to the (rather obvious) conclusion known as the Gibbs–Duhem equation [13, 14]:

$$(x_1 * d\mu_1 + x_2 * d\mu_2 + x_3 * d\mu_3 + \dots + x_c * d\mu_c) = 0. \quad (8)$$

Consequently, due to the composition, the homogeneity of the Gibbs function combined with the imposition of the Gibbs–Duhem equation (8) onto the G potential enforces $C - 1$ constraints on the Gibbs function. These constraints are defined by Equation (9):

$$x_1 * \left(\frac{\partial \mu_1}{\partial x_j} \right)_{x_k \neq x_j} + x_2 * \left(\frac{\partial \mu_2}{\partial x_j} \right)_{x_k \neq x_j} + \dots + x_c * \left(\frac{\partial \mu_c}{\partial x_j} \right)_{x_k \neq x_j} = 0, \quad j = 1, 2, \dots, C - 1. \quad (9)$$

It follows from Equation (9) that the values of this function are located not on a $C + 1$ –dimensional hypersurface of the topological manifold, but instead, on a two-dimensional one (because $(C + 1) - (C - 1) = 2$). It should be mentioned that the dependence of a closed isothermal-isobaric system on two variables is commonly known [14], which means that the above statement brings nothing new. However, note that the thermodynamic equilibrium in such systems has to date been described predominantly based on function theory and mathematical analysis. This paper proposes a topological interpretation of these equations, leading to conclusions that the classical approach does not produce. In conclusion, we will say that:

1. *The dependence of the function $G(p, T, x_1, x_2, \dots, x_c)$ on the composition, x_i , causes for isothermal-isobaric closed systems the first degree homogeneity of this function, which in turn reduces the dimension of the topological manifold of the Gibbs potential to the value 2.*

Let X, Y denote the two coordinates describing the equilibrium state in the analyzed systems. Naturally, both coordinates are functions of thermodynamic parameters. The form of these coordinates, in particular, their specific dependence on the aforementioned parameters, is unimportant at this point (nonetheless, they should not be identified with the coordinates of a 2-D Cartesian space!). The important aspect is that the values of these coordinates create a lattice of geodesics on the topological manifold of the Gibbs potential for a given phase of the system. The geodesic lattice $\mathbf{R} = R(X, Y)$ can be said to represent the topological manifold of the Gibbs function of a given phase of the analyzed systems.

Because the function G is continuous for a given phase, the topological manifold \mathbf{R} for a single phase is a continuous and smooth geometric construct (e.g., with no holes or sharp changes in value). Chemical thermodynamic systems with C components can only exist as a maximum of $C + 2$ different phases (Equation (1)). The states of equilibrium for each phase are represented by a 2-D continuous region of the surface \mathbf{R} of the topological manifold. The regions of two phases cross each other along the line of thermodynamic equilibrium between these phases. The location of the intersection line between the manifold of phase α and the manifold of phase β , of the i -th component of the system, is defined by the following conditions:

$$\mu_i^\alpha = \mu_i^\beta, \quad i = 1, 2, 3, \dots, C. \quad (10)$$

The dihedral angle at which the two manifolds intersect depends on the change in entropy and volume in both phases, caused by phase transformations. Thus, the angle changes along with the values of the parameters in a given transformation. For critical states in some phase equilibrium, $\alpha \leftrightarrow \beta$, the angle may reach 180° , which allows for a smooth transition from one phase to the other. However, because the angle is usually different from 180° , the topological manifold loses its smoothness along the phase transformation line. In topology, this behavior is classified as a piecewise smooth manifold. Consequently, the Gibbs function topological manifold is a 2-D construct consisting of smooth regions representing the individual phases of the system, glued together along the phase transformation line. The gluing together of the different regions should guarantee that the smoothness of the entire manifold is retained. As has already been mentioned, in classical thermodynamics, the maximum number of phases in systems with C components is $C + 2$, which creates a problem: how should the smooth regions of a 2-D manifold be glued together to ensure such smoothness? In particular, how to make sure that the last region is glued to the first one? At this stage, we may only assume that for systems with two or more components, the number of ways the regions can be glued together is greater than one.

1.1 TOPOLOGICAL MANIFOLD OF A GIBBS FUNCTION FOR ALL EN BLOC PHASES OF THE SYSTEM

It has been noted above that the topological manifolds of the Gibbs functions are 2-D dimensional smooth surfaces successively glued together along the phase transition line, Equation (10). The form of this line imposes on the glued manifold of each phase the presence of the same components that are contained in both adjacent (glued) phases. Due to the fact that $G(p, T, x_1, x_2, \dots, x_c)$ is a continuous function, therefore the question arises: (a) how to arrange the components in successive phases so that the patch of the last phase manifold is glued to the patch of the first phase (otherwise the topological manifold will be discontinuous); (b) how many ways of arranging C components between $C + 2$ phases satisfy the condition a). Both conditions come down to the search for an answer to the

question: how many different topological manifolds can be allowed for all *en bloc* phases of the system. We will now deal with these issues.

Let us come back for a moment to the problem of parallelism between Equations (1) and (2). As mentioned above, this parallelism can occur in one of two ways. Either the number of the degrees of freedom, f , corresponds to the number of faces of the planar graph, F ; or f corresponds to the number of vertices of the graph, V . Both ways have been investigated in studies conducted to date. This paper and study number [11] present the latter approach, i.e.,

$$f \leftrightarrow V, p \leftrightarrow F, C \leftrightarrow E, \quad (11)$$

Is there a rational explanation behind this choice? Indeed there is: the reason is that the former approach, where the number of degrees of freedom corresponds to the number of faces of a planar graph located on a 2-D surface that is isomorphic with a sphere, $f \leftrightarrow E$, leads to absurd conclusions. If we were to accept them, then, due to the existence of states of thermodynamic systems in which $f = 0$ (i.e., invariant states), we would also have to accept the absurd statement that there exist planar graphs located on the aforementioned 2-D surface for which $F = 0$, i.e., graphs with no faces at all! While absurdities may be an essential part of social life, science should avoid nonsensical statements. Following this principle, this paper from now on shall assume that the parallelism between the phase rule (1) and Euler's formula for planar graphs (2) is ensured through the correspondence (11). Let us now return to the problem of the number of ways in which the individual regions of a topological manifold corresponding to each phase of the system can be glued together while ensuring the smoothness of the entire construct.

The problem is identical to that of the number of planar graphs with 0 vertices that contain C edges and $C + 2$ faces. I am aware that many of the Readers, upon seeing the phrase "graphs with 0 vertices," would recommend that the author seek professional help. After all, while it is possible to imagine a planar graph with 0 edges, proposing a graph with no vertices (as well as no faces) is almost like proposing a sea with no water! This paper will demonstrate that graphs with 0 vertices are, in fact, possible, and that their existence and number do not follow exclusively from Euler's formula (2). Furthermore, their number is equal to the number of ways in which the smooth regions of the topological manifolds of each phase can be glued together to guarantee the smoothness of the entire geometric construct.

2.1.1 PLANAR GRAPHS WITH 0 VERTICES, C EDGES, AND C + 2 FACES

In graph theory, planar graphs with 0 vertices (as well as graphs with 0 edges), usually called *null graphs* or *empty graphs* [15], have an unclear definition. This is due to a lack of research on such graphs. In particular, the number of such graphs remains inconclusive. Consequently, this paper will take advantage of intuition supported by elementary knowledge about the properties of planar graphs. Intuition tells us that any point on a planar surface associated in

some manner with the other points (or not, as with null graphs) can be called a vertex of a planar graph. This association is represented by the edges of the graph: the position of the vertices can vary and is defined by the relationship between them. Figure 1 shows a visual and functional representation of selected graphs and the corresponding sets of vertices, edges, and faces. One may ask: what if the position of a given vertex is not defined by the relationship between the vertices but rather depends strictly on the relationships between other objects within the graphs, such as faces, as with the sixth graph in Figure 1?

The vertex in the sixth graph, marked with an asterisk, is the common point between three faces. Thus, the position of the vertex is determined by the relationship between the faces, rather than the edges. One may even go as far as to say that since such a vertex operates differently from a vertex defined by graph theory, it is not a vertex at all. In what circumstances is this true? Such a situation occurs in the description of the topological relationship between three or more planes (see Graph 6 in Figure 1). This relationship can have one of the following three properties:

- i. *The planes do not intersect with one another;*
- ii. *The planes intersect along one or more lines with no common intersection point;*
- iii. *All planes intersect along lines that have a single common point.*

In the third case, the intersection lines constitute the edge or edges of the graph. What about the common point between the intersecting planes? It gives the false impression that it can also be called a vertex of the graph. However, from a logical perspective, it is not a vertex, because its position results from the relationship between the faces of the graph rather than the edges. In other words, Graph 6 in Figure 1 has three planes and three intersection lines but zero vertices.

