

Should the cross-phenomenological coefficients be vectorial?

V. S. Vaidhyanathan and V. Sitaramam*

Department of Biophysics, State University of New York at Buffalo, Buffalo, NY, USA.

*Biotechnology, University of Poona, Pune 411 007, India

Coupling of matter flux with chemical/enzymatic reactions in biological processes implies the existence of cross phenomenological coefficients. Since material transport is often directional and an asymmetry of the system is equally identifiable, the former prompted the improvisation of vectorial cross coefficients while the latter appeared to justify such an improvisation. Transport as well as chemical, enzymatic reactions can be described as vectorial fluxes with appropriate dimensions such that the cross coefficients as well as the dissipation function can be correctly represented as scalars.

IRREVERSIBLE thermodynamics has made a major contribution to our understanding of complex biological processes in permitting their description in reasonably explicit thermodynamic terms¹⁻³. The nexus between chemical processes and physical processes in terms of thermodynamics found its natural path of development in a search for coupling between metabolism and transport, the latter representing a ubiquitous and relevant physical process, also mechanistically based on enzyme-related (catalytic) processes.

However, it is a matter of concern that thermodynamic approaches have contributed less than one would have expected of a formal rigorous approach. The assertion that free-energy coupling can be formulated¹ has not clarified the means deployed for such coupling. One does not have to look far for the underlying reasons. There are significant shortcomings in the formulation of a link between chemical and physical processes both from the point of view of a phenomenological description and in terms of proper dimensional consistency. The critical unanswered question remains: how does a scalar reaction cause a vectorial flux?

Let us examine the origins. Kedem⁴ argued that in the dissipation function,

$$\Phi = J_w \Delta \mu_w + J_1 \Delta \tilde{\mu}_1 + J_2 \Delta \tilde{\mu}_2 + vA, \quad (1)$$

where the subscripts w, 1 and 2 refer to water, cation and anion respectively, the importance is in the addition of the reaction term vA to the dissipation function owing to material fluxes. The corresponding phenomenological coefficients could be written as

$$\Delta \mu_w = R_{ww} J_w + R_{w1} J_1 + R_{w2} J_2$$

$$\Delta \tilde{\mu}_1 = R_{1w} J_w + R_{11} J_1 + R_{12} J_2 + R_{1r} v$$

$$\Delta \tilde{\mu}_2 = R_{2w} J_w + R_{21} J_1 + R_{22} J_2 + R_{2r} v$$

$$A = R_{r1} J_1 + R_{r2} J_2 + R_{rr} v. \quad (2)$$

The symbols v and A refer to velocity and affinity respectively, as defined by DeDonder⁵. The non-zero values for cross coefficients R_{1r} and R_{2r} indicate coupling between ionic flows and reaction; it is assumed that no direct coupling exists between flow of water and the reaction. These cross-coefficients coupling matter fluxes to the reaction are vectorial, unlike the other coefficients, which are all scalars. The meaning of a vectorial coefficient is sought within the asymmetry of the membrane since an isotropic phase will not permit coupling between a scalar and a vectorial flow⁶.

A few points in this connection are worth making. Asymmetry essentially implies inhomogeneity, implying that scalar phenomenological coefficients, like diffusion or frictional coefficient, are dependent on a position variable. If matter flux of the k th species, $J_k = -D_k (dc_k/dx)$, is to be maintained constant under stationary-state conditions, in the absence of chemical reactions, and if the concentration profile of k is not linear in the membrane system, it is necessary that the diffusion coefficient D vary as a function of x . Secondly, the dissipation function is obviously a scalar. A scalar can be arrived at as a product of two scalars or as a dot product of two vectors. Therefore, by necessity, the phenomenological coefficients, which represent the constants of proportionality, must necessarily be scalars. If one represents the cross-phenomenological coefficient between a scalar reaction and a vector matter flux as a vectorial coefficient, one obtains a somewhat strange matrix of phenomenological coefficients, in which all the diagonal elements and most of the off-diagonal elements are scalar, and two or four off-diagonal elements vectors. Since the purpose of an irreversible-thermodynamic description is to describe the processes in realistic terms, this postulation of vectorial phenomenological coefficients remained of doubtful value⁷⁻¹⁰.

