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Metaphysics of Systems: Complexity, Parent System, and the Graph-theoretical Interpretation of Chemical Reaction Mechanisms

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Abstract: The problem of the definition of the category of system as formulated by Karl Ludwig von Bertalanffy is investigated by using the chemical graph theory. General approach to the system within the metaphysical frame is based on the model in which the mechanistic scheme for the cyclopropylcarbinyl network of reactions is used as an example of the abstraction of the category of system. Here, the chemical graph theory is extended to the studies of the organic reaction mechanisms. The relationship between diversity and complexity, as well as the definition of the parent system is discussed.

Keywords: theory of complexity, system theory, chemical graphs, organic reaction mechanisms.

INTRODUCTION

AFTER the formulation of the general system theory by Karl Ludwig von Bertalanffy[1] in the middle of the last century and after the impressive development of the theory of complexity,[2] the intensive studies in this field of science were resulted with the deeper clarification of the principles of complexity and their relationship with the structure of systems. In my previous publications I have proposed the representation of complexity and systems by using the chemical graph theory.[3] In these studies, complexity was explained as a combination of three subclasses: synchronic, diachronic, and combinatorial complexity. Accordingly, any spatio-temporal object called the *actual entity*, or *actuality*, (by using the whiteheadian term) is charactrized with three components of complexity. It appears within the "complexity space" spanned by three "coordinates" (synchronic, diachronic, and combinatorial). A system emerges when the actualities become interconnected such that this aggregate of objects can execute a particular function in the environment. Historically, the system theory in this form has originated from the theory of cybernetics formulated 1948 by Norbert Wiener.[4]

However, the research in the field of the system theory, at the least one which is available in the recent literature, is primarily focused on the development of "system thinking" rather than on the original system science in the form in which it was formulated by Bertalanffy. The research about a rigorous definition of system is almost missing. For instance, the basic question, what is the system *versus* what is not the system, is still open. In rigorous science, the characterization of any category should be based on the heuristic formulation of *the parent structure*, i.e., the simplest arrangement that possesses the basic characteristics of this category. In this work I am trying to represent some proposals about the possible definition of the *parent system* within the classical general system theory by examining some case studies borrowed from chemistry, particularly from chemistry of molecular communications, as well as from the chemical theory of the organic reaction mechanisms. It is also demonstrated that such an approach to the definition of the system could be generalized to the abstraction in which the analogy to some basic physical and chemical principles could be recognized.

CHEMICAL GRAPH THEORY, SYSTEMS AND COMPLEXITY

Before the discussion of the central question of this work, let me review some basic principles of the application of the chemical graph theory to the representation of systems within the "complexity space". Complexity of any object (i.e., actuality) is defined by its positions in the complexity space consisting in three components ("coordinates"): synchronic, diachronic, and combinatorial (Figure 1).

In all of its basic forms (synchronic, diachronic, and combinatorial) complexity is constrained, i.e., it cannot progress *ad infinitum*.[3,5–7] While the synchronic complexity, which is characterized with its level structure, (for instance, atomic, molecular, supramolecular, biological, etc. levels) is limited because, as we go to the higher level, the energy of interaction to form more complex structures diminishes, and it tends to approach to zero. For instance, the energy for the formation of molecules from atoms is 10^6 orders of magnitude lower than the energy for the formation of atoms from subatomic particles, or the energy for the formation of van der Waals complexes is much smaller than the energy of the molecular bond, etc.[6,7]

Diachronic complexity reaches its maximum in oscillations which are in the middle between regular and chaotic behaviour. Good examples for the maximal complexity are movements of planets in the solar system (so called KAM theorem),[8] as well as the kinetics of chemical systems such as Belousov-Zhabotinski oscillator.[9] Maximum of the combinatorial complexity follows from the correlations between diversity and complexity. If the diversity is represented with the Shannon entropy,[10] then the maximal complexity does not appear at the maximal diversity (i.e., maximal Shannon entropy). Rather, it appears in between, even closer to lower diversity.[7]

As we have proposed previously, the system is formed by constructing particular interconnections between actual entities within the complexity space. These interconnections can be represented by graph in which the actualities are denoted by vertices (nodes), and the interconnections by edges (Figure 2).

