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Review Article

The Graph Model of the Transport Phenomena

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Abstract

The transport phenomena mean the variation in time and space of generalized forces when they generate flows for which conservation laws apply. The Onsager principles states that all the flows are linear functions of the gradients which act in the system, which is valid in the case of the processes slow enough to be a real hypothesis of the local equilibrium. We can interpret the conductibility coefficients (transport coefficients) defined by the phenomenological theory and determined experimentally based on the molecular theory of transport processes and we can calculate them with the help of the molecular parameters. The various transport processes can be coupled on the basis of Curie's principle, which says that in the isotropic systems, if there are interactions which can be described through linear laws, then the forces and flows of various tensorial orders and different characters do not interfere with one another. The biophysical models of crossed effects have not been elaborated too rigorously (detailed), this being the cause for which in the description of the processes found in the living organisms, there are bigger discrepancies between models and reality. We must underline the fact that the flow produced through the difference of hydrostatic pressure is not considered a real transport phenomenon; this is why the crossed effects they participate in are not real crossed effects.

Keywords: Transport phenomena, Graph model, Onsager's postulate

Introduction

Transport phenomena mean the variation in time and space of generalized forces when they generate flows for which conservation laws apply (*J. Vincze* 1967). This general and strongly scientific definition of the transportation phenomena has two major merits:

1) Forms of transportation can be deducted from it (mass transport - diffusion; energy transport - thermal conductibility; impulse transport - viscosity; task / load transport - electric conductibility, crossed effects and other)

2.) It allows a quantitative characterization of the product exchange, which was impossible based on the previous definitions [1,2].

Definition of the Transport Phenomena

If W-the amount of the transported parameter, for which the conservation law is valid; K-a constant dependent on the type of transportation and the nature of the transported parameter; grad a-the generalized force, then the amount of the parameter (flow) transported through the surface dS in the dt time frame will be given by the relation:

$$W = K\int_{t_1}^{t_2} \iiint_{S(x,y,z)} grad\ a\, dS\, dt$$

If the transportation takes place only after a direction x, then we obtain the formula:

$$W = K\int_{t_1}^{t_2}\int_{x_1}^{x_2} grad\ a_x dx\ dt$$

The differential form is the following:

$$\partial W = K\cdot\frac{\partial a}{\partial x}\cdot\Delta S\cdot\Delta t$$

By making the proper replacements in the relation above, we obtain the classical laws which describe simple transportation phenomena. With nonstationary transportation we understand those forms of transportation where the value of the flow is modified in time from one point to the other.

The Onsager Principles

By synthesizing the equations which describe the transport phenomena, we reach the general conclusion according to which that flow (φ) is directly proportional with the conjugated thermodynamic Force (F), that is φ = A.F, where A is the matrix of the conductibility coefficients. Matrix A does not contain the gradient explicitly, but it can contain several sizes connected to that phenomenon, among which measures appear in the formula of the gradient. This is the first linearity law of Onsager [3]. We already demonstrated for simple transport phenomena, that the fact that each flow is in linear relation with the conjugated generalized force. The linear relation can be extended to the case of the coupled transport processes, which allows the discussion and the general description of the transport processes [4,5]. Therefore, the flow of an extensive measure is not determined only by the non-homogeneity of the conjugated intensive measure, but it can also be influenced in principles by all the present thermodynamic forces [6].

The Onsager principles state that all the flows are linear functions of the gradients which act in the system, which is valid in the case of the processes slow enough to be a real hypothesis of the local equilibrium [7]. In a first approximation, we can accept these conditions, obtained the following relation among all the flows (φ_i) for the general case and all the generalized forces (Fj) from the given system (from a system):

$$\begin{aligned}
\varphi_1 &= A_{11}\cdot F_1 + A_{12}\cdot F_2 + \cdots + A_{1n}\cdot F_n \\
\varphi_2 &= A_{21}\cdot F_1 + A_{22}\cdot F_2 + \cdots + A_{2n}\cdot F_n \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\varphi_n &= A_{n1}\cdot F_1 + A_{n2}\cdot F_2 + \cdots + A_{nn}\cdot F_n
\end{aligned}$$

The relations which establish the various flows and forces which generate them are called phenomenological equations [8].

The phenomenological equation obtained can be written as matrix, in the form of:

$$(\varphi_k) = (A_{ki})\cdot(F_i)(K = 1,2,\cdots,n; i = 1,2,\cdots,n)$$

According to Onsager's postulate [3] referring to the coupled processes, the coefficient matrix is symmetrical, hence the symmetric coefficients are equal: Aij = Aji. The value of the determinant formed by the conductibility coefficients $\| A_{ki} \|$ is equal, according to the law of algebraic calculation, to the amount of the products between the elements of a line (Aji) and its algebraic complement $\| A_{ik} \|$ that is

$$\| A_{ki} \| = \sum_{k=1}^{n} A_{ki}\cdot \| A_{ki} \|$$

A coupled transport process formed of n flows and n forces, contains n processes of direct transports and . crossed effects. From here it results that the equation system includes several pairs of crossed effects, so the number of the independent conductibility coefficient which must be determined experimentally will be n+[9]. We can interpret the conductibility coefficients (transport coefficients) defined by the phenomenological theory and determined experimentally based on the molecular theory of transport processes and we can calculate them with the help of the molecular parameters [10]. Let us take the case in which n=4 and have the following processes of simple transport: diffusion, thermal conductibility, electric conductibility, and the internal rub (viscosity) as well as all the pairs of corresponding crossed effects.