One may also question the validity of the explicit assumption that no direct coupling exists between flow of water and chemical reaction. Living systems are

compartmentalized; cotransport of water affects internal volume and thereby the concentration of the reactants, and secondarily the reaction rates and possibly their equilibria. Further, dimensional consistency requires that the coupling coefficient be vectorial between chemical reaction and matter flux in the formulations (see Appendix). One has two possible, though not mutually exclusive, solutions to the problem of phenomenological description of the influence of chemical reactions on matter fluxes: either one can find a vectorial matter flux expression arising from chemical reaction kinetics, or one may, as suggested by Kedem (see above)¹, invoke a vectorial phenomenological coefficient. Is the vectorial phenomenological coefficient notional or should it have substantive mechanistic interpretation? Though the latter is desirable, the interpretation does not appear to be clear at all. The Cartesian components of the so-defined vectorial phenomenological coefficient are also not evident. This lack of methodological transparency has led to valiant efforts even to identify and define operational fluxes and operational forces, which are pseudovectorial quantities¹. The direction of cycle of cyclic reaction has been invoked to give the sense of a vector.

In reality, since the dissipation function should be a scalar and since it is a product of the fluxes and their conjugate forces, it is clear that these should be either scalars or vectors and not both. The matrix of phenomenological coefficients must find its roots in the substrata of material interactions. For instance, a scalar coefficient such as electrical or thermal conductivity perfectly accounts for a vast phenomenology.

In this paper we formulate the vectorial component of matter fluxes that arise from a chemical reaction. Even for a simple enzyme reaction in the steady state, identification of a possible quantity with the proper dimensions of matter flux and its conjugate force may enable one to restrict the cross-coefficients to scalar quantities with a realistic description of the phenomenology.

The matter flux produced by a chemical reaction needs to be initially considered. Reaction rate, which we may call flux arising from a chemical reaction, has the dimensions of moles/volume·sec, while matter flux has the dimensions of moles/area·sec. Therefore, since reaction rate has the dimensions of moles/sec·volume, i.e. concentration/sec, one can obtain the proper flux dimensions by integrating over the length element, i.e.

$$\int [\partial C_k / \partial t] dx = \bar{J}_k, \quad (3)$$

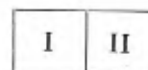
which is consistent with the equation of continuity at steady state,

$$\nabla \cdot \bar{J}_k = \pm J_R, \quad (4)$$

$$\bar{J}_k = \pm J_R(x) dx, \quad (5)$$

where J_R denotes the reaction rate of a reaction R , in which the species k participates. The reaction rate is sometimes expressed as number of moles per unit time, thus giving for the dissipation function the dimensions of energy per unit time. However, when one considers the diffusion of matter, recognizing that the dimensions of matter flux are moles per unit area per unit time, of concentration moles per unit volume, and of diffusion coefficient unit area per unit volume, one obtains the result that the dissipation function should be expressed as energy per unit volume per unit time. Thus, if one is to express the dissipation function as arising from matter transport and a chemical reaction, its dimensions should be energy/unit volume·sec. Also, the rate of chemical reaction, the velocity, should be in dimensions of variation of concentration per unit time, with affinity in dimensions of energy/mole.

The production of a matter flux with magnitude and direction can be best understood, with the figure shown below.



If it is presumed that an enzyme reaction of the kind



occurs in region I and steady state is maintained in region I, one has

$$(\partial C_P / \partial t) + \nabla \cdot \bar{J}_P = 0 \quad (7)$$

in region II, where the system is not in steady state nor can a steady state be maintained. This is analogous to water flowing at steady state in a river. When the river joins an ocean, i.e. an infinite sink, far from the river-ocean junction—the coast—the flux of water is zero, while the flux of water in the river is finite, and nonzero. Therefore, in the interfacial region, the flux should decay down from a finite nonzero value to a value of zero. Thus, though stationary state can be maintained in the river, it cannot be maintained at the interfacial region, i.e. at the mouth of the river. This is essentially the statement of the equation of continuity (equation 7). (Equation 7 stipulates, in addition, that the chemical flux, rate of chemical reaction, must have dimensions of moles/unit volume·sec if the matter flux is to have its correct dimensions of moles/unit area·sec. Recognition of this point leads to the conclusion that the dissipation function should be defined as energy/unit volume·sec.)

Similarly, though steady state exists for the enzyme reaction in region I, a stationary state does not exist in region II, into which the product P is injected. This enables one to equate emanation of P , dC_P/dt , and express equation 2.

$$\int (\partial C_P / \partial t) dt = Q_P, \quad (8)$$

where Q_P is the amount of P in region II collected over

a period of time,

$$\text{and } \int (\partial C_P / \partial t) dx = J_{Px}, \quad (9)$$

where J_{Px} is the x component of the matter flux vector J_P .