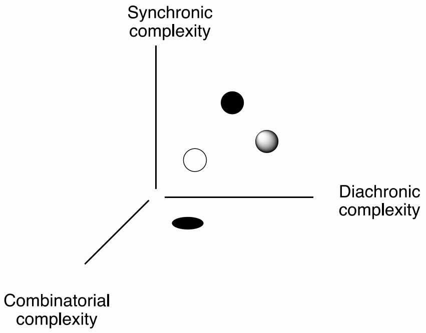

Figure 1. Complexity space: "coordinates" of the synchronic, diachronic, and combinatorial complexity. Actualities are depicted as circular shapes within the coordinate space.

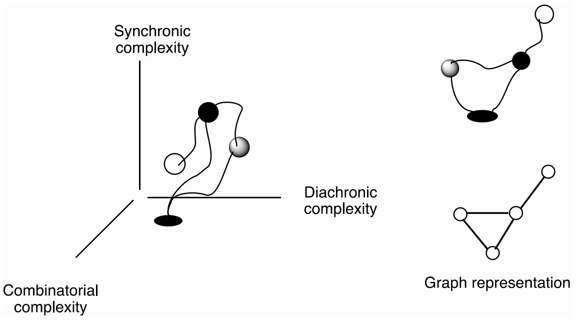

Figure 2. Formation of system by interconnecting of components (actualities), and its graph-theoretical representation. The use of the wiggly vertices on the left side of the Figure has meaning that *only the connections* are important not the nature of these connections.

The advantage of the use of graphs is that the systems can be mathematically represented by a corresponding matrix (*adjacency matrix*) whose determinant can be transformed to the characteristic polynomial. The order of such characteristic polynomial corresponds to the number of vertices. The solution of this characteristic polynomial is a set of values called the spectrum of the graph (Figure 3).

I argue, that the spectrum of the graph, which is the representation of particular system, characterizes also the degree of the complexity of this system. As the spectrum consists of more states (real solutions of the characteristic polynomial), the system is more complex. Accordingly, the statement that maximal complexity of the system does not correspond to the maximal diversity[3,7] can be *inter alia* demonstrated by analysing the complexity of its graph representation focusing on the number of possible real states in its spectrum. For instance, let us analyse two systems, A and B, which both have 6 vertices (which represents actualities), but they are interconnected in different ways (Figure 4). Graph A in the figure is less interconnected than the graph B. Since B possesses more connections between vertices than A, it exhibits higher diversity, i.e., many more paths in walking between the nodes are possible. However, by calculating the spectra of both the graphs it becomes evident that, in spite to its much lower diversity, graph representing the system A is characterized with the spectrum with with 6 states (only real solutions are taken into account) x_1 to x_6, in the comparison with the system B which can only appear in two states. Thus, *the system* A *is more complex than the system* B *in spite to the fact that the vertices in* A *are interconnected to a lesser extent*.

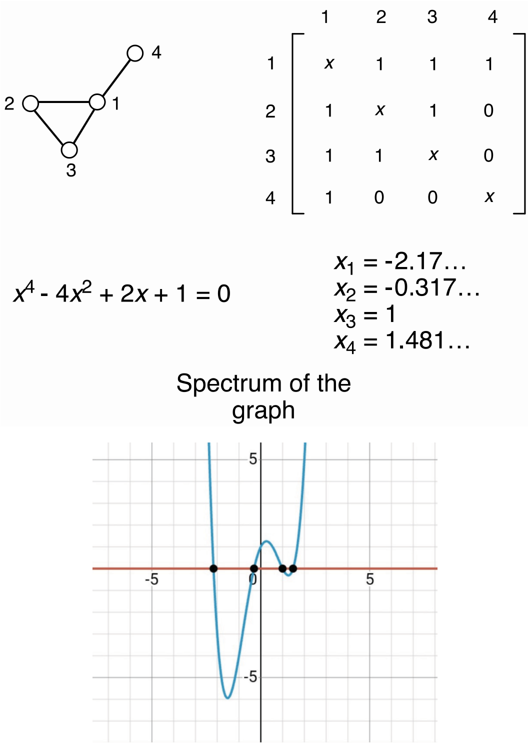

Figure 3. Analysis of the graph representing the system: adjacency matrix, characteristic polynomial, and the graph spectrum (solution of the polynomial, x_1 to x_4). The curve on the lower right corner represents the graph-function of the characteristic polynomial where the dots on the x axis are the solutions x_1 … x_4.