$$\begin{aligned}
\varphi_1 &= A_{11}\cdot F_1 + A_{12}\cdot F_2 + A_{13}\cdot F_3 + A_{14}\cdot F_4 \\
\varphi_2 &= A_{21}\cdot F_1 + A_{22}\cdot F_2 + A_{23}\cdot F_3 + A_{24}\cdot F_4 \\
\varphi_3 &= A_{31}\cdot F_1 + A_{32}\cdot F_2 + A_{33}\cdot F_3 + A_{34}\cdot F_4 \\
\varphi_4 &= A_{41}\cdot F_1 + A_{42}\cdot F_2 + A_{43}\cdot F_3 + A_{44}\cdot F_4
\end{aligned}$$

Based on algebraic decomposing, the value of the determinant can be written as sum of the partial determinant products, with the corresponding algebraic complementariness. In the case of the given quadruple coupled process, the decomposing is effectuated taking determinants of 2nd rank and their algebraic complementary (also 2nd rank!):

$$\begin{vmatrix} A_{11} A_{12} \\ A_{21} A_{22} \end{vmatrix} \cdot \begin{vmatrix} A_{33} A_{34} \\ A_{43} A_{44} \end{vmatrix} + \cdots + \begin{vmatrix} A_{13} A_{14} \\ A_{23} A_{24} \end{vmatrix} \cdot \begin{vmatrix} A_{31} A_{32} \\ A_{41} A_{42} \end{vmatrix}$$

This discomposure is extremely important from the biological point of view, because it proves that for any even n the coupled transport processes can be considered interactions of the crossed effects. If n is odd, then the coupled processes must be seen as interactions between the crossed effects and the simple transports [11]. The various transport processes can be coupled on the basis of Curie's principle, which says that in the isotropic systems, if there are interactions which can be described through linear laws, then the forces and flows of various tensorial orders and different characters do not interfere with one another. This principle is very important for the study of transport processes and chemical reactions [12]. The measures which interfere in the chemical reactions are scalar, while the generating forces and flows are vectorial or tensorial. According to Curie's principles, the coupling is produced only in anisotropic systems (membranes with asymmetrical structure) and the living systems are almost always anisotropic. The maintaining of the generalized forces requires certain sources which can be found either in the given system or outside it or on the limit of the surface between the phases. Generally, we can state that the source's tensoric order is always equal to the one of the flow and the one of the generating force is higher by one.

For the anisotropic systems studied by Prigogine and Bălescu [13,14], in which the transport processes take place fast, Curie's principles is not valid anymore. Kedem and Katchalsky [15] have established that according to their nature, the coefficients which characterize the phenomenological systems are rubbing coefficients, being scalar in a first approximation, but with a better approximation they have tensorial character [16].

The phenomenological equations can also be represented by grafts, Berge and Ore - the fathers of the graft theory - elaborated a series of mathematical models which are used widely for solving various technical problems. Let us take the case of a system in which we find three flows and three forces, characterized by the following phenomenological equations:

$$\varphi_1 = A_{11} \cdot F_1 + A_{12} \cdot F_2 + A_{13} \cdot F_3$$
$$\varphi_2 = A_{21} \cdot F_1 + A_{22} \cdot F_2 + A_{23} \cdot F_3$$
$$\varphi_3 = A_{31} \cdot F_1 + A_{32} \cdot F_2 + A_{33} \cdot F_3$$

The corresponding graft is represented in Figure 1.a.

The question is, however, what will this graft look like when the generalized forces interact with one another? The illustration of such a case can be seen in the graft in Figure 1.b.

If we write the algebraic equations corresponding to this graft, we obtain exactly the generalized phenomenological equations [17,18]. On the writing of the first equations system, we will introduce an intermediary variable (fi), which makes the connection between forces and flows:

$$\varphi_1 = A_{11}' \cdot f_1 + A_{12}' \cdot f_2 + A_{13} \cdot f_3$$
$$\varphi_2 = A_{21}' \cdot f_1 + A_{22}' \cdot f_2 + A_{23} \cdot f_3$$
$$\varphi_3 = A_{31}' \cdot f_1 + A_{32}' \cdot f_2 + A_{33} \cdot f_3$$

$$f_1 = B_{11} \cdot F_1 + B_{12} \cdot F_2 + B_{13} \cdot F_3$$
$$f_2 = B_{21} \cdot F_1 + B_{22} \cdot F_2 + B_{23} \cdot F_3$$
$$f_3 = B_{31} \cdot F_1 + B_{32} \cdot F_2 + B_{33} \cdot F_3$$