The intersection lines between the three planes constitute the edge or edges of the graph, while the intersecting planes are the faces. Since there are three intersection lines in Graph 6, does this mean that the graph has three edges? Euler's formula for planar graphs indicates that if a planar graph with zero vertices has three faces, then it should only have a single edge. Thus, all three intersection lines jointly form a single edge that bifurcates at the intersection point between all the planes. Consequently, the single bifurcating edge and the three faces with a single common point introduce planar graphs with zero vertices to graph theory. Such graphs represent the intersection between planes or 2-D surfaces. For simplicity's sake, this representation of the intersection between the smooth regions of a manifold will be shown after mapping onto a plane (e.g., onto the p, T plane in thermodynamics) and will be referred to as a *0-vertex state graph* or *graph-map* interchangeably. If Equation (11) represents the correspondence *equilibrium thermodynamics* \leftrightarrow *graph theory*, then the planar graph-map represents the invariant state of a system with C components and $C + 2$ phases (0 degrees of freedom = 0 vertices; $C + 2$

phases = $C + 2$ faces; C components = $C + 2$ intersection lines, which constitute C edges, i.e., some edges bifurcate). The intersection lines constitute the edges of the graph, as defined by Equation (10). The faces of the 0-vertex state graph are the smooth regions of the Gibbs function topological manifold, and their number is equal to the maximum number of phases in a system with C components. At first glance, the only concerning aspect is that the $C + 2$ intersection lines are defined by C edges, rather than $C + 2$, as one would expect. Why is that? Consider that in accordance with Equation (10), an edge is a line that characterizes the equilibrium for a given i -th component of the system. This component may occur in several phases (which are represented by the faces of the graph), and consequently, several different intersection lines represent the equilibrium of the same component in different phases. Thus, the different intersection lines correspond to the same edge. One may ask, do such graphs even have different edges? According to Equation (10), the graph-maps of systems with $C > 1$ contain C different edges. Each edge corresponds to the equilibrium between the two phases of a specific (one of the C possible) components of the system. This number of edges is represented by $C + 2$ lines intersecting at the point of the invariant state that is not a vertex of this graph-map. Figure 2 shows all possible 0-vertex state graphs (i.e., state graphs that guarantee the continuity of the glued whole) for unary systems (containing component A) and binary systems (containing components A, B).

In Figure 2, the equilibrium lines of component A are marked with a solid line, and those of component B – a dashed line. The figure indicates that for unary systems, there exists only one graph-map that contains three intersection lines between the three regions of the manifold of each phase (α, β, γ). These lines are marked with the letters k, l, m . Because all regions represent the equilibrium states of the same component, A , all these lines constitute a single edge of the graph, which bifurcates at the invariant point (marked with an asterisk). Thus, we arrive at the trivial conclusion that there exists only one type of an invariant state in unary systems. However, binary systems operate differently. Figure 2 shows that for such systems, there are three ways to continuously glue together the regions of the topological manifolds of the four phases ($\alpha, \beta, \gamma, \delta$) within the system. Thus, from a topological viewpoint, there are three possible forms of binary systems, which correspond to three different types of an invariant state. The first form represents the 0-vertex graph marked with the letter a in Figure 2, the second – the letter b , and the third – the letter c . In the first form, phases α and β contain only component A , whereas phases γ and δ are binary. This form of the system is marked $\{(A), (A), (A, B), (A, B)\}$. In the second form, marked $\{(A), (A, B), (B), (A, B)\}$, the phases α and γ are unary: the first phase contains component A , and the second phases contains B , while phases β and δ are binary. Lastly, the third form is marked $\{(A, B), (A, B), (A, B), (A, B)\}$. It is worth reiterating that the number of ways the regions of the topological manifold of binary systems can be glued together indicates that such systems may support three types of an invariant state. Note that this does not mean that

the same binary system can have three different invariant states; rather, the invariant state may differ between some binary systems.

Graph	Math. graph formula	Vertices	Edges	Faces
	$E_1(x,y)E_2(y,z)$	$\{x, y, z\}$	$\{E_1, E_2\}$	$\{F_1\}$
	$E_1(x,y)E_2(x,y)$	$\{x, y\}$	$\{E_1, E_2\}$	$\{F_1, F_2\}$
	$E_1(x,y)E_2(y,y)$	$\{x, y\}$	$\{E_1, E_2\}$	$\{F_1, F_2\}$
	$x E_2(y,y)$	$\{x, y\}$	$\{E_2\}$	$\{F_1, F_2\}$
	x	$\{x\}$	$\{\emptyset\}$	$\{F_1\}$
	$k: (F_1(x,y)=F_2(x,y))$ $m: (F_1(x,y)=F_3(x,y))$ $l: (F_2(x,y)=F_3(x,y))$	$\{\emptyset\}$	$\{E_1 = \{k \wedge l \wedge m\}\}$	$\{F_1, F_2, F_3\}$

Figure 1: Sample graphs provided to compare 0-vertex graphs with other graphs. The last three columns in the figure present the individual constituents (vertices, edges, and faces) of each graph. The last line presents a sample 0-vertex graph obtained as a result of three faces of the same type intersecting at a single point. The intersection lines of the two planes determine the edge of the graph. The intersection point of the three faces cannot be interpreted as a vertex of the graph.

The reader will likely now ask: why can the regions of each phase’s manifold in binary systems only be glued together in three ways? In other words, why can binary systems only appear in three forms that differ in the distribution of each component between the phases? Why is it impossible to have forms with different distributions of components, such as $\{(A), (A), (A), (A, B)\}$, $\{(A), (A), (B), (A, B)\}$, or $\{(A), (A, B), (A, B), (A, B)\}$? The answer is simple: because such forms would involve a discontinuous Gibbs function topological manifold. The Gibbs potential is a continuous function, which means that its manifold must likewise be continuous. The issue surrounding the discontinuity is illustrated in Figure 3 based on a system given by $\{(A), (A), (B), (A, B)\}$. The individual phases in Figure 3 have the following compositions: $\alpha = (A, B)$; $\beta = (A)$; $\gamma = (A)$; and $\delta = (B)$. As

we can see, such a distribution of components between the phases creates a discontinuous Gibbs function topological manifold. The discontinuous area is marked with “?” in Figure 3.

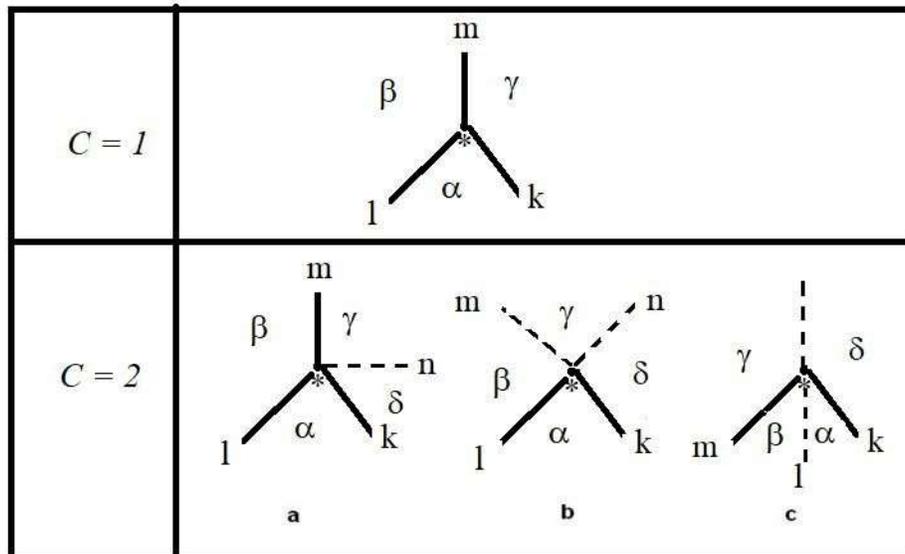


Figure 2: Mapping the Gibbs function topological manifold for unary and binary systems onto the plane (p, T) creates a graph-map of an invariant state. The phase equilibrium lines (10) of component A are marked with a continuous line and those of component B – a dashed line. The edges of the graph constitute the equilibrium lines of a given component. Thus, the edges may bifurcate at the point of intersection between all equilibrium lines. This intersection point is not a vertex of the graph because it represents the relationship between the faces, rather than between the different points (vertices). Consequently, the graphs shown in the figure are 0-vertex graphs. The faces of these graphs are the smooth 2-D regions of the Gibbs function topological manifold that represent the single-phase states of the system (marked with Greek letters). The invariant state is marked with an asterisk.

