

## Phase Diagrams and Physicochemical Graphs. How did it start

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### Abstract

Physicochemical graphs, a concept introduced in 1961 by two Russian scientists, A.L. Seifer and V.S. Shtein, were actually foreshadowed by another Russian scientist in 1928, N.S. Kurnakow. His ideas were further developed by I. Levin in 1946, even if he did not know Kurnakow's work and even if his own work went unnoticed to Seifer and Shtein. Physicochemical graphs were the end result of an attempt to encode by the aid of graph concepts the two- and three-dimensional (and even n-dimensional in Kurnakow's mind) physicochemical phase diagrams. It remained a side-attempt as the main stream of chemical graph theory decided to develop along different directions, centering its attention, mainly, on the properties of molecular structure and dynamics. Nevertheless, visiting again the pages of these four authors a glimpse of the richness of the possibilities of chemical graph theory can be caught, as well as the deepness that hides behind some graph algorithms, which can be used in connection with phase diagrams.

### Prelude

Trinajstić in his opus on chemical graph theory [1] happens to spend some words about the intent, developed by some authors, to use phase diagrams as topological objects [2,3]. It seems that this point of view on phase diagrams went nearly unnoticed among the chemical graph theoreticians and physical chemists. In fact, it did not undergo any further interesting development. The chemical graph community preferred either to further deepen and develop the line started by Wiener in 1947, or develop their own line, both based on a graph representation of molecules, and lately on a graph representation of reaction mechanisms [5 - 20]. Now, the proposed graph objects, named physicochemical graphs by Seifer and Shtein, [4] offer, among other interesting things, an appealing way to rediscover the strange parallelism that exists between the Gibbs phase rule and the Descartes-Euler rule for simple polyhedra. The Gibbs phase rule is a general chemical thermodynamics relation between the

variance  $V$ , the number of components  $C$ , and the number of phases  $P$  for a simple system of any composition [21], i.e.,

$$V + P = C + 2 \quad (1)$$

Here, simple system means a system without fields of any sort (magnetic, gravitational, electric). The variance (or degrees of freedom) can be defined as the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium. Normally, the intensive variables are the temperature, the pressure, and the composition, as expressed as the mole fraction of one component. A phase is a state of matter that is uniform throughout, not only in chemical composition but also in physical state. Thus, we speak of the solid, liquid, and gas phases of a substance (i.e., ice, water, and steam), but also of its various solid phases (i.e., Ice I, II, III, ...). By a component we mean a species present in the system, as for the solute and solvent in a binary solution.

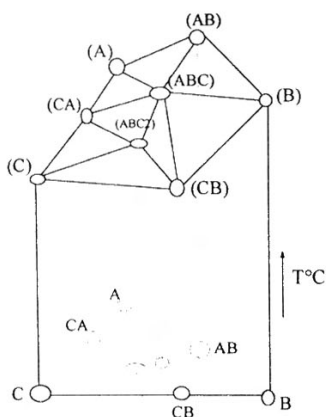
The Descartes-Euler rule for simple polyhedra is a mathematical-geometrical relation between the number of vertices,  $V$ , the number of connections  $C$ , and the number of faces  $F$ , for any simple polyhedra [1]. For simple polyhedra it is meant a polyhedra without holes, such that its surface can be transformed, by a series of continuous deformations, into the surface of a sphere,

$$V + F = C + 2 \quad (2)$$

The physicochemical graphs are, practically, the objects where the two rules meet, as all phase diagrams are of the simple geometric type. These last types of graphs underline not only the versatility of the concept of graphs in chemistry, but it introduces a new way to look at phase diagrams. Aim of this paper is to reopen the chapter on physicochemical graphs giving a rather detailed exposition of the three fundamental papers that have been published on the subject. The exposition will follow a historical thread. It starts with Kurnakow's paper introducing the phase diagram as topological object, goes on with the paper of Levin developing some of the considerations introduced by Kurnakow, and ends up with the paper of Seifer and Shtein widening some Kurnakow's thoughts about the topological character of phase diagrams. These two authors introduced the term physicochemical graphs.

