

Pattern Recognition and Alternative Physical Chemistry Methodologies

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Alternative formalisms for two different domains in physical chemistry are considered here: thermodynamics and chemical kinetics. In thermodynamics the performance of a diagrammatic method based on geometric and algebraic considerations is illustrated here. This method based on the particular symmetry of a thermodynamic diagram allows one to obtain the most important thermodynamic expressions of a simple system and to solve thermodynamic problems strictly related to these expressions. The different thermodynamic expressions can be developed with the application of various geometric patterns to the proposed diagram. Furthermore, the particular structure of this diagram allows one to develop a matrix formulation of the pattern formalism. The matrix formalism requires one to recast the thermodynamic parameters of the diagram into a vectorial form. The number of thermodynamic relations that can, thus, be “discovered” is enormous. In chemical kinetics, two new approaches for writing kinetic equations in matrix form or directly in the integrated form are introduced here. The first method is based on the derivation of the rate **K** matrix of a kinetic systems of any order in a direct and straightforward way. This method, which allows one to solve first-order and some second-order kinetics with the normal matrix algebra methods, is mainly based on rate matrices which show interesting “patterns” due to their internal structure, which can further be used to check their validity and help to construct more complicated rate matrices. In fact, it is possible to derive a set of rules, which offers the possibility to construct rate matrices in a total mechanical way. The convolution approach to chemical kinetics applies to species that are consumed solely through first-order steps, regardless of the complexity of its formation pathways. This last method offers the possibility to formulate the rate equation directly in the integrated form, a form which shows an interesting structure, especially in the case of consecutive reaction schemes. A careful lecture of the different topics of this paper will not overlook the fact that the real subject of the proposed formalisms is the detection and recognition of patterns and to show that, sometimes, behind impressive relations or matrices a very “unimpressive” pattern is hiding.

INTRODUCTION

Normally an interested lector is overrun by the number of relations that he or she finds during a normal physical chemistry course and by the lack of an unitary and straightforward formalism in many fields and topics of physical chemistry. Thus, the first (and not only the first) impact with thermodynamics is always intimidating with all those relations popping out from everywhere, and the feeling is not rare that there must be a shorter and easier way to derive all those relations. Officially, we can trace this feeling back to 1935, when such a problem first appeared in the literature in a paper by F. O. Koenig,¹ even if it seems that Max Born was the first who in 1929 introduced a simple mnemonic diagram to remember the most useful Maxwell relations, as reported by Callen.²

Recently, some studies about the application of pattern recognition to the problem of deriving relations among thermodynamic parameters have been reported.^{3–5} Pattern recognition is a subfield of artificial intelligence and a large fraction of the effort in this area must be devoted to the recognition of appropriate geometric patterns from given

“objects”. The first purpose of this paper is, thus, to review and further develop the geometric formalism,^{2–5} which allows one to derive the many different relations of a simple thermodynamic system of pure substances,^{6,7} and to encode these relations by the aid of a matrix formalism, which is mainly based on the particular geometry of the thermodynamic diagram. For simple thermodynamic systems is here understood systems whose equilibrium states are described by the three thermodynamic coordinates (one of which being always the temperature) and by a single equation of state, which robs one of them of its independence. In this work hydrostatic systems will mainly be considered, that is, systems where the other two thermodynamic extensive (generalized displacement) and intensive coordinates (generalized force) are the volume *V* and the pressure *P*, respectively. Nevertheless, the mnemonic diagram can easily be adapted to other types of simple systems as it will be explained in the discussion section. The diagrammatic method can also be a valuable powerful method to solve specific problems, in fact, the solution of these problems can be reduced into a series of symmetry operations performed on the diagram. The parameters of this diagram are two sets of thermodynamic objects, defined by their position in the diagram: the corner set, {A, G, H, U}, and the diamond

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set, $\{P, S, T, V\}$ whose handling is governed by neighborhood relations. The derived thermodynamic relations are functions of the relative position and connection of these two sets in the diagram, that is, they are determined by the topology of the diagram, which is an energy-dimensioned diagram. In fact, while the corner set is a potential set, the parameters of the diamond set when multiplied with each other (along an arrow) give also rise to an energy dimensioned term.

Another important field in physical chemistry is surely chemical kinetics where the treatment of the different kind of chemical reactions gives the impression of a "random walk" through a system which is looking for a unitary formalism. The second aim of this paper is, then, to review and further deepen some recent developments in this field and discover how patterns, that is, characteristic regularities can be detected in the rate matrices, whose construction represent the first step to solve the kinetic equations. Normally,⁸⁻¹⁰ the evaluation of the kinetic rate laws, which are differential equations, consists in studying the fate of a specific reagent or product along several specific cases, that is, first-order, first-order opposing or reversible and consecutive, second-order, second-order reversible, etc. This "state of the art" gives the impression of a lack of unity and leaves the feeling that each case is somewhat unique. The use of matrices in chemistry and chemical engineering allows the formulation of chemical kinetic models in an elegant and compact way. The matrix formalism of the rate equations (a set of interconnected differential equations, one for the concentration time variation of each species) is particularly convenient since it allows the integration of the rate equations, using a uniform set of procedures. In addition, the time evolution of the concentrations of all species (reagents, products, and intermediates) is obtained simultaneously. This formalism has been treated in some basic texts on chemical kinetics and mathematics for chemistry¹¹⁻¹³ and has been recently reconsidered and further developed by different authors.¹⁴⁻¹⁸ Here we will not be concerned with matrix algebra, which is also used in quantum chemistry (the two fields becoming, thus, rather similar), but mainly with the mechanical construction of rate matrices, which show in many cases interesting regularities from which a set of rules for their construction can be derived. These rules, together with the principle of microscopic reversibility, allow one to insert the rate constants in a rate matrix in a direct and straightforward way, like the chessmen on a chessboard.