From such graph-theoretical representations of systems we could conclude (i) that the number of the states which (**in this approach!**) represent the complexity of systems cannot be larger than the number of actualities (nodes), and, (ii) that the number of states in the graph spectrum is not correlated with the level of the interconnectivity (diversity).

An illustrative model for such relationship between complexity and diversity should be found in the analysis of the mechanical systems, for instance, in the assembly and function of the timing belt, which is the heart of every standard car engine (Figure 5). The level of the interconnectivity of the machine components by timing belt described with **A** (Figure 5) is lower than the level of the interconnectivity in **B** in which four additional connections between the components are added (red lines in Figure 5). In contrast to **A**, and in spite to its higher diversity, **B** is not functional at all. Thus, **A** is more complex than **B**, and the six states of the graph spectrum which represents the assembly **A** (see the Figure 4, left) can be associated with the six particular machine components and their functions.

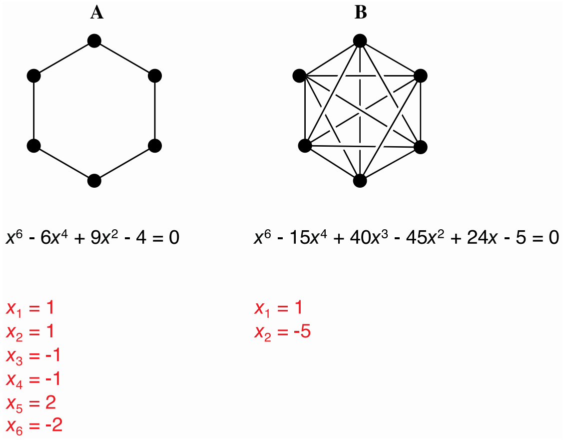

Figure 4. Different levels of interconnectivity of 6 actualities, and the number or states (number of the real solutions of the characteristic polynomial) of their graphs of different diversity.

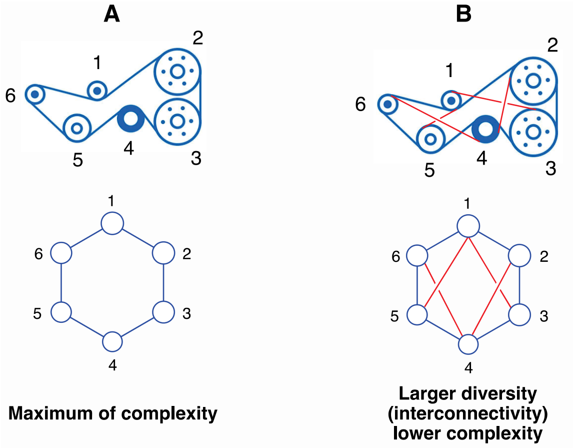

Figure 5. Mechanical model in which the timing belt in the automobile engine is represented by graph. For clarity, 4 additional interconnections between the components 1 … 4 in **B** are labelled in red). As in the Figure 4, the more interconnected engine components (case **B**) decrease the level of complexity, and it is not functional.

INTERMOLECULAR COMMUNICATIONS AND THE PROBLEM OF THE PARENT SYSTEM

Now, when we have already developed our theoretical approach to the problem of the definition of the complexity of systems, we have the tool for the more general, but at the same time more useful characterization of the basic category of system: the search for the *parent system*. The convenient models for the systems which can be represented by graphs appear in the arrangements of intermolecular communications.[11] The examples of such the simplest systems are shown in the Figure 6. The representation of these systems requires the introduction of the *directed graphs* in which the node A is connected with the node B, but not vice versa: the node B is not related to the node A. For instance, in the linear and cascade communication (Figure 6) the left nodes are connected to the right nodes but not in opposite direction. In contrast, in the interactive communication (Figure 6) both of the nodes are interconnected in both the directions.

The connections between nodes in the directed relations are in the graphs labelled with arrows. In some systems such as the communications in the Figure 6 some of nodes are directed and some are in undirected communications. Some examples of directed, and undirected graphs are shown in the Figure 7.