The two equation systems make together the generalized phenomenological equations, where the nature of the matrix coefficients (Aij) results from the classic phenomenological coefficients, hence it coincides with the nature of the matrix coefficients (Aij). The coefficient of the matrix (Bij) are the correlation coefficients about which we know that are characterized by reciprocity conditions, that is Bij = Bji which is also the condition of Onsager's postulate. Hence, we reached the extension of Onsager's postulate, because if Bii = 1 and Bij = 0 and we obtain exactly the initial phenomenological equations [19,20]. In certain conditions, the Onsager's reciprocity principles can be considered a natural law (Figure 1).

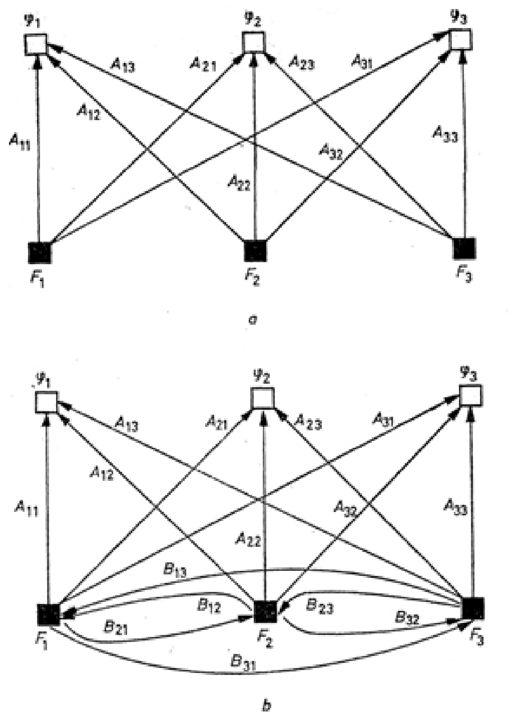

Figure 1: Graph model in three cases.

Crossed Effects

The biophysical models of crossed effects have not been elaborated too rigorously (detailed), this being the cause for which in the description of the processes found in the living organisms, there are bigger discrepancies between models and reality. The biophysical processes which characterize the biological systems can be better described by knowing the coupled transport processes [21]. In these systems the flows are not independent from one another, but they influence one another. Hence, in the living organisms, flows are not generated only by the conjugated generalized forces, but also by the simultaneous action of other forces. Generally, in the system there are as many flows as generalized forces and each force partially participated at the generation of each flow, so the simple types of the transport processes interfere with one another. It is extremely important the fact that the coupled transport systems can be reduced to the interconnected effect of the crossed effects.

In most biological systems, more gradients act in general. For example, in the case of electrolytes, the concentration and the potential gradient cam function all the same. Several flows can coexist simultaneously. A certain type of flow is determined not only by the corresponding gradient, but basically it can be influenced by any force. In a simpler case, when there are two flows and two corresponding gradients, then, except for simpler transport phenomena, there are interactions between the existing flows and forces, namely the so-called crossed effects [22,23]. Thermos diffusion is the most typical crossed effect between the non-equilibrium thermodynamic processes. Under the influence of a permanent temperature difference, in a gas mixture or solution, there is a separation of the components or a concentration difference. Because of the temperature gradient a mass transport takes place, which is nothing else but the transfer of caloric energy through convection. The crossed effects in which gradient act and reciprocally interconnect flows form pairs of reverse effects. In the following paragraphs we briefly explain those above through the effect dealt with in the previous paragraphs.

a. Seebeck effect: Peltier effect (under the influence of a temperature difference there is an electric current and vice versa).

b. L. Soret effect: Dufour effect (the temperature difference produces the modification of the concentration and vice versa).

c. Thermal mechanical effect: mechanical caloric effect (in an osmometer containing a semi-permeable membrane a water current starts from the warmer area to the colder one, producing a difference of hydrostatic difference and the other way around).

The couples of crossed effects are included in Figure 1. We must underline the fact that the flow produced through the difference of hydrostatic pressure is not considered a real transport phenomenon; this is why the crossed effects they participate in are not real crossed effects. The hydrostatic pressure difference produces a volume flow for which no conservation law is valid, hence it is not a real transport phenomenon. Moreover, in the solution we cannot talk about their hydrostatic pressure and the gas, without a constant liquid volume, respects other laws. But since the liquids' hydrostatic pressure has a remarkable importance, we considered it useful to include this phenomenon in the discussion of the transport phenomena. The frequency with which we find different types of reverse effects shows great variations. In table I. we denoted with * the very frequent pairs which lie at the basis of a lot of physiological processes, the action potential, absorption, substance transport in blood from the interstitial liquid and from here in the cells, secretion, breath, hence they lie at the basis of most of the metabolic processes.

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Conflict of Interest

None.

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