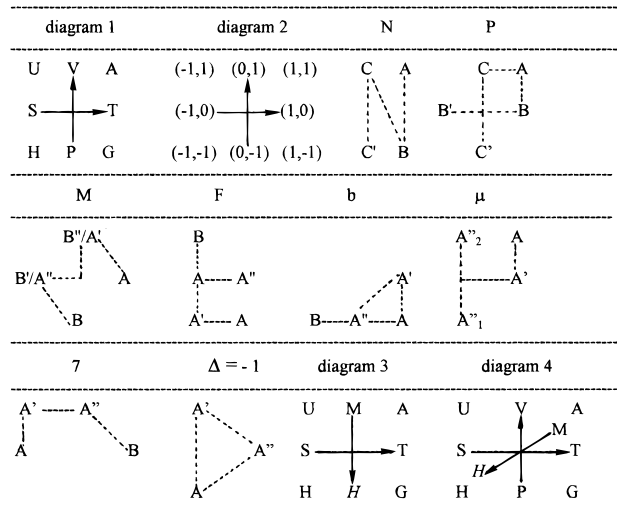
Recently,¹⁸⁻²⁴ another and more direct formalism for first-order kinetics has been further developed and used. It is a formalism which uses a convolution approach and allows one to write the kinetic equations directly in the integrated form. Even if this approach is limited to kinetic schemes composed of first-order or pseudo-first-order elementary steps it gives a synthetic and straightforward view of these chemical kinetic processes. The method has been recently used for the analysis of complex photochemical kinetic systems, and in these cases it seems much more powerful and rich than the conventional kinetic formalism. In many cases, for the consecutive reaction scheme especially, but, in a minor way, also for other reaction schemes, the convolution equations show a very simple pattern-like

structure, which helps to construct these equations in a direct way, even if their solution can be rather "convoluted".

For those who want to expand some of these topics in a different direction and to have a brief overview of other methods, which are rather loosely coupled with the foregoing discussion, refs 25 (chemical thermodynamics), and 8, 22, 26, 27, and 28 (chemical kinetics) are strongly recommended. To underline the importance of pattern recognition and how pattern recognition can have different facets, it can be added that, recently,²⁹ attention has been focused on the fact that electrical networks follow a pattern based on Fibonacci sequences.

THERMODYNAMIC DIAGRAM. METHOD

The thermodynamic mnemonic diagram given in Table 1 consists of two square arrows pointing upward toward the midside of an imaginary square whose corners are labeled with the four common thermodynamic potentials A , G , H , and U in alphabetical clockwise order, the Helmholtz potential A at the right top. In alphabetical order, but starting at the low side of the vertical arrow and going upwards (like a 45°-rotated Z) are the parameters P , S , T , and V , where P and T are the intensive parameters and S and V are the extensive parameters. Parameters A , G , H , U , P , S , T , and V represent Helmholtz free energy, Gibbs free energy, enthalpy, internal energy, pressure, entropy, temperature, and volume. It is well-known, that in simple systems of pure substances anyone of the eight quantities may be expressed as a function of any two others, but the particular structure of the thermodynamic diagram shows further that the potentials can be imagined to be function of the neighboring quantities in the diamond. Let us define this property the main property (MP) of the diagram. Thus, the natural or special variables of the potential functions are S and V for U , $U = U(S, V)$, V and T for A , $A = A(T, V)$, S and P for H , $H = H(S, P)$, and finally $G = G(T, P)$. Strictly speaking a main property of the diagram can be considered also the relations, $V = V(T, P)$, $P = P(T, V)$, etc. Further, as T and P are the only intensive properties of the diagram, A , adjacent to T , can be considered the available energy at constant temperature, particularly convenient in problems involving T . Thus, G , adjacent to both intensive properties T and P , can be considered the available energy at constant T and P , particularly convenient for problems involving T and P , and H , adjacent to P only, as the available energy at constant P and especially convenient for problems involving P . An arrow pointing away from a natural variable implies a positive sign, whereas an arrow pointing toward a natural variable implies a negative coefficient, as it will become evident with the introduction of the geometric patterns. In fact, a series of geometric patterns can be identified and used to obtain the most important thermodynamic expressions of simple systems. The various thermodynamic expressions result from the application of a series of operations based on these patterns when they overlay diagram 1. The geometric form of the patterns is easy to remember as they trace the shape of a Latin or Greek letter or of a number: F , N , M , P , b , μ , Δ , 7 , etc. This trace should indicate the relation among the parameters of the diagram and determine

Table 1. Diagram for Thermodynamic Relationships (Diagram 1, 3, and 4), the Vector Diagram for Thermodynamic Relationships (Diagram 2), and the Geometric Patterns N, P, M, F, b, μ , 7, and Δ 

also the sign of the variable controlled by the direction of the arrow. Two rules are worth remembering: (a) to generate the thermodynamic relationships, terms are used in alphabetical order and in unprimed, primed, and twice primed order, and (b) when going from one term on an arrow to the other term on the same arrow, the sign is positive when the direction of tracing the letter approaches the arrowhead and negative when the same direction approaches the arrowtail. After some practice these rules become evident.

The given geometric method is mainly based on the particular symmetry of the thermodynamic diagram, which can be used to develop a matrix formalism to derive the different thermodynamic relations. In this formalism the parameters of the diagram A, G, H, U, P, S, T , and V are replaced by two component (x,y) row matrices (diagram 2, Table 1):

$$\begin{array}{cccccccc} A & G & H & U & P & S & T & V \\ (1,1) & (1,-1) & (-1,-1) & (-1,1) & (0,-1) & (-1,0) & (1,0) & (0,1) \end{array}$$

These thermodynamic vectors possess an interesting mathematical property: adjacent potentials (corner vectors) or adjacent variables (diamond vectors) in diagram 2 are orthogonal to each other, that is, when multiplying a thermodynamic vector by the transpose t (= column vector) of another adjacent thermodynamic vector (not on the same arrow), the result is always zero, i.e.:

$$(-1,1) \cdot (1,1)^t = 0; (-1,0) \cdot (0,1)^t = 0; \\ \text{but: } (-1,0) \cdot (1,0)^t \neq 0$$