The existence of such an area indicates that this specific distribution of components between the phases makes it impossible to glue together the region corresponding to phase δ with the region corresponding to phase γ , and thus, the continuity of the entire manifold is impossible to achieve. Consequently, invariant states such as this one cannot physically exist. Some authors of chemical thermodynamics textbooks do not take this fact into account [16], providing $\text{H}_2\text{O}-\text{NaCl}$ as an example of an invariant state in a binary system, even though such a state does not, in fact, exist. Specifically, the invariant state in the $\text{H}_2\text{O}-\text{NaCl}$ system provided by the aforementioned textbook as an example [16] is a state in which a saturated water solution of salt coexists with ice crystals, precipitated salt crystals, and water vapor. Figure 4 demonstrates that this invariant state cannot physically exist because its Gibbs function topological manifold would have to be discontinuous, as water vapor (or ice

crystals) cannot exist in equilibrium with NaCl crystals. The figure suggests that in the invariant state of this system, one other phase must also be binary. The ice crystals will most likely contain NaCl molecules.

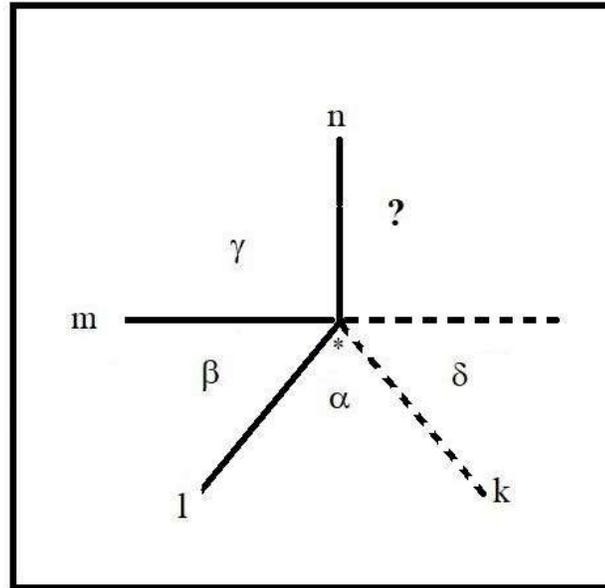


Figure 3: An invariant state within a binary system consisting of the phases $\{(A, B), (A), (A), (B)\}$ cannot exist because its Gibbs function would be discontinuous, as shown by the discontinuity of the manifold that contains the graph of the invariant state (the discontinuous area is marked with a question mark). The markings in Figure 3 as the same as in Figure 2.

Unary and binary systems are relatively simple, which means that finding all permitted gluing procedures that create continuous regions of the manifold is not difficult. However, what about systems with $C > 2$? It is possible to count all permitted ways to glue together the regions of the Gibbs function topological manifold? To put it differently, is it possible to count all permitted types of invariant states for systems with three or more components? Because the permitted types of gluing are represented by graph-maps, the problem comes down to the procedure for counting these graphs. Before we address this issue, let us explain the characteristics that a 0-vertex graph must have in order to represent a permitted gluing procedure, i.e., to represent a real invariant state of a thermodynamic system. Note that the phase equilibrium line of each component adjoins two phases (each phase is represented by a face of the graph). Therefore, the edge of the state graph-map representing any component must in total adjoin an even number of faces. Taking this into account, we may move on to the problem of counting state graph-maps for complex thermodynamic systems, and consequently, to counting invariant states in such systems.

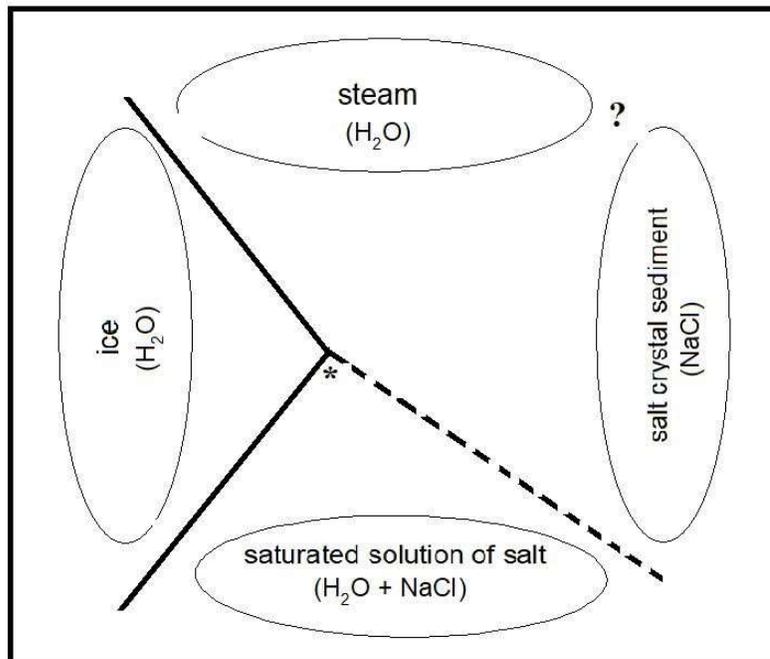


Figure 4: An example of a “false” invariant state within the H_2O - NaCl system, which does not exist in reality because it would have to be represented by a discontinuous Gibbs function. Some authors [16] mistakenly claim that such a state exists.

2.1.2 PROBLEM OF COUNTING PLANAR GRAPH-MAPS WITH C EDGES AND $C + 2$ FACES

A simple counting of non-isomorphic 0-vertex planar graphs by drawing them is, without a doubt, more difficult than counting normal graphs that have even more vertices than there are edges in the graph-maps. As has been stated above, there exist one and three 0-vertex state graphs for unary and binary systems, respectively. It is slightly more difficult to demonstrate “by hand” that for a ternary system, there are five such graphs, i.e., ternary systems may contain five types of invariant states that differ in terms of the distribution of the components A , B , and C between the five coexisting phases. The difficulties in counting encourage seeking a more convenient graph-based representation for such “demanding” 0-vertex graphs. Consequently, the following correspondence is proposed between the elements of graph-maps and the more “convenient” *normal graphs* that have more than 0 vertices:

$$\begin{aligned} \text{edge graph-map} &\leftrightarrow \text{vertex of the normal graph} \\ \text{face graph-map} &\leftrightarrow \text{edge of a normal graph.} \end{aligned}$$

Thus, the definition of a normal graph for a given 0-vertex graph is similar to the definition of a dual graph [10]. Of course, as with the 0-vertex graph, the normal graph is

planar. This obvious conclusion follows from the satisfaction of Euler’s formula (2) by the constituents of the graph. In other words, every normal graph created in this manner has $V^* = C$ vertices (which is the number of edges in a graph-map) and $E^* = C + 2$ edges (which is the number of faces in a graph-map). And how many faces, F^* , does it have? The answer can be found by substituting V^* and E^* into the Euler equation (2): $F^* = 4$. The invariant state of a system with any number of components always represents a normal state graph with four faces.

There is a one-to-one correspondence between a given 0–vertex graph and its normal counterpart. This is the difference between dual graphs and normal graphs. The relationship between a dual graph and a graph is only one-to-many, whereas for normal graphs, it is one-to-one. As has been mentioned above, in 0–vertex graphs, each edge adjoins an even number of pairs, whereas in normal graphs, each vertex should have an even valence. This correspondence, *0–vertex graph* \leftrightarrow *normal graph*, constitutes a proposal for counting 0–vertex state graphs and their normal equivalents. Study number [12] shows sets of all normal graphs for systems with fewer than nine components. Figure 5 presents some of these graphs, i.e., those related to systems with $C \leq 3$.

These sets of normal graphs include those whose graph-maps were shown in Figure 2. Table 1 provides the number of normal graphs, $\eta_0(C)$, for more complex systems.

The table indicates that the values of $\eta_0(C)$ constitute an increasing numerical sequence. An elementary analysis [17, 18] of the sequence shows that for even values of $C = 2k$, $k = 0, 1, 2, \dots$, the value of η_0 differs by $k(k + 3) / 2$ from the corresponding value for both neighboring systems when C is odd (i.e., $C = 2k - 1$ and $C = 2k + 1$):

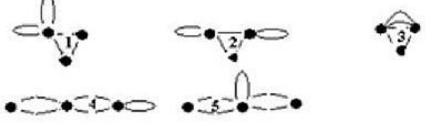
C	Normal graph	$\eta_0(C)$
1		1
2		3
3		5

Figure 5: Normal graphs are the one-to-one counterparts of 0–vertex graphs. They are equally as effective in describing the invariant state as easier to count compared to the latter. The vertices of these graphs represent the components of the system, the edges (including loops) represent the phases, the composition of which is determined by the vertices connected with a given edge. Normal graphs always have four faces and an even valence of the vertices. The graphs in the first two rows in the figure correspond to the 0–vertex graphs in Figure 2.