Now, as a case study, let us use two examples of cybernetic arrangements of which the first is constructed only from two components, heater and sensor, and the second is extended with the addition of the thermostat (Figure 8). The *linear* arrangement (which is analogous to the linear intermolecular communications) is represented with the directed graph because the information flows only in the direction from the heater to the sensor. However, in the *interactive* arrangement the communications between heater and sensor are in both directions because the sensor can turn the heater OFF or ON depending on the *required temperature* that is set "*from outside*", by **our** free decision.

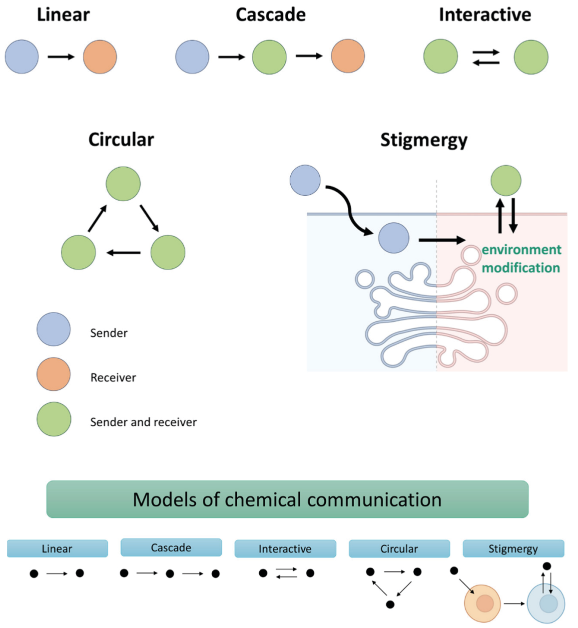

Figure 6. Models of chemical communications between complex molecules. Reproduced with the permission from Ref. [11].

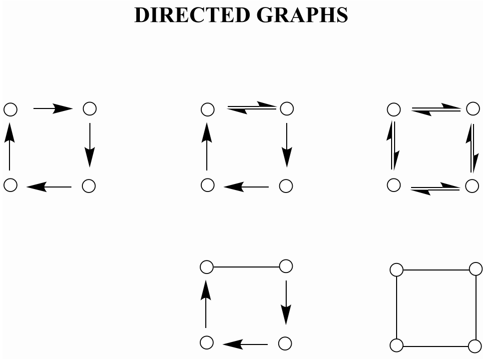

Figure 7. Directed, undirected and partially directed graphs.

By using graph theoretical interpretation, these arrangements can be analysed in the way represented in the Figure 9. The determinant representation of the directed graph (left on Figure 9) is non-symmetrical because there is the communication between H and S (the matrix element is 1), but not the communication between S and H (the matrix element is 0). After the transformation of the determinant to the polynomial, the spectrum of the graph of the linear combination (Figure 9 left) consists from only one state ($x = 0$). In contrary, the spectrum of the interactive communication (Figure 9 right) consists from two states: $x_1 = 1$, and $x_2 = -1$, respectively. Consequently, the interactive communication heater-sensor-thermostat is the system

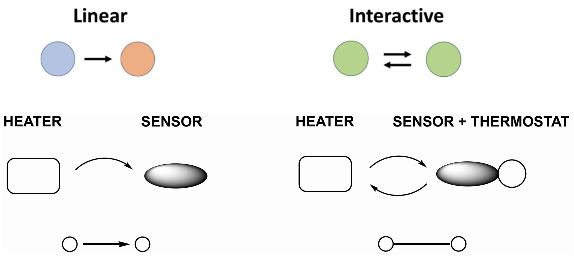

Figure 8. The representation of the parent system.

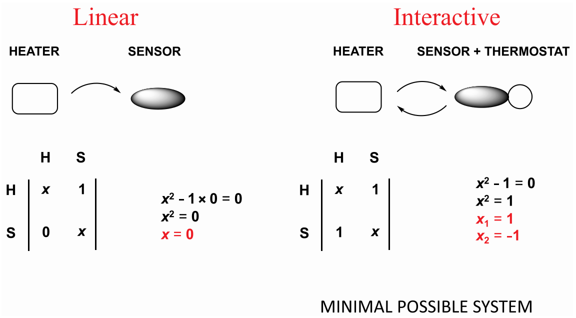

Figure 9. Number of states that are characteristic of the minimal possible system (parent system) must be 2 or higher. H is label for heater, and S is label for sensor.

because it transforms the environment characterized with the "superposition" of all possible temperatures to the narrow range of temperature determined by the *programmed function* of this system. Within the scientific conventionalism, interactive communication could be used as an example of the parent system, the simplest one. Or, conversely, the **parent system** is a combination of actualities which appears minimally in two states (characterized with the two solutions of the characteristic polynomial)!