The value of flux of P , \bar{J}_P , obtained thus will have the correct magnitude and direction of matter flux. The conjugate force appropriate to this flux can be evaluated from the dissipation function

$$-T(dS/dt) = \bar{J} \cdot \bar{X}, \quad (10)$$

and the dimensions of the conjugate (force per unit area) can be evaluated to be calories/mole.

In this manner, we are able to define an appropriate matter flux and its conjugate force caused by the enzyme reaction occurring in region I. If one expresses the chemical flux and chemical force in the usual manner of irreversible-thermodynamics formulation (e.g. refs. 2, 11), as

$$-T(dS/dt) = v \cdot A, \quad (10)$$

where S is the entropy, one has the left hand side with dimensions of energy/sec, while A , the affinity, has dimensions of energy/mole, and the rate v , called velocity or chemical flux, has dimension of moles/sec, instead of moles/unit volume · sec. Thus the question of whether volume should be present in the dimensions and definition of dissipation function, which persisted after the previous formulations (see above), is now clarified. In the appendix, the difficulties encountered from the point of view of dimensional analysis are outlined for the more traditional approaches used in the literature thus far.

Concluding remarks

To summarize the influence of a chemical reaction on matter flux of a species that participates in the chemical reaction in a system under steady state, one can express the dissipation function as

$$\Phi = \bar{J}_k \cdot \nabla \bar{\mu}_k + \bar{J}_{k*} \cdot \bar{X}_{k*}, \quad (12)$$

$$\bar{J}_{k*} = \int_{\text{volume}} (\partial C_k / \partial t) dx, \quad (13)$$

$$\bar{X}_{k*} = -(T\dot{S})/\bar{J}_{k*}, \quad (14)$$

where \bar{J}_{k*} is the additional contribution to flux of k caused by the chemical reaction. In terms of scalar phenomenological coefficients, L_{kj} and L_{kR*} , the matter flux of species k can be expressed as

$$\bar{J}_{k*} = L_{kj} \nabla \bar{\mu}_j + L_{kR*} \bar{X}_{Rk*} \quad (15)$$

To reiterate, when one considers matter fluxes and

influence of the chemical reaction, together or individually, it is essential that the dissipation function is considered as per unit volume. The asymmetry present in the membrane can be satisfactorily taken into consideration by recognition of space dependence of scalar phenomenological coefficients in the inhomogeneous phase, without invoking vectorial phenomenological coefficients. When water flows down a mountainous stream, though the terrain is inhomogeneous and the force causing the flow is gravity, the proportionality constant between flow under stationary-state conditions, and the force will be scalar and not vectorial. The asymmetry of the inhomogeneous character of the terrain evidently leads to vectorial flow without in any way stipulating a vectorial phenomenological coefficient!

The importance of volume *per se* in energetics appears to be profound. Many physical processes in cells and organelles, such as contraction or expansion, that lead to volume changes could result in dissipation of free energy and entropy changes. Indeed, volume regulation in cells and organelles is ubiquitous in living systems. This intimate relationship between volume and energetics can indeed be sought at many levels of organization. At an elementary level, infinite dilution would be inimical to life processes based on chemical reactions. Conservation of volume in the face of various fluxes remains a major theme in biological regulations. Volume relates to the activities of various systems which can be altered through osmotic pressure since these are interrelated by an appropriate equation of state. In recent years, the influence of osmotic pressure on the activities of various membrane proteins and coupled processes has been outlined in considerable detail¹²⁻¹⁶. Osmotic compression would tend to decrease the pockets of free volume in the membrane phase. There exists adequate consensus that such pockets of free volume would be critical to fluctuations attendant to catalysis and transport¹⁷⁻¹⁹. This link between osmotic pressure and free volume critical to activity would also find its roots in thermodynamic formulations. Recognizing the existence of a relationship between communal entropy and free-volume changes²⁰, arising from oscillations of tails of lipid or chains of proteins in the membrane space, one can recognize and venture to relate such effects to changes in thermodynamic functions of the membrane systems²¹. Thus one can hope to unravel the intimate relationship between volume and energetics at many levels.