### Kurnakow's 'Verbindung und Raum' [2]

Kurnakow's elaborate work tells us that the physicochemical analysis is studying the relationships between composition and properties of physicochemical systems at equilibrium. This relationship finds its best expression in the diagram composition-property. A closer analysis of the diagram composition-property show an interesting analogy between change in the state of materials (or physicochemical transformations of matter) and positional (situs) changes in the figure (or geometrical transformation of the space). Every information these diagrams enclose about component, phases, and properties is, in fact, expressed by a complex of edges, faces, and vertices that are the main geometrical constituents of these of diagrams, which could be called '*closed connected complex (CCC)*'. The geometry of the *CCC* gives us information about its physicochemical content. The edges and faces of this *CCC* encode information about the stability of every phase. The topological structure of a composition-property diagram reminds, in some way, the structure of a topographic map. It should here be reminded that already Cayley and Maxwell had discussed the topological character of a map of the earth [22, 23].



Let us examine the three-component ( $C = 3$ ) system of the nearby Figure. The system has the shape of a simple polyhedron, whose horizontal isothermal projection is the well-known triangular phase diagram. Here,  $V=5-P$  and, hence the maximum variance is four, as at least one phase ought to be present. Then, holding pressure and temperature constant the variance equals two, i.e., the mole fractions of two components.

This physicochemical polyhedron consists of eight secondary prisms, which are characterized by the A, B, and C components, by the AB, AC, and CB binary species and by the ternary species, ABC, and  $ABC_2$ .

We can now formulate the following topological rule: *the number of secondary triangles (systems) equals the number of Eutectics*. This rule can be used to study the physicochemical diagram, as the exceptions to this rule can be used to detect abnormal equilibrium systems.

The geometric elements of this *CCC* (vertices, edges, and faces) have a special meaning as the meeting point of edges and faces correspond to compounds, which belong to specific phases. It should here be remarked that while topological properties are not dependent on coordinates and neither is the phase rule *per se*, the phase diagram is absolutely dependent on coordinates, which determine the physical conditions of the system, a fact that Kurnakow, to simplify matters does not consider. Thus, in the above Figure the species that are composition and temperature dependent are shown in parenthesis.

Kurnakow, in his work, talks about n-dimensional phase diagrams and gets interested about the problem of time, space and matter, i.e., a problem as old as Plato, and Aristotle and as new as modern physics [24, 25]. His goal is to justify the definition of a chemical space and its metrics, i.e., the space of chemical transformations that should be studied with topological concepts. Interesting here is a citation by Clifford that matter is nothing else than folded space, and a chemical compounds can be seen as a singular folding in space. Kurnakow does not deepen the subject of phase diagrams further, but hopes that the next future will solve the problem of a multidimensional space, which will be able to solve in a topological way any geometric *CCC* complex. In the remaining paper he gets, then, interested in a topological representation of molecules, and rewrites the Descartes-Euler formula for polyhedra in the following way,

$$\alpha_0 - \alpha_1 + \alpha_2 - 2 = 0 \quad (3)$$

Here,  $\alpha_0$  are the number of zero-dimensional objects (vertices),  $\alpha_1$  the number of one-dimensional objects (edges), and  $\alpha_2$  the number of two-dimensional objects (faces). Closed surfaces obey, instead, the following Cauchy relation,