CYCLOPROPYL CARBINYL PROBLEM AND THE METAPHYSICAL DEFINITION OF SYSTEMS

One of the most prominent models in the discussions about the "nonclassical" structures of carbocations as the reaction intermediates has been focused to the study of the so called "cyclopropylcarbiniy problem". The most interesting finding was that the solvolysis of both, cyclopropylcarbinyl chloride, or cyclobutyl chloride results in the same mixture of the products (Figure 10). In the studies using the low-temperature NMR,[12] and superacid matrix isolations,[13] the phenomenon has been explained by the structure of the reactive intermediate, which is described as the fast equilibrium of bicyclobutonium and cyclopropylcarbinyl cation.

Here we wish to demonstrate how this reaction mechanism could serve as a model for the investigation of the category of system in the most general form. The mechanistic scheme of this reaction and its graph-theoretical representation are shown in the Figure 11. The vertices (nodes) in the graph (Figure 11, bottom) represents the reactant/product structures (A, B, C, D) and the reactive intermediate (#) in its simplified description.

Graph-theoretical approach to this mechanistic reaction scheme can be represented by the matrix,

$$\begin{array}{c|ccccc|}
 & A & B & C & D & \# \\
A & x & 0 & 0 & 0 & 1 \\
B & 0 & x & 0 & 0 & 1 \\
C & 0 & 0 & x & 0 & 0 \\
D & 0 & 0 & 0 & x & 1 \\
\# & 1 & 1 & 1 & 1 & x
\end{array}$$

whose solution provides the polynomial $x^5 - 3x^3 = 0$ with the solutions $x_1 = -1.7320\ldots$, $x_2 = 0$, and $x_3 = 1.7320\ldots$ Thus, the rearrangement cyclopropylcarbiny-bicyclobutyl-methylallyl, if it is considered as a system, has a degree of complexity characterized with three states ($x_1 = -1.7320\ldots$, $x_2 = 0$, and $x_3 = 1.7320\ldots$). This representation could serve for the deeper explanation of the category of system in its general form, i.e., how it has been proposed by original work of Bertalanffy, in which a system is characterized primarily with its function. What is the function of the cyclopropylcarbiniy system? If the components, cyclopropyl carbinyl chloride, and cyclobutyl chloride are mixed in any ratios, they will under solvolytic conditions always transform to the product composition 48 %, 47 %, 5 %, as it is shown in the Figure 10. The function of this system could be considered as if it is an "operator" that transforms the environment with random composition of the reactants to the "predetermined" proper composition (Figure 12).

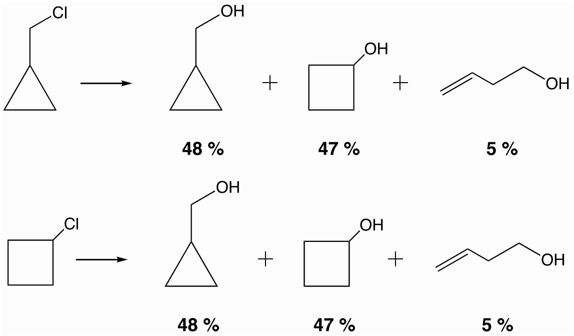

Figure 10. Products of the solvloysis of cyclobutyl and cyclopropylcarbinyl chlorides.

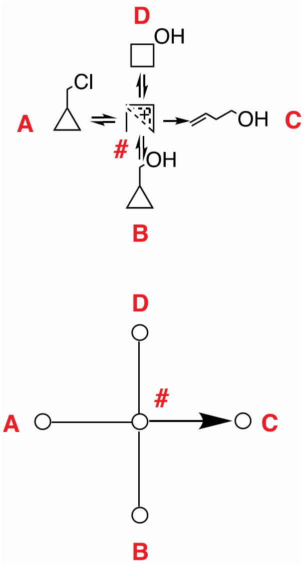

Figure 11. Mechanistic scheme of the cyclopropylcarbinyl rearrangement (top), and its graph-theoretical representation (bottom). The symbol for the reactive intermediate equilibrium is simplified and labelled with #. The reaction from # to C is almost irreversible, and this part of the graph is directed.