Appendix

Let us consider the dissipation function of a system of fluxes:

$$\Phi = -T\dot{S} = \text{Energy/sec} \cdot [^*]. \quad (A1)$$

For matter flux,

$$\begin{aligned} \varphi = \bar{J} \cdot \nabla \bar{\mu} &= [\text{moles}/(\text{cm}^2 \cdot \text{sec})] [\text{Energy}/(\text{mole} \cdot \text{cm})] \\ &= \text{Energy}/[\text{sec} \cdot \text{cm}^3]. \end{aligned} \quad (A2)$$

For a chemical reaction (flux), when we consider changes in the concentration rather than amounts to describe the velocity of the reaction.

$$\begin{aligned}\phi &= v \cdot A = \partial C / \partial t \left[\sum_i (v_i \cdot \nabla \mu_i) \right] \\ &= [\text{moles}/(\text{cm}^3 \cdot \text{sec})] [\text{Energy}/\text{mole}] \\ &= \text{Energy}/(\text{sec} \cdot \text{cm}^3).\end{aligned}\quad (\text{A3})$$

To be consistent, we should consider

$$[*] = \text{cm}^3, \quad (\text{A4})$$

and, thus, one refers to 'dissipation/unit volume', be it matter flux or be it a chemical reaction. If one has both vectorial matter fluxes and scalar chemical reaction occurring simultaneously in a system, then, if

$$\phi = \bar{J}_i \cdot \bar{X}_i + vA, \quad (\text{A5})$$

$$J_i = L_{ij} \nabla \mu_j + \bar{L}_{ir} A; \quad (\text{A6})$$

i.e. the cross-phenomenological coefficients, L_{ir} and \bar{L}_{ir} should be vectorial!

If, as Caplan² described,

$$\phi = J \Delta \mu + vA \quad (\text{A7})$$

$$J \Delta \mu = \text{Energy}/\text{cm}^2 \cdot \text{sec}, \quad (\text{A8})$$

while $vA = \text{Energy}/\text{cm}^3 \cdot \text{sec}$, and hence the dimensional problem,

$$\text{If } A = \sum_i v_i \cdot \nabla \mu_i, \quad (\text{A9})$$

and $V = \text{mole}/\text{sec}$, then $[*]$ should be unity. However, there now exists a conflict between equations A1 and A2 as well as equation A3. Therefore the dissipation function should be defined as per unit volume.

If one has in a system a chemical reaction and matter flux existing simultaneously, and the dissipation function can be expressed as

$$\phi = J_i \cdot X_i + v_r A_r, \quad (\text{A10})$$

$$J_i = L_{ij} \nabla \mu_j + L_{ir} A_r, \quad (\text{A11})$$

where r is the chemical reaction, the cross-phenomenological coefficients should be vectors.

If, as Caplan² writes the dissipation function as presented in equation A7, v has dimensions of concentration/time or moles/time and A the affinity has dimensions of energy/mole, giving the dissipation function dimensions of energy/volume·sec or energy/sec depending on whether free-energy dissipation should be defined per unit volume or not. If matter flux J_k is still defined as moles/unit area·second, the first term of equation A11 has the dimensions of energy/area·sec, which is different from the dimension of the second term!

Lastly, the question of dimensionality of forces and fluxes pertains to a transition from transport kinetics to enzyme kinetics. Consider the kinetic representation of transport as

$$T + S_o \rightleftharpoons TS \rightleftharpoons T + S_i.$$

The velocity of reaction would have the dimensions of moles/sec in the conventional manner. The notion of a vectorial flux being moles/area·sec would be possible only when velocity of reaction has the dimensions of moles/volume·sec, as justified in the main text between equations 2 and 7. When the reaction is confined to the membrane phase, the thickness of the membrane arises naturally in the definite integral.

By the same token, one may consider an enzyme-mediated chemical reaction as of transport returning the substrate in the same direction that it has come from, product formation being a somewhat less relevant issue for the moment. Here, the homology between a transport and an enzyme reaction becomes clear once we correct for the dimensions as seen before. Thus we are left with an explanation

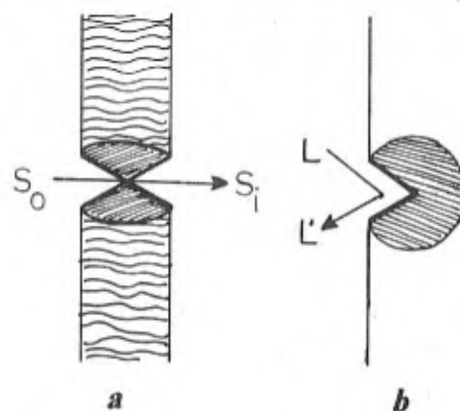


Figure A1. A comparison of the length dimension as relevant to a transporter (a) and an enzymatic reaction (b). **a.** The membrane is represented by the wavy-line area; the dashed area represents the domain of the molecular dynamics of a membrane-spanning transporter molecule; S_o , substrate for transport on the 'outside' (o) and the 'inside' (i) of the membrane, direction of mass transport indicated by the arrow. **b.** The enzyme as a putative surface is indicated by an extended line such that the ligand L traverses the active site and leaves as L' after chemical transformation. The arrow indicates the path, highlighting the relevance of the length dimension as in **a.**