Thus, the only combinations allowed in the diamond set (P, S, T , and V) are the following energy-dimensioned combinations: $S \cdot T$ and $P \cdot V$. While adjacent combinations in the corner set are mathematically forbidden, diagonal combinations are forbidden per definition. In order to obtain, by matrix formalism, the thermodynamic expressions, the following matrices are used (equation numbering will be

preceded by the letter of the section to which it belongs: T = thermodynamics; M = matrix, C = convolution)

$$C_4^+ = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \quad (T1)$$

$$C_4^- = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad (T2)$$

$$\sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (T3)$$

$$\sigma_y = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \quad (T4)$$

These matrices perform a 90° (clockwise) or a -90° rotation about the axis of diagram 2 of Table 1 and a x - or y -reflection parallel to the x or y axis, i.e., $(-1,1) \sigma_x = (-1,-1)$ and $(-1,-1) \sigma_y = (1,-1)$.

The following four idem- and nil-potent matrices are also needed to transform potentials lying over or under the x or y axis into a variable function lying on the axis

$$L_x = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad (T5)$$

$$L_{-x} = \begin{pmatrix} -1 & 0 \\ 0 & 0 \end{pmatrix} \quad (T6)$$

$$L_y = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad (T7)$$

$$L_{-y} = \begin{pmatrix} 0 & -1 \\ 0 & 0 \end{pmatrix} \quad (T8)$$

The sign conventions for this formalism are as follows: negative sign for a term in a thermodynamic expression is contributed only by vectors $(-1,0)$ and $(0,-1)$ when (s1) these vectors are not differentiated, excluding the constant parameter, (s2) they are the second factor in nondifferentiable energy-dimensioned term, and (s3) they are a constant parameter in a wholly differentiable expression, otherwise the sign is always positive.

Geometric Relations between Neighboring Potentials. The N Pattern. The relationships controlled by this pattern when overlaid on diagram 1 (see Table 1) have the following general algebraic form

$$A = B - CC'$$

As from C to C' we are moving toward the arrowtail, a minus sign is required before the third term of this equation.

By superimposing the dashed lines of the N pattern to diagram 1 rotated by 90° and by substituting the alphabetical terms with the corresponding thermodynamic terms we obtain the following equation (90° substitution):

$$G = H - TS \quad (T9)$$

$$H = U + PV \quad (T10)$$

Rotating the N pattern around its CC' axis by 180° (a 180° substitution, followed by a 90° substitution) we obtain the other equivalent expressions, like, i.e.,

$$U = H - PV \quad (T11)$$

Matrix Formalism for the Neighboring Potentials. Generating step: the matrix form of the well-known $H = U + PV$ relation, shown in eq 12 (capital letter is omitted whenever cited equation belongs to the same chapter)

$$(-1, -1) = (-1, 1) + (0, -1)(0, 1) \quad (\text{T12})$$

can be obtained operating on potential $H \equiv (-1, -1)$ with matrix succession, σ_x , L_y , L_{-y} , as shown in the following equation

$$(-1, -1) = (-1, -1)\sigma_x + (-1, -1)L_y(-1, -1)L_{-y} \quad (\text{T13})$$

Operating, instead, only on potential $(1, -1) \equiv G$ with matrix succession σ_y , L_x , L_{-x} , (like in eq 14), we obtain eq 15, i.e., $G = H - TS$

$$(1, -1) = (1, -1)\sigma_y + (1, -1)L_x(1, -1)L_{-x} \quad (\text{T14})$$

$$(1, -1) = (-1, -1) - (1, 0)(-1, 0) \quad (\text{T15})$$

while with the former matrix succession we can obtain $G = A + PV$.

The generating step converts the starting vector into a neighboring vector and, then, adds to it the product of the projections of these two vectors on the corresponding x or y axis; the σ operation could be replaced by a C_4 operation. As further multiplication between two row vectors is not possible, matrix operations stop at this level. Operations $\sigma_{x,y}$, $L_{y,x}$, $L_{-y,-x}$ (the generator) could be used to generate the remaining thermodynamic relations, which can also be generated by the aid of the following propagating step.

The propagating step, formally easier than the generating step, operates on the terms of a well-known starting relation with rotation or reflection matrices only. Repeating this process with the terms of the newly obtained relation we can generate every thermodynamic expression. Performing a C_4^+ operation on eq 12, that is, $(12)C_4^+$,

$$(12)C_4^+: (-1, -1)C_4^+ = (-1, 1)C_4^+ + (0, -1)C_4^+(0, -1)C_4^+ \quad (\text{T16})$$

eq 17 is obtained, that is, $U = A + ST$

$$(-1, 1) = (1, 1) + (-1, 0)(1, 0) \quad (\text{T17})$$

While performing a $(12)\sigma_y$ operation, expression, $G = A + PV$, can be obtained

$$(12)\sigma_y: (1, -1) = (1, 1) + (0, -1)(0, 1) \quad (\text{T18})$$

and so on. The negative signs in eqs 15 is supported by the s2 sign convention.

Geometry of the Differential Forms of the Potentials. The P Pattern. The relationship for this geometric pattern when overlaid on diagram 1 (see Table 1) are given by an algebraic equation of the following form

$$dA = -dB(B') - dC(C')$$

For the sign convention see the preceding paragraph (from B to B' arrowtail is approached). With a successive 90°

substitution and rearranging (that is, $dB(B') = B'dB$) we obtain the following equations

$$dG = VdP - SdT \quad (\text{T19})$$

$$dH = TdS + VdP \quad (\text{T20})$$

$$dU = -PdV + TdS \quad (\text{T21})$$

Matrix Formalism for the Differential Forms of the Potentials. Propagating step: starting with the matrix expression of the well-known differential form, $dU = TdS - PdV$, shown in eq 22

$$d(-1, 1) = (1, 0)d(-1, 0) - (0, -1)d(0, 1) \quad (\text{T22})$$

and performing a $(22)C_4^+$ operation, eqs 23, that is, $dA = -PdV - SdT$, can be obtained. The same equation but with interchanged terms could be obtained with a $(22)\sigma_y$ operation. Performing instead a $(23)C_4^+$ operation, like in eq 24, eq 19 is retrieved

$$(22)C_4^+: d(1, 1) = -(0, -1)d(0, 1) - (-1, 0)d(1, 0) \quad (\text{T23})$$

$$(23)C_4^+: d(1, -1) = -(-1, 0)d(1, 0) + (0, 1)d(0, -1) \quad (\text{T24})$$

Equation 22 can also be derived by the aid of the following generating step performed on vector $(-1, 1) \equiv U$ alone

$$d(-1, 1) = (-1, 1)L_{-x}d(-1, 1)L_x + (-1, 1)L_{-y}d(-1, 1)L_y \quad (\text{T25})$$