Table 1: The number, η_o , of methods of continuously gluing $C + 1$ of the fragments of the topological manifold of single-phase systems into the manifold of the whole system. This number is equal to the number of allowed classes of invariant states in C -component systems, ($C \leq 8$).

k	0	1	2	2	3	3	4	4	k	k
$C = 2k + 1$	1		3		5		7		$2k + 1$	
$C = 2k$		2		4		6		8				$2k$
η_o	1	3	5	10	15	24	33	47	Eq. (14)	Eq. (13)

$$\eta_o(2k) - \eta_o(2k - 1) = \eta_o(2k + 1) - \eta_o(2k) = k(k + 3)/2, \tag{12}$$

where $k = 1, 2, 3, 4, \dots$. This correspondence, along with the boundary value $\eta_o(C = 1) = 1$, gives the following number of non-isomorphic C -vertex normal graphs:

$$\eta_o(C) = 3 + 2 * (k - 1)(k + 1) + k * (k - 1)(2k - 1)/6, \tag{13}$$

where $= 2k, k = 1, 2, 3, \dots$.

$$\eta_o(C) = 3 + 2 * (k - 1)(k + 1) + k * (k - 1)(2k - 1)/6 + k * (k + 3)/2, \tag{14}$$

where $= 2k + 1, k = 0, 1, 2, \dots$.

Equations (13) and (14) show that for large values of C (i.e., for a large number of vertices in normal state graphs), the number of invariant states increases proportionally to the third power of C . In graph theory, the number of graphs of a given type usually increases much faster, and consequently, the observed increase in the value of $\eta_o(C)$ is relatively slow. It seems that the slower rate of increase is caused by the constant, and independent from C , number of faces in these state graphs. The method for counting the gluing procedures of the smooth regions of the Gibbs function topological manifold (which also allows for counting of the invariant states) provides information about the composition of each invariant state. Of course, in order to obtain this information, we must first learn about the normal graph of an invariant state. Consider the invariant state represented by the last graph in Figure 5 for a ternary system. The vertices of the normal state graph represent the components of the system. Let these components be marked, from left to right on the graph, A, B , and C . Conversely, the edges connecting the vertices X and Y represent the phase containing X and Y . Thus, the graph can be said to represent an invariant state with the following phase composition: $\{(A, B), (A, B), (B), (B, C), (B, C)\}$. Let's summarize:

2. *The patches of topological manifolds of the individual phases of the C component system can be glued together into η_o (see Equations (13) and (14)) of allowed*

methods, i.e. those which satisfy the condition of the continuity of the whole manifold of the system.

- 3.** *The distribution of components between the various phases of the system is represented by normal graphs introduced in this work (see point 2.1.2).*

Finally, note that the lines of phase equilibria intersect at one point of a manifold called the invariant point. Therefore, as noted in [12], the number of invariant states in C -component systems is the same as the number of permitted methods of gluing the sheets of topological manifold of individual phases of the system.

This is how much information can be obtained using the elementary tools of topology to describe equilibrium, represented by a single point belonging to all planar regions of the topological manifold, in the invariant states of complex thermodynamic systems. What about equilibrium states located not on the entire manifold, but on one of its smooth regions? In classical thermodynamics, such a state is represented by a point on a planar region of the topological manifold of a given phase. Let us, therefore, discuss this topic.

2.2 TOPOLOGICAL MANIFOLD OF GIBBS FUNCTION FOR SINGLE PHASE OF THE SYSTEM

In the classical approach to the thermodynamics of equilibria, the state of a single-phase system represents a point on a smooth plane of a topological manifold of a Gibbs function. Quantitatively, such a state is expressed by the distance of this point from the point representing the so-called reference state. Of course, this distance is equal to the value of the function in the considered equilibrium state. In the topological approach to thermodynamics presented here, the equilibrium of a C -component single-phase system (parameter $p = 1$ in Equation (1)) is represented by a state graph with $C + 1$ vertices and C edges lying on a smooth patch of a topological manifold (see Equations (1), (2) and (11)). This graph will be a tree. The above-mentioned equations show that the vertices of this graph are degrees of freedom of the thermodynamic system, while the edges illustrate certain properties characterizing the individual components of the system. And here the problems arise: **a)** a single point on a 2-D dimensional manifold patch has two degrees of freedom, so the state graph would represent a system with $2 * C + 2$ degrees of freedom, while the state of a single-phase system has only $C + 1$ degrees of freedom. How to eliminate this incompatibility of the topological description of equilibrium? **b)** what are the properties of the individual components of the system that the edges of the state graph represent. The sum of these properties, along the individual edges, should give a quantitative characteristic of the equilibrium, i.e. the value of the Gibbs potential; **c)** a set of vertices can be joined by edges in many ways to form a tree. Which connection methods will the layout state graph represent? We will look for solutions to these problems in the following part of the work.

Points located on a smooth region of a manifold represent the single-phase equilibrium states of the system. Equations (1), (2) and (11) indicate that each of such states

is represented by a planar graph with C edges, $C + 1$ vertices, and one face, which is what graph theory refers to as a *tree*. The vertices and edges of the graph are located on the 2-D surface of a region of the manifold. Specifically, Equations (1) and (2) indicate that the state graph for a unary system has two vertices; for binary systems, three; for ternary systems, four; etc. This statement may be disturbing; after all, according to phenomenological thermodynamics, the state of a system is represented by just a single point in the space of thermodynamic parameters, made up of the values of the parameters of the system. It follows that such a representative of the state of a system can under no circumstances constitute the vertex or vertices of the state graph for a unary system, for several reasons. Firstly, the state graph has multiple vertices (specifically, $C + 1$). Secondly, every vertex of a 2-D manifold only has two degrees of freedom, whereas according to the classical definition, a thermodynamic state has $C + 1$ degrees. How do we translate a classically-defined equilibrium state, i.e., a point in the space of thermodynamic parameters, into a representation of a state defined by graph theory, i.e., a graph with $C + 1$ vertices? Note that this cannot be a simple translation, such as *one value of a state component* \leftrightarrow *one vertex of a state graph*. This is because every vertex of the graph on a planar patch of the manifold has two degrees of freedom. Thus, a graph representing a single-phase state of a unary system has four, rather than two, degrees of freedom. A question arises about how to translate vertices on a 2-D surface into object with only a single degree of freedom. We should look for the answer in phenomenological thermodynamics: the value of every thermodynamic function is always given in relation to a thermodynamic reference state. In the topological description of the equilibrium state, the only possible reference state for every phase is the invariant state. We shall denote the value of each parameter in the invariant state with the corresponding symbol with an asterisk. Consequently, both coordinates of the manifold, X and Y , for the invariant state of a system with C components, are given by:

$$X^* = X(p^*, T^*, x_1^*, x_2^*, \dots, x_c^*); \quad Y^* = Y(p^*, T^*, x_1^*, x_2^*, \dots, x_c^*), \quad (15)$$

whereas the invariant state on a region of the topological manifold is given by: $R^* = R(X^*, Y^*)$. A coordinate system located on the point of the invariant state straddles $C + 1$ axes. The coordinates of the k -th axis on the 2-D plane of the manifold can be found by substituting, in Equation (15), the constant value of the k -th parameter in the invariant state for the current value for the instance marked ξ , which defines the position on the axis. For instance, the second axis of the coordinate system is defined as follows:

$$X^* = X(p^*, \xi, x_1^*, x_2^*, \dots, x_c^*); \quad Y^* = Y(p^*, \xi, x_1^*, x_2^*, \dots, x_c^*). \quad (16)$$

Projecting the classically-defined equilibrium state $R_o = (p, T, x_1, x_2, \dots, x_c)$ onto such axes of a coordinate system changes every variable ξ into the current value of a thermodynamic parameter. Thus, the state R_o is represented by the set $C + 1$ of the values of positions R_1, R_2, R_3, \dots where, for instance:

$$X_1 = X(p^*, T^*, x_1^*, x_2^*, \dots, x_c^*); \quad Y_1 = Y(p^*, T^*, x_1^*, x_2^*, \dots, x_c^*), \quad (17)$$

$$X_1 = X(p^*, T, x_1^*, x_2^*, \dots, x_c^*); \quad Y_1 = Y(p^*, T, x_1^*, x_2^*, \dots, x_c^*), \quad (18)$$

and so on. The positions obtained in this manner are simply the subsequent constituents of a classical state mapped onto the axes of the coordinate system located on an invariant state. Equations (17) and (18) show that the subsequent constituents have only one degree of freedom, i.e., they can constitute the vertices of the sought state graph of a single-phase system. Consequently, the state of the system R_0 is represented by a graph tree with an appropriate number of vertices, as defined in Equations (17) and (18). Thus, the state of a unary system is represented by a graph with two vertices, R_1, R_2 , (see Figure 6); a binary system – three vertices, R_1, R_2, R_3 ; a ternary system – four vertices, R_1, R_2, R_3, R_4 ; etc.