for the physical meaning of integrating velocity of reaction over the linear distance. The idea of transport back into same phase essentially suggests that the distance covered would relate to the active-cleft dimension into which the substrate migrates. Since the chemical reaction of the enzyme with the substrate is confined within the active-site cleft, the linear dimension in the definite integral indicating flux would relate to the depth of the cleft as depicted in Figure A.1.

The physical picture may also be arrived at similarly. Consider one mole of enzyme of, say, 20 Å diameter. Let the molecules form a monolayer, which would cover about 1600 m². Since we consider a reaction volume of a litre (since the enzyme would be in a single phase), this area would correspond to a height of 4–5 Å, which in turn would be in the general ambit of active-cleft dimensions. Implicit in such a description is the awareness that the active cleft is but one solution relevant to enzyme catalysis to account for the length dimension, though catalytic/diffusive phenomena *per se* need not be restricted to this particular view of the length dimension. There have been other attempts to overcome the embarrassment of a vectorial coefficient^{3,4,11}. The use of the length dimension of the active-site cleft of enzyme or transporter, which regulates the diffusion component of the reaction/transport, is deeply satisfying and represents essentially a novel approach to dimensional consistency as well as consistency with physical reality.

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Long-term monitoring of vegetation in a tropical deciduous forest in Mudumalai, southern India

R. Sukumar, H. S. Dattaraja, H. S. Suresh, J. Radhakrishnan, R. Vasudeva, S. Nirmala and N. V. Joshi

Centre for Ecological Sciences, Indian Institute of Science, Bangalore 560 012, India

As part of an international network of large plots to study tropical vegetation dynamics on a long-term basis, a 50-hectare permanent plot was set up during 1988–89 in the deciduous forests of Mudumalai, southern India. Within this plot 25,929 living woody plants (71 species) above 1 cm DBH (diameter at breast height) were identified, measured, tagged and mapped. Species abundances corresponded to the characteristic log-normal distribution. The four most abundant species (*Kydia calycina*, *Lagerstroemia microcarpa*, *Terminalia crenulata* and *Helicteres isora*) constituted nearly 56% of total stems, while seven species were represented by only one individual each in the plot. Variance/mean ratios of density showed most species to have clumped distributions. The population declined overall by 14% during the first two years, largely due to elephant and fire-mediated damage to *Kydia calycina* and *Helicteres isora*. In this article we discuss the need for large plots to study vegetation dynamics.

RESEARCH on forests has been going on for several decades and yet we do not precisely understand their ecology. This is especially true of tropical forest ecology. It is well known that tropical forests are amongst the richest biological communities on earth. The disappearance of these forests, at an estimated rate of 1–2% per year¹, comes at a time when our knowledge of their structure and dynamics is woefully inadequate².

With a few exceptions, ecological studies of tropical forests have been largely isolated efforts, on small spatial scales and over short time periods. Notable

among the exceptions are the ongoing research on Barro Colorado Island in Panama by the Smithsonian Tropical Research Institute^{3,4} and the La Selva Biological Reserve in Costa Rica by the Organization for Tropical Studies⁵, both in the Neotropics.

Unlike in the relatively species-poor temperate forests, the study and characterization of species-rich tropical forests is a far more complex task. For one, the distribution of plant species is very heterogeneous, with most species having clumped distributions, making it necessary to study a large area in order to get an unbiased representation of the species present in the study sample. There is also a very wide variation in the relative abundance of species; a large study plot is again needed to provide sufficiently large sample sizes for the less common plants if one is to do any meaningful statistical analyses. Year to year variations in life-history phenomena of individuals and populations in response to climatic fluctuations (hurricanes, for instance, cause tremendous changes) also make long-term studies important.

Studies of tropical forests had been mostly confined to sampling trees within one or a few hectares until Hubbell and Foster^{6,7} took a bold step by setting up a 50-ha permanent plot in the tropical evergreen forests of Barro Colorado Island during 1980–82. Not only trees but also all other woody plants, excluding lianas, down to 1 cm stem DBH (diameter at breast height, in this case 1.3 m height) were enumerated and mapped. This provided an unprecedented opportunity to follow in detail the life histories of species, their interactions and the dynamics of plant communities.