$$\alpha_0 - \alpha_1 + \alpha_2 - 1 = 0 \quad (4)$$

To this type of surfaces belong the surfaces of a phase diagram, and the molecular formulas. For example,  $(\text{CH}_2)_3$  has:  $\alpha_0 = 9$ ,  $\alpha_1 = 9$ ,  $\alpha_2 = 1$ ;  $\text{CH}_2=\text{CH}_2$  has:  $\alpha_0 = 6$ ,  $\alpha_1 = 6$  (all type of bonds),  $\alpha_2 = 1$  (the double bond !);  $\text{CH}=\text{CH}$  has:  $\alpha_0 = 4$ ,  $\alpha_1 = 5$ , and  $\alpha_2 = 2$ ;  $\text{C}_6\text{H}_6$  has:  $\alpha_0 = 12$ ,  $\alpha_1 = 15$ ,  $\alpha_2 = 3+1$ ;  $\text{Ca}=\text{O}$ :  $\alpha_0 = 2$ ,  $\alpha_1 = 2$ , and  $\alpha_2 = 1$ ;  $\text{SO}_3$ :  $\alpha_0 = 4$ ,  $\alpha_1 = 6$ , and  $\alpha_2 = 3$ ;

H<sub>2</sub>SO<sub>4</sub>:  $\alpha_0 = 7$ ,  $\alpha_1 = 8$ ,  $\alpha_2 = 2$ , and so on. It should be noted that a triple bond contributes two cycles. If no cycles are present then the following Listing's relation should be used,

$$\alpha_0 - \alpha_1 - 1 = 0 \quad (5)$$

I.e., for water, H-O-H:  $\alpha_0 = 3$ , and  $\alpha_1 = 2$ , while for ethane, CH<sub>3</sub>-CH<sub>3</sub>:  $\alpha_0 = 8$ , and  $\alpha_1 = 7$ . From these relations some interesting results can be derived, i.e., about the overall number of atoms with odd valence in an organic molecule (always even). The given relations are nothing else than special cases of the following general relation found by Cauchy in 1811,

$$\alpha_0 - \alpha_1 + \alpha_2 - \alpha_3 - 1 = 0 \quad (6)$$

where  $\alpha_3$  is the number of three-dimensional bodies. This is the relation of a 'tree of bodies', which consists of  $\alpha_3$  polyhedra. From this relation a series of special cases can be derived, of which two have already been seen ( $\alpha_3 = 0$ , and  $\alpha_3 = \alpha_2 = 0$ , i.e., relations 4 and 5). Relation 6 can be generalized for n-dimensional bodies,

$$\alpha_0 - \alpha_1 + \alpha_2 - \alpha_3 + \dots + (-1)^n \alpha_n - 1 = 0 \quad (7)$$

For  $\alpha_n = 1$  we obtain the Poincaré's relation, which is valid for an n-dimensional polyhedron, which can be transformed, through a continuous transformation into a sphere,

$$\alpha_0 - \alpha_1 + \alpha_2 - \alpha_3 + \dots + (-1)^{n-1} \alpha_{n-1} = 1 - (-1)^n = \text{const.} \quad (8)$$

For  $n$  even: const. = 0, while for  $n$  odd: const. = 2. Thus, for  $n = 3$  we obtain the famous Descartes-Euler rule, which could be written as:  $\alpha_0 - \alpha_1 + \alpha_2 = 2$ . Relations 7 and 8 with  $n > 3$  could be used to study physicochemical systems with five or more components.

### Levin's 'Phase rule and Topology' [3]

Levin's work can be considered a discussion about some topics of Kurankow's work, with a special paragraph about nonsimple cases, even if Kurnakow is never cited. Levin starts

reshaping the Descartes-Euler rule into a form similar to eq. (6),

$$1 - F + C - V = -1 = (-1)^3 \quad (9)$$

The  $1$  on the left-hand side of this formula represents *one* volume or *one* three-dimensional item. This equation like eq. (6) now follows the geometric sequence,

$$\text{volume} \rightarrow \text{area} \rightarrow \text{line} \rightarrow \text{point}$$