In the aforementioned system of coordinates, the Gibbs function depends on the coordinates of the individual vertices: $\Delta G(R_1, R_2, R_3, \dots, R_{C+1})$. What about the edges of the state graph? The state graph represents the minimal value of the Gibbs function, $\Delta G(R_1, R_2, R_3, \dots, R_{C+1})$. Consequently, the value can be given as an integral over the path, located on the 2-D surface of the topological manifold, that runs across all vertices of the graph. This path consists of arcs connecting the adjacent vertices of the graph that can be interpreted as the edges of the graph. Because our state graphs are trees, the graph has one edge fewer than the vertices. Thus, each edge can be ascribed to a component of the system. The aforementioned total path must be minimal; it follows that it is also a geodesic (or arcs of the geodesic) located on the 2-D surface of the manifold. If this path consists of arcs of line segments: $R_1-R_2, R_2-R_3, R_3, R_1, \dots$, then, in accordance with the graph representation, the value ΔG equals:

$$\Delta G = \min_{R_i-R_j} \left(\sum_{i,j} \iint_{R_i}^{R_j} dR \right), \quad (19)$$

where the parameters i, j correspond to the neighboring vertices of the graph.

Because the pair R_i-R_j represents the edge ascribed to a given component, the summation over i, j in (19) can be substituted for summation over the subsequent components of the system: $X = A, B, C, \dots$:

$$\Delta G = \min \left(\sum_{X=A,B,C,\dots} \iint_{X_i}^{X_{i+1}} dR \right). \quad (20)$$

In other words, every component of the sum (20) describes the contribution of a given component of the system to the Gibbs function. Equation (6) indicates that the contribution is equal to: $x_X * \mu_X$. Thus, Equation (20) can be written as follows:

$$\Delta G = \min \left(\sum_{X=A,B,C,\dots} \iint_{X_i}^{X_{i+1}} dR \right) = \sum_{X=A,B,\dots} (x_X * \mu_X) \quad (21)$$

One may ask: how do we know that the sequence of edges, $X = R_i-R_j$, will give us the minimal-length path, i.e., the equilibrium value of ΔG ? This problem does not exist in unary systems for which the state graph only has two vertices that can only be connected in a single way through the minimal edge. However, binary systems already have three vertices, which gives three alternate paths: $1 = (R_1-R_2, R_2-R_3)$, $2 = (R_1-R_3, R_3-R_2)$, $3 = (R_3-R_1, R_1-R_2)$, (see Figure 7). All these paths create a linear graph in which the valence of the vertices is no greater than 2.

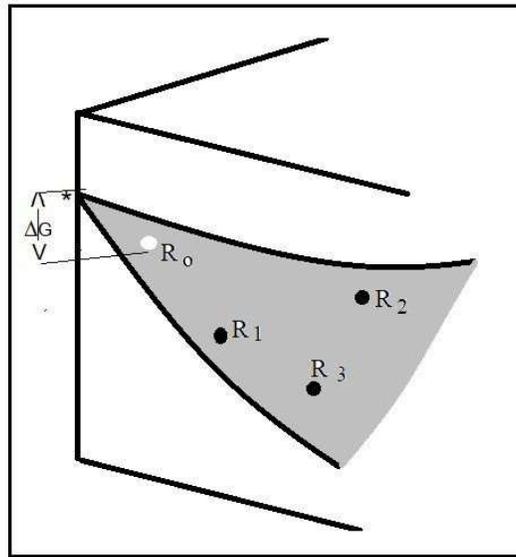


Figure 6: A model example of a topological manifold of a Gibbs function of a binary system. On the 2-D surface of the manifold, points are shown that represent: the classical equilibrium state (an clear circle), the invariant state (marked in the figure with an asterisk) and the individual degrees of freedom of the system (dark circles). Classical equilibrium state is represented by the point R_0 . The value of its Gibbs function relative to the invariant state is marked ΔG . Within the system of coordinates located on the invariant state, this point is represented by $C + 1$ components of the map of this point onto the axes of the system of coordinates: R_1, R_2, R_3 .

In ternary systems (see Figure 7), there are as many as 16 such paths, of which 12 are linear graphs, and 4 are branching trees in which one vertex adjoins all the others [19]. Cayley [20] (quoted based on Study No. [19]) showed that for systems with C components, there are $\eta_{\Delta G}^0 = (C + 1)^{C-1}$ such alternate paths. Is it possible to state which of the alternate sequences of edges will yield a state graph with minimal path length, i.e., a graph that represents the equilibrium state? Unfortunately, there is only one solution: to calculate the length of each arc of the potential graphs and determine the sequence that yields the shortest path via summation. This can be done for binary or ternary systems but for systems with 10 or more components, the task is unfeasible. Thus, the problem resembles the traveling salesman problem, known from graph theory, but is more complex. The traveling salesman problem involves finding the minimal path on linear graphs, whereas in the case of state graphs, we look not only for the shortest path of integration on linear graphs but also on branching trees. In sum, the value of the Gibbs function is contained within a graph with the minimal length of the path running through all its vertices. Let us briefly set aside the problem of finding a state graph corresponding to the value of the Gibbs function in equilibrium to discuss two other issues.

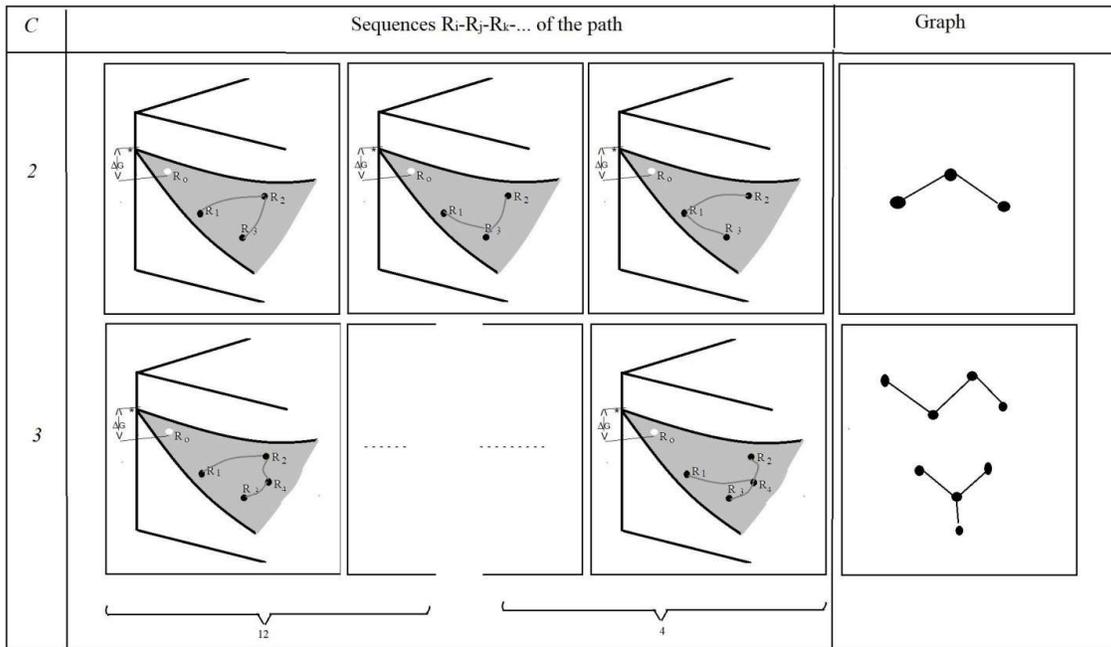


Figure 7: The state graph of a single-phase system is characterized by the minimum path through all the vertices of the graph (degrees of freedom). The length of the minimum path is equal to the ΔG at equilibrium. The figure shows typical paths for binary and ternary systems. For binary systems, the possible paths are represented by three sequences of vertices: $a = (R_1R_2R_3), b = (R_1R_3R_2), c = (R_3R_1R_2)$. For a ternary system, the figure shows 16 sequences of four vertices (12 of which are linear graphs and 4 are branching trees). Possible forms of state graphs for the systems considered here are shown in the last column in the figure.