Applying generator L_{-x} , L_x , L_{-y} , L_y to vector $(1, -1)$, like in eq 26, eq 27 is obtained

$$d(1, -1) = (1, -1)L_{-x}d(1, -1)L_x + (1, -1)L_{-y}d(1, -1)L_y \quad (\text{T26})$$

$$d(1, -1) = -(-1, 0)d(1, 0) + (0, 1)d(0, -1) \quad (\text{T27})$$

In the same manner we can generate every other relation.

Negative signs in the right hand side of eqs 23, 24, and 27 are supported by the s1 sign convention.

Geometry of the Maxwell Relations. The M Pattern. The relationships of this pattern when overlaid on diagram 1 are given by an equation of the following form (δ instead of the curly form of d stands for partial differentiation)

$$-(\delta A/\delta A')_{A''} = (\delta B/\delta B')_{B''}$$

The sign arises from the fact that tracing from A to A'' we approach an arrowtail, while from B to B'' the tracing approaches an arrowhead. With successive 90° substitutions we obtain, i.e., eqs 28 and 29

$$(\delta P/\delta T)_V = (\delta S/\delta V)_T \quad (\text{T28})$$

$$(\delta S/\delta P)_T = -(\delta V/\delta T)_P \quad (\text{T29})$$

Matrix Formalism for the Maxwell Relations. The generator for the Maxwell relation is the matrix succession: C_4^- , σ_y , C_4^+ , σ_y , C_4^- , which applied to vector $(1, 0) \equiv T$, like in eq 30, generates eq 31, that is, $-(\delta T/\delta V)_S = (\delta P/$

$\delta S)_V$. Partial derivatives of vectors will from now on be denoted with a prime, namely, $\delta(1,0) \equiv (1,0)'$

$$[(1,0)'/(1,0)'C_4^-]_{(1,0)\sigma_y} = [(1,0)'C_4^+/(1,0)'\sigma_y]_{(1,0)C_4^-} \quad (T30)$$

$$-[(1,0)'/(0,1)']_{(-1,0)} = [(0,-1)'/(1,0)']_{(0,1)} \quad (T31)$$

while with the aid of the propagating steps, $(31)C_4^+$ and $(32)\sigma_x$ the following relations are obtained

$$(31)C_4^+: [(0,-1)'/(1,0)']_{(0,1)} = [(1,0)'/(0,1)']_{(1,0)} \quad (T32)$$

$$(32)\sigma_x: [(-1,0)'/(0,-1)']_{(1,0)} = -[(0,1)'/(1,0)']_{(0,-1)} \quad (T33)$$

that is, eqs 28 and 29 respectively. The negative sign is supported by the s3 sign convention.

Geometric Relations for the Coefficients. The F Pattern. The form of the relationships of this pattern when overlaid to diagram 1 is given by

$$(\delta A/\delta A')_{A''} = -B$$

Tracing from A' to B we approach the arrowtail, thus, one of the two terms (A' or B) should be negative. With successive 90° substitutions we obtain the following equations

$$(\delta G/\delta P)_T = V \text{ (F upside down)} \quad (T34)$$

$$(\delta H/\delta S)_P = T \quad (T35)$$

With a 180° substitution around the A'' axis, followed by 90° substitution we obtain the other relations, like, i.e.,

$$(\delta A/\delta V)_T = -P \text{ (F rightside up)} \quad (T36)$$

Matrix Formalism for the Coefficients. Equation 37 is the vector representation of the F relation (it can be derived by the aid of the F pattern): $(\delta U/\delta V)_S = -P$,

$$[(-1,1)'/(0,1)']_{(-1,0)} = -(0,-1) \quad (T37)$$

While with the aid of propagating steps, $(37)C_4^+$ and $(38)\sigma_x$ relations 38 and 39, respectively, are obtained, that is, $(\delta A/\delta T)_V = -S$ and $(\delta G/\delta T)_P = -S$,

$$(37)C_4^+: [(1,1)'/(1,0)']_{(0,1)} = -(-1,0) \quad (T38)$$

$$(38)\sigma_x: [(1,-1)'/(1,0)']_{(0,-1)} = -(-1,0) \quad (T39)$$

The negative signs in the right part of these equations are supported by the s1 sign convention. Ignoring every other vector in eq 37 but $(-1,1) \equiv U$, we could have used this vector in denominator, constant parameter, and coefficient with the generating sequence, L_y , L_x , and L_{-y} respectively, and derive, in this manner eq 37.

It is noteworthy that the given sign convention, which could be based on x and y directions of diagram 1, has the advantage of avoiding continuous reference to any form of diagrams.