This is the natural scheme that is followed when, a certain composition within a three-component three-dimensional isobaric phase diagram (previous Figure) cools from the upper homogeneous miscible liquid phase into the completely solid heterogeneous eutectic region. The last eutectic ABC2 has a lower free energy than the other points in the diagram. The phase rule can also be rewritten in a topological form similar to eq. (9), i.e.,

$$1 - P + C - V = -1 = (-1)^3 \quad (10)$$

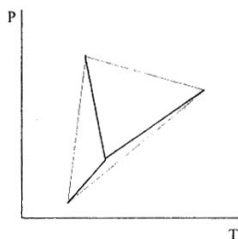
Number  $1$  on the extreme left and the exponent  $3$  represent one generalized three-dimensional phase diagram. As for two-dimensional diagrams, they are always projections or sections cut from a three-dimensional diagram regardless of the number of components. This for what concerns the simple surfaces. In the topology of non-simple surfaces a given surface (closed, one-sided, etc.) is placed in a certain *genus*,  $p$ , which is equivalent to the number of holes contained by the surface. A comprehensive form of eq.2, including such non-simple cases is

$$V + F = C + 2 - 2p \quad (11)$$

Where  $2 - 2p$  is called the Euler characteristic. A cube with a cubic hole in it has  $p = 1$ , 16 vertices ( $V$ ), 16 faces ( $F$ ), and 32 edges ( $C$ ) and satisfies eq. 11. This formula is similar to the phase rule if it is modified as follows,

$$V + P = C + 2 - r \quad (12)$$

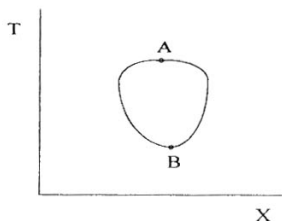
Where  $r$  may represent other variables, such as gravitational forces, electric or magnetic fields, or capillarity. Two examples can be used to underline the correlation between phases and faces, components and edges, degrees of freedom and vertices, as, in Levin's words: *for phase diagrams the phase rule imposes physically what the Descartes-Euler equation describes geometrically.*



Among the different examples Levin discusses there is an application of equation 4, where a P-T water phase diagram should be modified as in the nearby figure to become apparent. The real phase diagram is open, made up of the three converging curves only.

Here,  $\alpha_0 = 4$ ,  $\alpha_1 = 6$ , and  $\alpha_2 = 3$ , and eq. 4 holds

He then considers the nicotine-water type of system in a two-dimensional T-X temperature-composition isobaric diagram, shown in the nearby figure. Here the closed curve encloses the region of the immiscible phase. To satisfy eq. 4 the two critical points A and B should be considered, then,  $\alpha_0 = 2$ ,  $\alpha_1 = 2$ , and  $\alpha_2 = 1$ .



When this figure is transformed into three dimensions, with pressure  $P$  as the third dimension, the result is a conoid. Then to hold eq. 6 (or 9) the critical curve joining  $A$  and  $B$  along the conoid, i.e., halving the conoid, should be considered and then,  $\alpha_0 = 2$ ,  $\alpha_1 = 3$ , and  $\alpha_2 = 3$ , and  $\alpha_3 = 1$ .

Levin, after having emphasized how the phase rule and the Descartes-Euler rule are synonymous and how the phase diagrams can be treated as topological objects, ends his work with the hope that further work on the subject will be done in the near future.

#### **Seifer and Shtein's 'Topology of Composition/Property Diagrams for Binary Systems' [4]**

Seifer and Shtein took up Levin's hope, without citing him but largely citing Kurnakov's work, even if here Kurnakov is cited ending with a  $v$  (maybe a printing error of the English edition). In this paper these two authors introduced the concept of physicochemical graphs.

The paper is written with the aim (i) to define a machine language of physicochemical analysis, and (ii) to describe the composition/property diagrams of binary systems in a topological way. They develop, thus, some principles for the topological description of phase diagrams for the memory of electronic computers, which could allow a search of these records for a diagram of any structure.