4. *The first issue is the encoding of the value of the ΔG function within the geometry of the function's topological manifold. The value of the function is usually presented visually as the distance between a point located on the function's topological manifold and a reference point (Figure 6). Equation (21) shows that the Gibbs potential, ΔG , in equilibrium states has a particular property: the potential constructs its manifold in such a way that its value is contained (encoded) within the geometry of that manifold. Put simply: the geometry of a topological manifold of a Gibbs function contains information about the value of this function at equilibrium.*

There is an easily noticeable resemblance to gravity in Einstein's general theory of relativity. It is worth investigating in the future whether this resemblance is a simple coincidence or some deeper connection exists.

5. *The second issue concerns the number of potential state graphs for systems with many components (conventionally, $C = 10$ or more) that need to be analyzed in order to find the graph with the shortest integration path, as in Equation (19). Cayley's formula [20] indicates that for such complex systems, at least 10^9 would*

have to be analyzed in order to determine the one with the shortest integration path.

Taking into account the number of $\eta_{\Delta G}^0$ paths connecting $C + 1$ vertex tree one can expect existence of more than one graph with the shortest path. Let us denote this number by the symbol, $\eta_{\Delta G}$. Of course, if $\eta_{\Delta G} > 1$, the equilibrium state of a single-phase system will be degenerate. That is, the properties of such a phase will be determined by the properties of several / a dozen structures differing in the set of values of the chemical potentials $\{\mu'_i(k), i = 1, 2, \dots, C; k = 1, 2, \dots, \eta_{\Delta G}\}$. The value of the weighted sum of these potentials for each set, k , will be the same and equal to, ΔG . In other words: the topological approach to the thermodynamics of equilibria suggests the occurrence, in complex chemical systems, of the degeneration of the state of equilibria, i.e. the multistructure of this state. At this point, it should be emphasized that the multistructure does not mean that individual structures, differing in the sets of chemical potentials, coexist simultaneously in the analyzed state. Degeneration, i.e. multistructure, should be understood as the current structure with the k -th set of chemical potentials: $\mu'_i(k)$, $i = 1, 2, \dots, C$, at the right moment transforms into a structure characterized by a different set of chemical potentials, eg: $\mu'_i(j)$, $j \neq k$. Obviously, the Gibbs potential ΔG of both structures will be the same.

Of course, the theses discussed in Point 5 can be accused of being mere speculation. While this is correct, it is my belief that speculation can sometimes inspire future explorations. I think that such an inspiring influence on the research on the discussed problem can be fulfilled by the considerations on the maximum value of the degree of degeneration, $\eta_{\Delta G}^{\max}$ included in Appendix.

Coming back to the problem at hand, we can state that through our analysis, we have determined the graphs with the shortest integration paths, i.e., we have found the appropriate state graphs. Consequently, the number of graphs describing the state of single-phase systems has decreased drastically. For instance, binary systems had three such potential graphs; but after finding those with the shortest path, only one is left. For ternary systems, the number decreased from 16 to 2. For systems with $C = 4$, the number decreased from 125 to 3 non-isomorphic graphs. Figure 7 shows all such state graphs (obtained by selecting those with the minimal path) for systems with $C \leq 4$ components.

However, Figure 7 indicates that the number of such graphs, η , increases with an increase in C . Thus, for $C = 5$, the value $\eta = 6$, and for $C = 10$, $\eta = 235$ [19]. Harary and Palmer [21] demonstrated that the asymptotic value of the number of single-phase state graphs, for $C \rightarrow \infty$, changed according to the following equation:

$$\eta = 0.535 * \frac{d^{-(C-1)}}{(C-1)^{2.5}}, \quad (22)$$

where $d = 0,338322$.

Every such graph, as long as it has previously met the minimum path criterion, presents a single equilibrium state of an isothermal-isobaric system. Consequently, from a topological perspective, single-phase unary and binary systems can take only one form. However, for ternary systems, the number of equilibrium forms increases to two, one represented by a linear graph with four vertices and the other by a branching graph-tree (see last column of Figure 7).

It goes without saying that more complex systems have more state graphs. However, one of these state graphs is always a linear graph (analogous to the one in unary and binary systems) and the rest are more or less branching trees. A non-branching graph can be transformed into a branching one by gluing together and breaking up its vertices. Some such operations performed on graphs describe the transformation of one phase into another through a two-phase state of the system. In fact, these operations describe two types of phase transformations: congruent and non-congruent [11].

Are there any indications of the difference between the state represented by a linear graph and that represented by a branching tree? Taking into consideration that the states represented by branching graphs only appear for $C \geq 3$, Studies Nos. [11, 22–24] suggested that such graphs represent stable QCs, based on the fact that stable QCs form by means of non-congruent solidification in systems with three or more components. Studies Nos. [11, 23, 24] show that through non-congruent solidification, linear graphs representing crystalline structures can be transformed into branching graph-trees representing an exotic (by implication, quasicrystalline) phase. Later studies by A. P. Tsai [25] and Goldman et al. [26, 27] reported the synthesis of stable QCs in binary systems. However, considering that both elements in these “binary QCs” have multiple isotopes, such QCs should rather be considered pseudobinary, as they achieve thermodynamic stability through the entropy of mixing of the isotopes. Therefore, the findings of Studies Nos. [11, 22–24] related to the interpretation of the state graphs of single-phase systems lead to the following conclusion:

6. *The linear state graphs of single-phase systems describe the systems in a normal state, e.g., a crystalline state. State graphs that are branching trees represent systems in an exotic state, e.g., quasicrystalline.*

The great number and diversity of equilibrium states in systems with many independent components, C , provokes a bold question: how many equilibrium states are possible in systems with the same number of independent components as in an average living organism? The question is impossible to answer for several reasons. We do not know what constitutes an average living organism; we do not know when two or more chemical entities should be treated as a single component, rather than separate components; we do not know how many components the average organism consists of; nor do we know how many reactions connect these components. In other words, the number of independent components in these systems

is ambiguous, to say the least. Under some conditions, we do have a specific answer to a more general question: how many different equilibrium states are possible for the entire biosphere? The aforementioned conditions stem from Brinkey's and Zhao's thesis [28, 29] that associates the number of independent components, C , with the number of: the elements making up each component of the system, M ; r' , i.e., the number of independent reactions that do not occur due to kinetic restrictions; and Z , which differs from zero if, for instance, the composition of one phase is the same as the composition of another one. If such special cases are ignored, then $Z = 0$, as is assumed in our further considerations. An equation follows from this thesis:

$$C = M + r' - Z, \quad (23)$$

Study No. [22] shows that only about 30 elements take part in the functioning of the biosphere as a system. Assuming that all kinetically allowable reactions occur within this model biosphere, i.e., $r' = 0$, the number of different equilibrium states is equal to the number of non-isomorphic state graphs, i.e., trees with about 30 edges. Then, using Equation (21), we can calculate that the system has at least $\eta = 4.03 * 10^{10}$ different equilibrium states. Unfortunately, the number only refers to state graphs in which all edges are of the same type. As has already been mentioned, the edges in such graphs represent the contribution of each component to the Gibbs potential (Equation (21)). Thus, in order to find the number of different equilibriums, we should count the trees with 30 different, rather than same, edges. The distinguishability of the edges does not change the number of graphs for unary or binary systems. However, beginning with systems with $C = 3$, the value η for graphs with distinguishable edges increases dramatically. For instance, whereas only two graphs with same-type edges corresponded to ternary systems, ($\eta = 2$); for graphs with three different edges: A, B, C , $\eta = 4$, i.e., (ABC) , (BCA) , (CAB) and a branching tree $((A)(B)(C))$. How much will the number of state graphs with 30 different edges increase compared to $4.03 * 10^{10}$? I can give no answer because I do not know the solution to the problem of counting graphs with different edges. Another issue to consider is whether the aforementioned number η has anything in common with Earth's biodiversity. From a thermodynamic viewpoint, the representatives of the individual units of biodiversity (varieties, species, genera, etc.) correspond to systems that are from equilibrium. Therefore, if their state is described by the Gibbs function, then it is the function $\Delta G_{n.eq}$, which depends not only on the value of thermodynamic parameters but also on their gradients, i.e., the difference between their values within the system and outside it [22]:

$$\Delta G_{n.eq} = \Delta G_{n.eq} (p, T, x_1, x_2, \dots, x_c; \nabla p, \nabla T, \nabla x_1, \nabla x_2, \dots, \nabla x_c). \quad (24)$$