DISCUSSION

More complex form of patterns can be used to derive more elaborate thermodynamic relations. A μ pattern (see Table

1) can, for example, be used to derive relations 40–42. This pattern obeys the following general algebraic relation

$$(\delta A/\delta A')_{A''1} = (\delta A/\delta A')_{A''2} - (\delta A''_2/\delta A')_{A''1}(A''_1)$$

The following should be noticed about this relationship: (a) A' appears only as a denominator, (b) constant terms are the two primed terms in 1,2,1 order, and (c) A''_1 term behaves like a constant and multiplicative term, respectively, in the third member of this equation. Notice also the diagonal positioned A''_2 term in the second and third member on both sides of the minus sign. Now, with successive 90° rotations and substituting the corresponding thermodynamic parameters and rearranging we obtain the corresponding thermodynamic equations

$$(\delta G/\delta P)_S = (\delta G/\delta P)_T - S(\delta T/\delta P)_S \quad (T40)$$

$$(\delta H/\delta S)_V = (\delta H/\delta S)_P - V(\delta P/\delta S)_V \quad (T41)$$

$$(\delta U/\delta V)_T = (\delta U/\delta V)_S - T(\delta S/\delta V)_T \quad (T42)$$

Another problem that could geometrically be solved is to derive the value of $(\delta S/\delta U)_V$ that establishes an important link between thermodynamics and statistical mechanics, as it is used to define the Lagrange multiplier β .⁶ This quantity can be derived by the aid of a seven-like (or ?-like) pattern (see Table 1) whose general equation could be $(\delta A/\delta A')_{A''} = 1/B$, that is,

$$(\delta S/\delta U)_V = 1/T \quad (T43)$$

The vectorial form of this equation is

$$[(-1,0)'/(1,1)']_{(0,1)} = 1/(1,0) \quad (T44)$$

Applying, then, sequentially a C_4^+ operation we obtain the other relations, where the minus sign is controlled by the s1 rule, (where eq 45 is given by a rightside up 7)

$$[(0,1)'/(1,1)']_{(1,0)} = -1/(0,-1) \quad \text{or} \quad (\delta V/\delta A)_T = -1/P \quad (T45)$$

$$[(1,0)'/(1,-1)']_{(0,-1)} = -1/(-1,0) \quad \text{or} \quad (\delta T/\delta G)_P = -1/S \quad (T46)$$

Notice, here, how the first vector of the first term and the vector of the second term of each equation just change the sign of the nonzero component.

The fact that only two variables out of PVT are independent is expressed by the corresponding use of a triangular Δ pattern (see Table 1, sometimes this pattern is more similar to a right-angled or skewed triangle), that cyclically rotates around three parameters of the diagram. A minus sign could here be justified by the VTP arrowtail of the middle term, but it is more advantageous to justify it with the simple rules of calculus for cyclic differentiation (shortly: $\Delta = -1$).

$$(\delta P/\delta V)_T(\delta V/\delta T)_P(\delta T/\delta P)_V = -1 \quad (T47)$$

The corresponding matrix equation can be generated from the first $[(0,-1)'/(0,1)']_{(1,0)}$ term with the sequence $\sigma_x C_4^+ C_4^+$

Table 2. Schematic Representation of the Main Relations for the U, H, and G Representations

<i>MP</i> property :	$U = U(S,V)$	$H = H(S,P)$	$G = G(T,P)$
<i>N</i> pattern :	$U = H - PV$	$H = U + PV$	$G = H - TS$
<i>F</i> pattern :	$(\delta U/\delta S)_V = T$	$(\delta H/\delta S)_P = T$	$(\delta G/\delta P)_T = V$
" :	$(\delta U/\delta V)_S = -P$	$(\delta H/\delta P)_S = V$	$(\delta G/\delta T)_P = -S$
<i>N + F</i> :	$U = H + (\delta U/\delta V)_S V$	$H = U + (\delta H/\delta P)_S P$	$G = H + (\delta G/\delta T)_P T$
<i>M</i> pattern :	$(\delta P/\delta T)_V = (\delta S/\delta V)_T$	$(\delta V/\delta T)_P = -(\delta S/\delta P)_T$	$(\delta S/\delta V)_T = (\delta P/\delta T)_V$
<i>P</i> pattern :	$dU = dS \cdot T - dV \cdot P$	$dH = dS \cdot T + dP \cdot V$	$dG = -dT \cdot S + dP \cdot V$
rearranging :	$dU = TdS - PdV$	$dH = TdS + VdP$	$dG = VdP - SdT$
Δ pattern :	$(\delta U/\delta S)_V(\delta S/\delta V)_T(\delta V/\delta U)_S$	$(\delta H/\delta S)_P(\delta S/\delta P)_T(\delta P/\delta H)_S$	$(\delta G/\delta T)_P(\delta T/\delta P)_T(\delta P/\delta G)_T$

for the second term and $C_4^- \sigma_x C_4^-$ for the third term (for numerator, denominator and constant term, respectively).

Simultaneous use of the main property (*MP*) and of the different patterns allows one to find the most important relationships of the different energy representations and to detect sometimes new patterns, that is, new symmetries. In Table 2 the main relationships of the *U*, *H*, and *G* representations have been summarized. The *MP* property can be used to derive the total differential of the potentials, i.e., $dU = (\delta U/\delta S)_V dS + (\delta U/\delta V)_S dV$, where $(\delta U/\delta S)_V$ and $(\delta U/\delta V)_S$ can be derived with the aid of the *F* pattern, the final result being the *P* pattern relation of Table 2. Further, the total differential of $T = T(A,V)$: $dT = (\delta T/\delta A)_V dA + (\delta T/\delta V)_A dV$, can be solved with pattern 7 and with the Δ pattern, in fact, $(\delta T/\delta A)_V = -1/S$, and, $(\delta T/\delta V)_A = -(\delta T/\delta A)_V(\delta A/\delta V)_T$. The two terms of this relation can be obtained with the aid of the 7 and *F* patterns, respectively, the final result being $dT = -dA/S - PdV/S$, that is, $SdT = -dA - PdV$, a relation which can be obtained with the *P* pattern. In a similar way the relation for $(\delta S/\delta V)_U$ can be obtained to solve the differential $dS = (\delta S/\delta U)_V dU + (\delta S/\delta V)_U dV$.