The diagram of a binary system is seen as a two-dimensional closed complex of points, lines, and surfaces (fields), which is called *primal complex*. The conversion of this primal complex into a physicochemical graph is shown in Fig.4, where the diagram of a eutectic system is taken as primal complex. A graph dual to the primal one is first constructed, where each field of the diagram corresponds to a point of the '*vertex-field*' dual graph (Fig. 4-left). The whole region lying outside the closed complex forms a null field, which corresponds to the '*null N*' vertex of the graph. The graph at the left describes only the relative position of the fields in the primal diagram. Further, each intersection of the edges of the dual graph with the edges of the primal complex is marked by a '*vertex-boundary*' point. In the new graph (Fig. 4-middle) vertices-boundaries are between the vertices-fields. For every field their number is equal to the number of lines separating the given field from the others. Thus, the field lying below the *solidus* line in Fig.4 is described by a vertex-field, *b* (open circle) and five vertices-boundaries, *a* (black circle), which brings about the appearance of new edges in the graph.

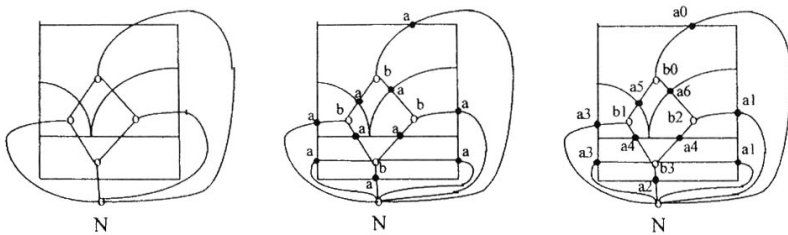


Figure 4. Successive construction of a physicochemical graph: (left) dual from the primal complex, (middle) graph with vertices of two colors, (right) physicochemical graph (for the sake of clarity use of subscripts has been avoided in the rightmost figure).

While *a* vertices are second-order vertices, with two arcs, *b* vertices have an order not less than two and some of them are nodes with an order equal to or greater than three. Hence, in the middle graph vertices are of two '*colors*'. In the right graph of Fig. 4 vertices are marked.



Now, it is possible to have in a single record information about the general structure of the diagram and about its specific chemical compounds. In this, all vertices,  $a$ , which are formed from one line of the initial diagram, always have the same color (see in Fig. 4-right). One of the simplest ways of recording graphs is through the construction of a table of stars. Let  $a_0, a_1, \dots, a_i$  be vertices-boundaries, and  $b_1, b_2, \dots, b_i$  be the vertices-fields of the physicochemical graph. These vertices-fields would record *liquid, solid solution*, and other forms. Then each row of the table of stars has this form:  $b_q — a_i b_s, a_{i+1} b_{s+1} \dots$

That is, following the symbol of every vertex-field are all the branches of the graph recorded in succession, proceeding from this vertex. Every branch consists of two vertices - a neighboring  $b$  vertex and the vertex  $a$  lying between two  $b$  vertices. Essentially each row of the table is a symbolic record of one of the determined fields of the diagram with an indication of the neighboring fields and bounding lines. The complete assembly of rows for all type  $b$  vertices of the physicochemical graph can be recorded linearly, with separation of the rows by some symbol. As an example are given the linear records of physicochemical graphs for equilibrium diagrams of binary systems with unlimited solubility of the components in the solid and liquid states with a maximum (*l*-carvoxime-*d*-carvoxime system), or a minimum (Cu-Au system) melting point, and without them (Ge-Si system). The primal diagrams of these systems and their physicochemical graphs are shown in Figures 5 - 7.