Furthermore, biodiversity should be counted by state graphs representing the function from Equation (24) rather than the equilibrium counterpart of the function. Of course, it is unknown how such graphs should be constructed, let alone counted. However, all is not lost; we can still use indirect measures. Assume that the gradients in Equation (24) have only a negligible effect on the equilibrium number of the different states of the system. Then, the

number will differ only slightly from the number related to the corresponding equilibrium function:

$$\Delta G_{eq} = \Delta G_{eq}(p, T, x_1, x_2, \dots, x_c; 0, 0, \dots, 0), \quad (25)$$

The number of different states representing this function has been discussed above, and we know that it is much larger than 4.03×10^{10} . The same is true for the number of basic units of biodiversity (species?), i.e., as long as no deviation from the equilibrium significantly affects the number of states, then there are no fewer than 4.03×10^{10} living organisms. I am aware that there are many faults to be found with these musings of a chemist about biodiversity; and such critique would indeed negate this study, if there were any competing approaches to the issue of Earth's biodiversity from the chemical perspective. Unfortunately, I do not know of any such approach. It should be stated that these musings do not pretend to be strict scientific findings; rather, they are meant to indicate a different path leading from chemistry to biology. Let us end with the following conclusion:

7. *Assuming that all kinetically permitted reactions take place within the biosphere and that the non-equilibrium conditions have a negligible effect on the number of types of equilibrium in nature, we may propose that the global number of biodiversity units is counted by trees with 30 different edges, and that this number is greater than 4.03×10^{10} .*

3. SUMMARY

This study investigated two issues related to the properties of the Gibbs function topological manifold in systems with C independent components. The first issue concerned the manifold as a whole, which is piecewise smooth and consists of glued-together regions that each represent the state of a single phase of the system. The second issue concerned the topological properties of the smooth regions of the manifold, in particular, the topological properties of the various single-phase states represented by the individual points of a region.

With respect to the first issue, the topological manifold of any chemical system was found to consist of $C + 2$ smooth regions, glued together along the equilibrium lines, that represent the states of the phases of the system. The state of the system (there is only one, i.e., the invariant state) is represented by 0-vertex state graphs (also referred to as the *graph-maps* of the system), which are inconvenient to use. Due to this inconvenience, a more useful representation of the 0-vertex state graphs was proposed. Such representations were named *normal graphs* because, as with any "typical" graph, they have more than zero vertices (specifically, C vertices, each with an even valence), $C + 1$ edges, and always only four faces. Normal graphs are more convenient than graph-maps in that they can easily be counted for systems of any complexity (Equations (13) and (14)). The ability to count graphs helps to determine the number of permitted ways that the smooth regions of the topological manifold can be glued together into a smooth whole (Equations (13) and (14)). The number

of these ways is also the number of classes of invariant states in complex systems, while the form of the state graph for a given class indicates the composition of each phase of the invariant state.

With respect to the second issue concerning the states of systems represented by a point on a smooth region of the manifold, it was noted that the quantitative measure of such a state is the value of the Gibbs function at a given point relative to a reference state. The reference state for all equilibria of the system is the invariant state. It was found that, according to the topological description of equilibrium, a single-phase thermodynamic state is represented by a tree located on the 2-D surface of a manifold with $C + 1$ vertices, which are all connected by a minimal path. Consequently, the Gibbs function has a particular property: its value is contained within the geometry of its topological manifold. The path on the state graph consists of C edges corresponding to the contribution of each component to the Gibbs function (i.e., $x_X * \mu_X$). For systems with many components, finding a tree with a minimal path is equally as difficult (or even more so) as finding such a path in the traveling salesman problem. In the case of such systems, we may assume that there can exist more than one graph with a minimal (or close to minimal) path for a classically-defined thermodynamic state, i.e., this state can be multistructural. There is a large variety of state trees, including non-branching trees (also called *linear trees*) and branching trees for systems with $C \geq 3$. A non-branching graph can be transformed into a branching one by gluing together and breaking up some its vertices. Some of these operations on graphs describe the transformations of a phase into another phase through a two-phase state of the system. Such operations performed on graphs were found to describe two types of phase transformations, congruent and non-congruent. Until recently in crystallography, QCs were obtained by means of a non-congruent transformation of a crystal. Only a non-congruent transformation of graphs with three or more components can lead from a linear graph to a branching graph [11, 22, 24]. Consequently, this study suggested ascribing linear state graphs to the states of normal phases (such as crystalline phases) and branching state graphs to exotic phases (such as QCs).

The study also proposed that the number of organizational units (e.g., species) of the living organisms within Earth's biosphere can be tied to the number of equilibrium states in systems with about 30 elements.

4. APPENDIX

4.1 THE MAXIMUM VALUE OF THE DEGREE OF DEGENERATION OF THE STATE OF THERMODYNAMIC EQUILIBRIUM

In classical thermodynamics, the quantitative equilibrium in the C -component isobaric-isothermal system is determined by the minimum value of the Gibbs potential measured in

relation to a certain reference state, ΔG . Let us denote by the symbol $\{\mu_i, i = 1, 2, \dots, C\}$ the set of values of chemical potentials of individual components in the equilibrium state. Classical thermodynamics implicitly assumes that for each state of equilibrium, in a single-phase system, there is only one such set which gives the minimum ΔG according to equation (A1):

$$\Delta G = \mu_1 * x_1 + \mu_2 * x_2 + \mu_3 * x_3 + \dots + \mu_C * x_C. \quad (A1)$$

This assumption is equivalent to saying that the state of thermodynamic equilibrium is non-degenerate.

The topological interpretation of the equilibrium shows that the equilibrium state represents a planar state graph, which is a $C + 1$ vertices tree lying on the 2-D surface of a Gibbs function topological manifold. The vertices in the graph are the individual degrees of freedom, the edges connecting the vertex pairs-weighted chemical potentials, $\mu_i * x_i$. Thus, equation (A1) can be interpreted as the statement that the value of ΔG is equal to the length of the minimum path connecting the individual degrees of freedom in the state graph. The problem is that for systems with large C values, there is a huge number of paths connecting the vertices of the state graph ($C + 1$ vertex tree), $\eta_{\Delta G}^o$, namely the number of paths equals: For $C = 2, \eta_{\Delta G}^o = 3$; for $C = 3, \eta_{\Delta G}^o = 16$ (see Figure 7) and $\eta_{\Delta G}^o(C) = (C + 1)^{C-1}$ [19]. The theorem of non-degeneration of the equilibrium state is therefore equivalent to the assumption that in such systems only one path can be of minimal length.

From a topological point of view, the opinion that among the enormous number of paths only one has the minimum length is at least debatable. In the following considerations, we will assume that there are $\eta_{\Delta G}$ of different sets of chemical potentials $\{\mu'_i(k), i = 1, 2, \dots, C; k = 1, 2, \dots, \eta_{\Delta G}\}$ such that for each set μ'_i , the weighted sum (A1) is equal to the Gibbs function. Hence, $\eta_{\Delta G}$, will be the degree of degeneration of the equilibrium state. How to calculate this parameter? To answer this question, let us note that in our search we should take into account two conditions. First, we are looking for a C -element set of numbers, μ'_i , whose weighted sum (A1) gives the same value as the set, $\{\mu_i\}$. Secondly, each product of numbers, $x_i \mu'_i$ should be equal to the distance between the corresponding vertices in the state graph. Since for abstract states of systems we do not know the specific form of the topological manifold, let alone the position of individual vertices in the state graph, we can say that the second condition practically excludes the possibility of calculating $\eta_{\Delta G}$. However, in order not to be content with this impotence, we will continue to try, taking only the first condition into account, to calculate the maximum degree of degeneration $\eta_{\Delta G}^{\max}$.

Of course, a parameter defined in this way may drastically overestimate the real degree of degeneracy, because its calculations also take into account such edges in the state graph that do not connect the real vertices-degrees of freedom of the system. In the presented calculations, the properties of the Heaviside function, $h(x)$, and the Dirac delta $\delta(x)$ will be used. Specifically, we will use the following properties of these functions [30]:

$$h(x) = \begin{cases} 0, & x < 0 \\ 1, & x \geq 0 \end{cases} \quad (\text{A2})$$

$$\delta(x)dx = \begin{cases} 0, & x \neq 0 \\ 1, & x = 0 \end{cases}. \quad (\text{A3})$$

The integral of the second of these functions will be different from zero only if the region of integration contains 0. If we integrate a Dirac delta function whose argument depends on many variables then the value of the integral will be equal to the number of zeros of the argument.