Pattern recognition can also be used to solve practical problems by geometric convention. Let us derive, i.e., some thermodynamic properties of binary gas or liquid mixtures. From the Gibbs mixing function ΔG_{mix} ⁷ the relation for the entropy of mixing can be obtained with pattern *F*, $(\delta G/\delta T)_P = -S$, with *G* and *S* replaced by ΔG_{mix} and ΔS_{mix} , respectively. Application of patterns *N* and *F* provide, $\Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T\Delta S_{\text{mix}}$, and $(\delta \Delta G_{\text{mix}}/\delta P)_T = \Delta V_{\text{mix}}$, respectively. Finally, pattern *N* provides the last result: $\Delta U_{\text{mix}} = \Delta H_{\text{mix}} - P\Delta V_{\text{mix}}$.

An interesting application of pattern methodology is represented by exercise 5.4 on page 119 of Atkins' textbook.⁷ This exercise asks one to determine the equation for the temperature dependence of *A* (Helmholtz free energy) that corresponds to the well-known form of the Gibbs–Helmholtz equation

$$(\delta(G/T)/\delta(1/T))_P = H \quad (\text{T48})$$

This exercise can geometrically be solved once the pattern relating to the parameters of this equation has been recognized in diagram 1 of Table 1. Closer examination of this diagram shows that by superposing to it pattern b of Table 1, every thermodynamic variable involved in the given relation will be encompassed in a specific order given by the alphabetical letters *A*, *A'*, *A''*, and *B*, while the algebraic relationship for this geometry is $\delta(A/A')/\delta(1/A')_{A''} = B$. Thus, to find out the temperature dependence of potential *A*

we have to overlay the dashed lines of pattern b to diagram 1, rotate it by 180° around the *ST* axis and substitute the alphabetical terms with the corresponding thermodynamic terms, in the same order, obtaining, easily, the right answer

$$(\delta(A/T)/\delta(1/T))_V = U \quad (\text{T49})$$

With the same diagrammatic method we could try to solve another exercise, that is, the equation for the temperature dependence of the volume that corresponds to the well-known form of the Clapeyron equation^{1,6,7} for the phase transitions of a pure substance occurring at constant *T* and *P* (considering molar quantities): $dP/dT = \Delta H/T\Delta V$. Rotation of the Clapeyron pattern (a kind of broken arrow: $\nearrow \rightarrow$), results in an equation for a hypothetical phase transition occurring at constant *T* and *V* (a minus sign is needed as *P* is on an arrowtail): $dV/dT = -\Delta U/T\Delta P$. The parent equation of the more general expression, $dP/dT = \Delta S/\Delta V$, can easily be obtained operating on a kind of dashed *Z* pattern ($\nearrow -$) that is, $dV/dT = -\Delta S/\Delta P$. Such an equation can also be obtained by the aid of the *M* pattern.

Up to now only hydrostatic simple systems have been considered. In reality, the given diagrammatic method can easily be applied to other type of systems, like linear (wire), surface (films), electric (reversible cells), and dielectric (dielectric slab) or magnetic (paramagnetic rod) systems. In these cases the extensive *V* and intensive *P* coordinates of the diagram have to be replaced by the corresponding new extensive and intensive coordinates of the considered system. For example, in magnetic systems *V* and *P* have to be replaced by the total magnetization *M* of the magnetic material and by the magnetic intensity *H* respectively (Table 1, diagram 3). Further, in these cases, as work has to be done on the system in order to increase the extensive quantity by an infinitesimal amount *dEx* (*Ex* \equiv extensive quantity) the arrow changes direction pointing now toward the newly introduced intensive quantity (*H*). Now, application of *P* pattern to this diagram for magnetic materials gives rise to

$$dU = HdM + TdS \quad (\text{T50})$$

$$dH = -MdH + TdS \quad (\text{T51})$$

And, with the aid of the *M* pattern it is possible to derive the corresponding Maxwell relations, like, i.e.,

$$(\delta T/\delta M)_S = (\delta H/\delta S)_M \quad (\text{T52})$$

$$(\delta T/\delta H)_S = -(\delta M/\delta S)_H \quad (\text{T53})$$

The fact that only two variables out of *HMT* are independent is expressed even here by the corresponding use of the triangular ΔHMT pattern.

$$(\delta H/\delta M)_T(\delta M/\delta T)_H(\delta T/\delta H)_M = -1 \quad (\text{T54})$$

At this point it should be clear that the diagram and the corresponding patterns have a wide general utility that encompasses different systems. With surface systems, i.e., all is needed is to substitute the generalized force *H* (of the *HMT* system) with the surface tension \mathcal{T} and the generalized displacement *M* with the area *A*, likewise for an electric system *H* has to be replaced by the emf *E* of a reversible cell and *M* by the quantity of charge *Z*.

Three-dimensional diagrams based on generalized extensive and intensive parameters and on Legendre transformations have also been proposed.³² Such diagrams are rather elaborated and their direct mnemonic and mechanical quality is no more straightforward. Anyway, less elaborated three-dimensional diagrams can be constructed simply by adding an arrow passing through the center of the diagram (Table 1, diagram 4), i.e., with H and M along the arrowhead and arrowtail respectively. In this case a rather elaborated three-dimensional P pattern would give rise to the following relation for a composite hydrostatic-magnetic system:

$$dU = TdS - PdV + HdM \quad (T55)$$

Along this arrow the chemical potential μ_k (arrowhead) and the total number of chemical constituents (arrowtail) $\sum n_k$ could be added instead of H and M , and the three-dimensional P pattern would now give rise to the well-known relation for a multicomponent system (likewise for dU , dA , and dH)

$$dG = -SdT + VdP + \sum \mu_k dn_k \quad (T56)$$

Clearly, the matrix formalism here would be rather convoluted involving three-dimensional vectors and transformation matrices.