Diagram without melting point extremum (Fig. 5):

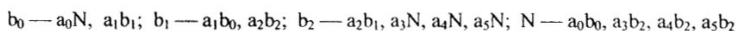


Diagram with a maximum melting point (Fig. 6):

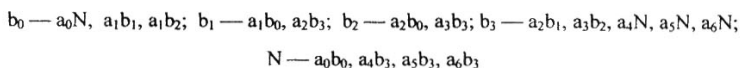
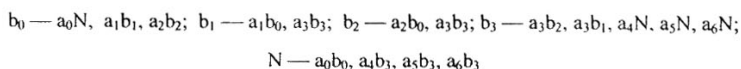


Diagram with minimum melting point (Fig. 7):



A search in the memory of the machine for all the diagrams of similar general structure, or of all the diagrams with the same structure of the individual parts is reduced to finding by means of a special program an enclosed subgraph in the graph. Such subgraphs will be linear subgraphs  $a_i b_j a_k$ , where  $b_j$  is a non-nodal vertex (cf. Figs. 5 - 7). Thus, to find systems with a maximum melting point, we just determine the inclusion in the physicochemical graph of the cyclic subgraph  $b_0 a_1 b_2 a_3 b_3 a_2 b_1 a_1 b_0$  with vertex  $b_0$  (liquid) directly connected with two type  $a$  vertices of the same color ( $a_1$  in Fig. 6).

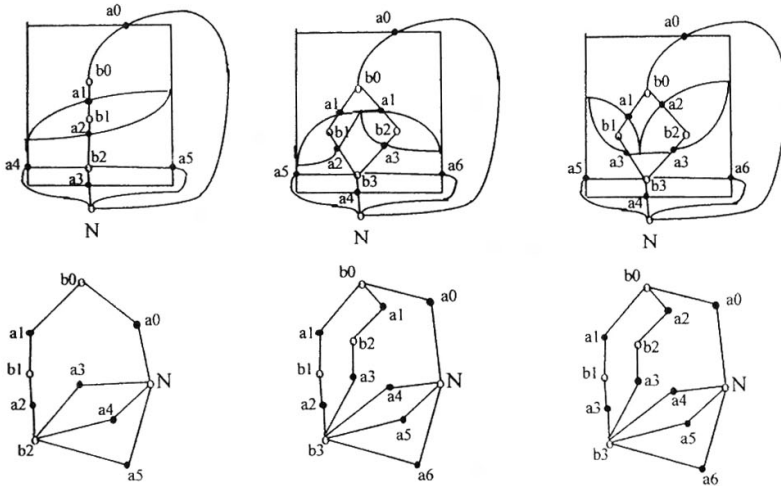


Fig. 5. Ge-Si system and its physicochemical graph. Fig. 6. l-carv-d-carv system and its physicochemical graph. Fig. 7. Cu-Au system and its physicochemical graph.

This cyclic subgraph distinguishes it from the cyclic subgraph for the system with a minimum melting point,  $b_0 a_2 b_2 a_3 b_3 a_3 b_1 a_1 b_0$ , which has  $b_3$  directly connected to two  $a_3$  vertices (Fig. 7). The physicochemical graph of the diagram of the Ge-Si system (Fig. 5), with neither a maximum nor a minimum, does not have such a type of cyclic subgraph. The given procedure can be used with other types of diagrams, with the limitation that it is possible for a planar representation of chemical equilibrium systems only.

## Finale

And, how did it end ? Practically, the discussion about physicochemical graphs ended here. The impossibility to encode quantitative information about temperature, composition and other physicochemical properties of the system, like pressure, fields, and so on, played a no minor role in their fading from the forefront of the chemical graph scene. While chemical graphs, through the definition of an abundant series of invariants could be used for quantitative prediction, physicochemical graphs, instead, suffered from the lack of invariants that could have helped them to enter into the field of quantitative predictions. They suffered also from the lack of a deeper systematization of the type developed by Temkin, Zeigarnik and Bonchev for the kinetic aspects of the chemical reactions.

Thus, if on one side Levin's hope is still open, on the other side the present application of topology to phase diagrams shows the righteousness of *Lobatschewsky's* dictum : *'There is no branch of mathematics, however abstract, which may not some day be applied to phenomena of the real world'*.

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