Let us assume that the set of chemical potentials corresponds to me, according to (A1), the values of ΔG . Let us denote by the symbol M_i the quotient:

$$M_i = \frac{\mu_i'}{\Delta G}, \quad i = 1, 2, \dots, C. \quad (\text{A4})$$

It is easy to verify that the values of this parameter meet the following condition:

$$0 \leq M_i \leq \frac{1}{x_i}. \quad (\text{A5})$$

We will now write the dependence (A1) as:

$$1 = M_1 * x_1 + M_2 * x_2 + M_3 * x_3 + \dots + M_C * x_C. \quad (\text{A6})$$

The maximum value of the degree of degeneracy, $\eta_{\Delta G}^{\max}$ of the classical state of equilibrium, will be equal to the number of sets M_i satisfying the equality:

$$[1 - (M_1 * x_1 + M_2 * x_2 + M_3 * x_3 + \dots + M_C * x_C)] = 0. \quad (\text{A7})$$

This number will be equal to the integral of the Dirac delta function:

$$\eta_{\Delta G}^{\max} = \frac{1}{x_1 x_2 \dots x_C} \int \int_0^1 \delta[1 - (m_1 + m_2 + \dots + m_C)] dm_1 dm_2 \dots dm_C. \quad (\text{A9})$$

With the above integration limits after m_1 , the argument of the delta Dirac function, marked with the symbol x , satisfies the condition:

$$-(m_2 + m_3 + \dots + m_C) \leq x \leq 1 - (m_2 + m_3 + \dots + m_C). \quad (\text{A10})$$

So the integral over m_1 is going to be equal to $h[1 - (m_2 + m_3 + \dots + m_C)]$. Thus, the equation (A9) as a result of integration after m_1 takes the form:

$$\eta_{\Delta G}^{\max} = \frac{1}{x_1 x_2 \dots x_C} \int \{ \int_0^1 h[(1 - (m_3 + \dots + m_C)) - m_2] dm_2 \} dm_3 \dots dm_C. \quad (\text{A11})$$

The integral over the variable m_2 gives:

$$\eta_{\Delta G}^{\max} = \frac{1}{x_1 x_2 \dots x_C} \int \{ \int_0^1 [1 - (m_3 + \dots + m_C)] * h[1 - (m_3 + \dots + m_C)] dm_3 \} \dots dm_C. \quad (\text{A12})$$

Successive integrations finally lead to the following result:

$$\eta_{\Delta G}^{\max} = \frac{1}{(C-1)!} * \frac{1}{x_1 x_2 \dots x_C}. \quad (\text{A13})$$

Equation (A13) shows that the maximum value of the degree of degeneration of the thermodynamic equilibrium state depends only on the phase composition, and is greater the more components in this phase are present at low concentrations. This parameter reaches the minimum value at equal concentrations of the system components. Unfortunately, the value of this parameter is not equal to 1, which would indicate no degeneration. Due to the above-mentioned shortcomings of this coefficient, its calculated value also does not prove the existence of degeneration, but only suggests its presence in some equilibrium states. The

question is: How much does the calculated $\eta_{\Delta G}^{max}$ parameter differ from the actual degree of $\eta_{\Delta G}$ degeneration? The writer of these words does not know the answer to this question, but he thinks that he knows what path to look for (this answer). Now let us note that the path set $\{\eta_{\Delta G}^o\}$ is composed of two subsets. One is a subset of minimum length paths through all the vertices of the graph; the second are paths of a different length (greater than the minimum) also passing through all the vertices. On the other hand, the set $\{\eta_{\Delta G}^{max}\}$ is also composed of two subsets. In both subsets the lengths of the paths are the same, but in one subset the paths run through all the vertices (degrees of freedom) of the graph, and in the other the paths omit at least one vertex in the state graph. Thus, the actual degree of degeneration of the thermodynamic equilibrium state, $\eta_{\Delta G}$, will be the number of elements in the intersection of the two sets mentioned above. The question is how to find the common part of these sets?

REFERENCES

1. O. Rüdell, The phase rule and the boundary law of Euler, *Z. Electrochem.* **35** (1929) 54–57.
2. M. A. Klochko, Analogy between phase rule and the Euler theorem for polyhedrons, *Izvest. Sectora Fiz.-Khim. Anal., Inst. Obshei. i Neorg. Khim., Akadd. Nauk SSSR* **19** (1949) 82–88.
3. D. R. Rouvray, Uses of graph theory, *Chem. Br.* **10** (1974) 11–15.
4. T. P. Radhakrishnan, Euler's formula and phase rule, *J. Math. Chem.* **5** (1990) 381–387.
5. L. Pogliani, Phase diagrams and physiochemical graphs. How did it start?, *MATCH Commun. Math. Comput. Chem.* **49** (2003) 141–152.
6. A. I. Seifer and V. S. Stein, Topology composition-property of diagram phase, *Zh. Neorg. Khim.* **6** (1961) 2711–2723.
7. J. Mindel, Gibbs' phase rule and Euler's formula, *J. Chem. Educ.* **39** (1962) 512–514.
8. F. A. Weinhold, *Theoretical Chemistry, Advances and Perspectives*, vol. 3, (Eds.: H. Eyring, D. Henderson), Academic Press, NY, 1978, pp. 15–54.
9. J. Turulski and J. Niedzielski, Use of graph theory in thermodynamics of phase equilibria, *J. Chem. Inf. Comput. Sci.* **42** (2002) 534–539.
10. N. Trinajstić, *Chemical Graph Theory*, 2nd Ed., CRC Press, Boca Raton, FL, 1992.
11. J. Turulski, Dimension of the Gibbs function topological manifold, *J. Math. Chem.* **53** (2) (2015) 495–513.
12. J. Turulski, Number of classes of invariant equilibrium states in complex thermodynamic systems, *Amer. J. Chem. Phys.* **8** (1) (2019) 17–25.
13. H. DeVoe, *Thermodynamics and Chemistry*, (November 2021 web version at: <https://open.umn.edu/opentextbooks/textbooks/715>, pp. 231, 405, 419 .
14. H. Bukowski and W. Ufnalski, *Solutions* (in Polish), W. N.-T. Warsaw, 1995, p. 39.

15. F. Harary and R. C. Read, Is the null-graph a pointless concept? *Graphs and Combinatorics*, Proc. Capital Conf., George Washington Univ., Washington D.C., 1973), pp. 37–44. Lecture Notes in Math., Vol. 406, Springer, Berlin, 1974.
16. M. Ch. Karapientantz, *Chemical Thermodynamics* (in Russian), Khimia, Moscow, 1975, p.122.
17. N. J. A. Sloane and S. Plouffe, *The Encyclopedia of Integer Sequences*, Academic Press, San Diego, 1995.
18. J. H. Conway and R. K. Guy, *The Book of Numbers*, Copernicus, Springer-Verlag New York, Inc., 1998.
19. J. V. Knop, W. R. Müller, K. Szymanski and N. Trinastić, *Computer Generation of Certain Classes of Molecules*, SKTH/Kemija u Industriji: Zagreb, Croatia, 1985.
20. A. Cayley, A theorem on trees, *Quart. J. Pure Appl. Math.* (1889) 376–378.
21. F. Harary and E. M. Palmer, *Graphical Enumeration*, (Chapter: Asymptotics), Academic Press, NY, 1973.
22. J. Turulski and J. Niedzielski, Earth's biodiversity as interpreted by a chemist, *J. Math. Chem.* **36** (1) (2004) 29–40.
23. J. Turulski, Binary self-similar chemical structures, *J. Math. Chem.* **56** (2018) 850–863.
24. J. Turulski, Dimension of the Gibbs function topological manifold: 2. Thermodynamically stable binary quasicrystals: Reality or artefact?, *J. Math. Chem.* **53** (2) (2015) 517–526.
25. A. P. Tsai, J. Q. Guo, E. Abe, H. Takakura and T. J. Sato, Stable binary quasicrystals, *Nature* **408** (2000) 537–538.
26. A. I. Goldman, A. Kreyssig, S. Nandi, M. G. Kim, M. L. Caudle and P. C. Canfield, High-energy X-ray diffraction studies of i-Sc₁₂Zn₈₈, *Phil. Mag.* **91** (19-21) (2011) 2427–2433.
27. A. I. Goldman, T. Kong, A. Kreyssig, A. Jesche, M. Ramazanoglu, K. W. Dennis, S. L. Bud'ko and P. C. Canfield, A family of binary magnetic icosahedral quasicrystals based on rare earths and cadmium, *Nat. Mater.* **12** (2013) 714–718.
28. S. R. Brinkley, Calculation of the equilibrium composition of systems of many constituents, *J. Chem. Phys.* **15** (1947) 107–110.
29. M. Zhao, Z. Wang and L. Xiao, Determining the number of independent components by Brinkley's method, *J. Chem. Educ.* **69** (1992) 539–542.
30. G. A. Korn and T. M. Korn, *Mathematical Handbook for Scientists and Engineers*, (Chapter: 21.9), McGraw Hill Book Company, NY, 1961.