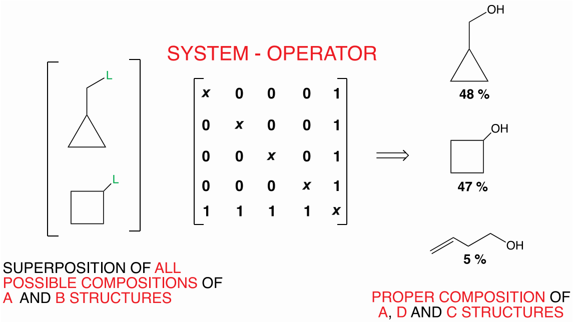

Figure 12. Generalization of the category of system. System as an operator which transforms the environment, i.e. the composition of molecular structures. L symbolizes a leaving group.

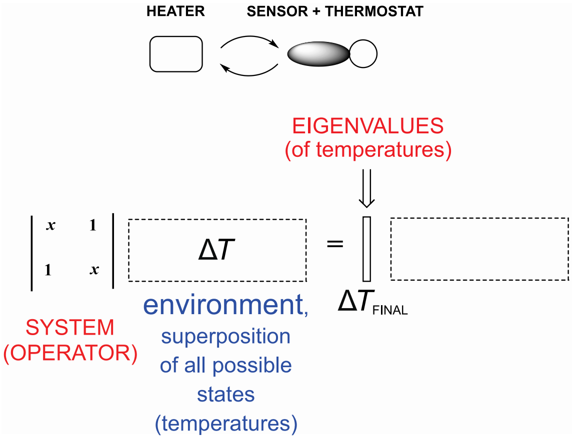

Figure 13. Generalization of the category of system. System as an operator which transforms the environment.

Similar explanation of the relationship between general definition of system and its function can be demonstrated also on the parent system represented in the Figure 8 (*vide supra*). As in the example of the cyclopropylcarbinyl mechanistic system, the parent system, heater-sensor-thermostat, can, in general, be explained as an operator whose function is to transform the "superposition" of all the possible temperatures of the environment to the projected narrow temperature range (Figure 13). The *symbolic* analogy with the Schrödinger equation is not very difficult to recognize.

CONCLUSIONS

In this work we demonstrate how the category of system in the form how it was imagined by Bertalanffy can be represented by using the chemical graph theory. In this approach, complexity of the system is in the relationship with the complexity of its graph spectrum. The larger number of states (i.e., the larger number of the real solutions of the characteristic polynomial) in the spectrum correspond to the more complex system, independently on the level of the interconnectivity. In, addition, the maximal number of states cannot exceed the number of actualities represented by vertices.

Using this approach, we have proposed the way for the definition of system starting with the construction of the parent system, the simplest combination of the actualities that characterizes a system. In this frame, the organic reaction mechanism of the cyclopropylcarbinyl rearrangements has been analysed on the way that all the reactants/products together with the reactive intermediate were symbolized as vertices (actualities) on the graph representing the system, which is in this way considered as a general abstract category. In both the analysed models, the parent system, and the cyclopropylcarbinyl model, the function which is their central characteristic is represented as a number of the real states (i.e., graph spectra).

Finally, in the most general form, perhaps in the metaphysical form, the system is characterized as an operator which transforms the superposition of a plenty of the states in the environment to the narrow definite states. In the parent system example, it is the transformation of wide spread temperatures of the environment to the narrow range values. Similarly, the function of such an operator in the cyclopropylcarbinyl mechanism transforms the random composition of the reactants/products to the final ratio of the compounds. Besides of the use of this reaction mechanism as a model for the study of the general properties of systems, in this work is also demonstrated how the chemical graph theory can be extended to the study of the organic reaction mechanisms in a way that not only the stable products, but also the transition structures (and/or transition states) could be represented as vertices in chemical graphs. This aspect is a matter of our further investigations.

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