Sometimes, to find the equilibrium conditions for a system composed of two subsystems separated by a diathermic wall,² there is the need to find the value of the partial derivative, $(\delta S/\delta V)_U$, which by the aid of Δ plus 7 and the F pattern is equal to P/T . Now, these three patterns can be unified on the thermodynamic diagram to build the new relation with the aid of a $\{\supset + \Gamma = \supset\}$ pattern (\supset = first and Γ = second term), and this new pattern can further be used to derive, through reflection operations along the PV and ST axis, relations 58 and 59

$$(\delta S/\delta V)_U = P/T \quad (T57)$$

$$(\delta S/\delta P)_H = -V/T \quad (T58)$$

$$(\delta T/\delta P)_G = V/S \quad (T59)$$

Signs are given by the product of the directions of the two parameters in the second term along the Γ pattern, i.e., in eq 59 from V to S two negative directions along Γ are encountered, thus the overall sign is positive, as it is the product of two negative signs. With vector notation an interesting symmetry can be detected, which allows one to obtain the second term directly from the first term

$$[(-1,0)'/(0,1)']_{(-1,1)} = (0,-1)/(1,0) \quad (T60)$$

$$[(-1,0)'/(0,-1)']_{(-1,-1)} = -(0,1)/(1,0) \quad (T61)$$

$$[(1,0)'/(0,-1)']_{(1,-1)} = (0,1)/(-1,0) \quad (T62)$$

The second term can also be obtained interchanging the x and y components of the (x,y) vectors of the first term. When both components are negative or positive also their signs should be changed, with the result that the second term becomes negative.

The thermodynamic diagram can be of some help even to derive relations whose terms are not included in the diagram,

like, i.e., the well-known TdS equations⁶ which allows one to derive the expressions for reversible isothermal ($dT = 0$) and reversible adiabatic ($TdS = 0$) changes of volume (the first TdS equation) as well as reversible isothermal and reversible adiabatic changes of pressure (the second TdS equation). Substituting in the corresponding positions of the first TdS equation, $TdS = C_v dT + T(\delta P/\delta T)_V dV$, P with V and vice versa, the second TdS equation, $TdS = C_p dT - T(\delta V/\delta T)_P dP$, is obtained (the negative sign is due to the fact that from V to P the direction is negative). In the corresponding matrix forms the passage from the first to the second TdS equation is accomplished by a σ_x operation with the help of the $s3$ sign rule. Other terms which do not appear in the thermodynamic diagram are the three coefficients: volume expansivity, α , isothermal compressibility, κ_T , and adiabatic compressibility, κ_S . Let us imagine that in diagram 1 of Table 1 the S , T , and P terms are rewritten in the following way: $S(\kappa_S)$, $T(\kappa_T)$, and $P(\alpha)$. Now, let us define $(\delta V/\delta T)_P = \alpha V$ and extract from this definition the corresponding pattern, which can now be used to define the other two coefficients, sign inclusive (from V to P the direction is negative), $(\delta V/\delta P)_T = -\kappa_T V$ and $(\delta V/\delta P)_S = -\kappa_S V$. The corresponding relation for $(\delta T/\delta P)_V$ can be derived by the aid of the main property, $V = V(T,P)$ and of the triangular $\Delta = -1$ VTP pattern: $(\delta V/\delta T)_P(\delta T/\delta P)_V(\delta P/\delta V)_T = -1 = (\alpha V)(\delta T/\delta P)_V(1/(-\kappa_T V))$, clearly, $(\delta T/\delta P)_V = \kappa_T/\alpha$.

Before leaving this subject let us reconsider the following F pattern equation, $(\delta U/\delta S)_V = T$. This equation has been used to define negative Kelvin temperatures, that could be achieved with a population inversion of a spin system.⁶ It can here be noticed that with an arrow inversion preceding equation becomes negative, that is, $(\delta U/\delta S)_V = -T$. Thus, inverting the ST direction in the thermodynamic space defined by the thermodynamic diagram it is possible to achieve a negative temperature. The corresponding matrix equation would be very alike eq 38 but with a different meaning, as, vectors are, now, redefined in the following way: $(1,1) \equiv U$, $(1,0) \equiv S$, $(0,1) \equiv V$, and $(-1,0) \equiv T$, thus parameter T would be negative thanks to the $s1$ rule. A similar reasoning is also valid for eq 35 of pattern F , for which a negative temperature can also be defined.⁶

MATRIX KINETICS. METHOD

The K Rate Matrix. The easiest way to start a discussion about matrices is to choose elementary matrices and from these derive the rules which can be extended to matrices of every kind and dimension. We will start by considering three-dimensional first-order rate K matrix, that is, a process with three chemical constituents, A , B , and C , that undergo a first- or pseudo-first-order reaction. Such a process can be described by a 3×3 square $K = [k_{ij}]$ matrix, which is normally the transpose of a mathematical matrix. The first-order rate matrix is a zero- k matrix, with $k_{ij} = \{k_{ij}, 0\}$, k_{ij} if i belongs to the set of reactants and j to the set of products, and 0 if i and j belong both to the set of reactants or to the set of products. In other words, the zero- k matrix has a k at its ij entry when i is related to j by a reaction path, and zero otherwise. For second- or higher n -order kinetic processes the K matrix becomes a $[k_{ij}C_k^{n-1}]$ matrix, as we shall see later on. The most general form for a first- or pseudo-first-order K rate matrix with three species is

$$\begin{bmatrix} -k_{AA} & k_{BA} & K_{CA} \\ k_{AB} & -k_{BB} & k_{CB} \\ k_{AC} & k_{BC} & -k_{CC} \end{bmatrix} = \mathbf{K} \quad (\text{M1})$$

where the minus sign along the main diagonal means that along that path species undergo chemical consumption. Terms k_{ij} are the rate constants for reactions, $\leftarrow I \rightarrow$, that is, reactions departing from reactant i , and k_{ij} cross-terms are the reaction rate constants for reaction $I \rightarrow J$. Thus, while k_{AB} and k_{BA} are the rate constants of $A \rightarrow B$ and $B \rightarrow A$, respectively, k_{AA} is the sum of the rate constants for $A \rightarrow B$ and $A \rightarrow C$ reactions.

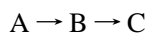
This general rule for the construction of rate matrices can be considered the main rule, but other rules can be derived from the striking regularities which can be detected in these matrices, especially when k_{ij} is replaced by the corresponding k_i and k_{-i} . Following are three properties,¹⁵ which can also help to check the validity of \mathbf{K} matrices which can easily be verified: (1) the sum of terms along a column is always zero as the term on the main diagonal is the negative sum of the terms along the respective column, (2) for reversible reactions the terms on symmetric sides of the main diagonal differ each other by their direction (normally indicated by i and $-i$ or f, forward and r, reverse), and furthermore, the rate matrices of triangular reactions at equilibrium (this topic will further be developed in the discussion section) due to the principle of microscopic reversibility,²⁵ which applies to each elementary reaction, possess the following property, (3) the ratio of the product of the rate constants along the secondary diagonals equals the ratio of the extreme terms along the antidiagonal, that is, $(k_{AB} \cdot k_{BC}) / (k_{BA} \cdot k_{CB}) = k_{AC} / k_{CA}$.

Adopting the matrix formalism the rate equation can be written in the following more succinct way (where $dC/dt = C'$),

$$C' = \mathbf{K} \cdot C \quad (\text{M2})$$

Thus, employing the normal methods of matrix algebra if nC' values are used as inputs, then nC values are obtained as outputs. Let us now apply the given rules to construct \mathbf{K} matrices of more complex and well-known reaction schemes.

Consecutive first-order reactions:



Here we have, $k_{AA} = k_{AB} = k_1$ and $k_{BB} = k_{BC} = k_2$, and the remaining $k_{ij} = 0$. The \mathbf{K} matrix will be

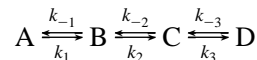
$$\begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{bmatrix} = \mathbf{K} \quad (\text{M3})$$

Notice that, while rule 1 is obeyed, rule 2 fails, as the reaction is not reversible.

Considering diverging side-reactions: $B \leftarrow A \rightarrow C$, the diagonal k_1 term has to be replaced with $(k_1 + k_2)$, in fact, now, two reactions are departing from A. The nondiagonal k_{AC} term becomes $k_2 = k_{AC}$. The k_2 terms in the second column are replaced by zeros, as $k_{BB} = k_{BC} = 0$.

Converging side-reactions, $B \rightarrow A \leftarrow C$, have, instead, the first column zeroed, as no reaction is departing from A, while in the second column, the first two terms are $k_{BA} = k_1$ and $k_{BB} = -k_1$ (diagonal term), and $k_{BC} = 0$. In the third column $k_{CA} = k_2$, and $k_{CC} = -k_2$, while $k_{CB} = 0$. Consecutive, and both types of diverging and converging reactions can easily be solved with the matrix eigenvalue method.

Opposing first-order consecutive reactions:



Here, $k_{AA} = k_{AB} = k_1, k_{BA} = k_{-1}, k_{BB} = (k_{-1} + k_2), k_{BC} = k_2, k_{CB} = k_{-2}, k_{CC} = (k_{-2} + k_3), k_{CD} = k_3, k_{DC} = k_{-3}, k_{DD} = k_{-3}$, while the remnant $k_{ij} = 0$. As the species are four the rate matrix is a 4×4 matrix, which shows an interesting regular pattern controlled by rules 1 and 2.

$$\begin{bmatrix} -k_1 & k_{-1} & 0 & 0 \\ k_1 & -(k_{-1} + k_2) & k_{-2} & 0 \\ 0 & k_2 & -(k_2 + k_3) & k_{-3} \\ 0 & 0 & k_3 & -k_{-3} \end{bmatrix} = \mathbf{K} \quad (\text{M4})$$

With $k_i = 0$ for $i > 1$ a simple first-order opposing reaction is obtained, which can easily be solved with the given eigenvalue method, while with $k_3 = k_{-3} = 0$ only, a system of opposing side-reactions of species A, B, and C is obtained. This last system can easily be solved with the eigenvalue method when, $k_1 = k_{-2} = k_c$ and $k_{-1} = k_2 = k_d$ (c and d stand for convergent and divergent, respectively).¹⁶

The Second-Order K Matrix. Rules for the construction of first-order rate matrices can be applied, with small modifications, to construct pure second-order (or higher-order) rate matrices with two reactants (A and B) and two products (C and D). Modifications are due to the introduction of the $(C_k)^{n-1}$ concentration term (for a second-order rate matrix, $n = 2$), that multiplies the k_{ij} rate constants.

$$\begin{bmatrix} -k_{AA}C_B & k_{BA}C_A & k_{CA}C_D & k_{DA}C_C \\ k_{AB}C_B & -k_{BB}C_A & k_{CB}C_D & k_{DB}C_C \\ k_{AC}C_B & k_{BC}C_A & -k_{CC}C_D & k_{DC}C_C \\ k_{AD}C_B & k_{BD}C_A & k_{CD}C_D & -k_{DD}C_C \end{bmatrix} = \mathbf{K} \quad (\text{M5})$$

Subscript k of the concentration term shows an inverted internal order, that is, $k = B, A, D, C$ relative to the concentration vector $C = (C_A, C_B, C_C, C_D)$. This matrix can be converted into a first-order rate matrix noticing that for $n = 1$: $(C)^{n-1} = 1, C_C = C_D = 0$ and $k_{iC} = k_{iD} = 0$. Terms outside the main diagonal of the given matrix can be simplified in two steps: (1) as there is no internal reaction between reactants or products (that is, A and C do not result from B and D respectively, and vice versa) then, $k_{AB} = k_{BA} = k_{CD} = k_{DC} = 0$, further, (2) as third and fourth term in the first and second rows as well as first and second term in the third and fourth rows are redundant, one of them can be eliminated. These redundancies, which can be eliminated in many ways, can easily be detected looking for terms in a row,¹⁵ which differ each other by internal exchange of reactants or products (namely, by internal exchange of subscripts of C and k, i.e., $k_{AC}C_B$ and $k_{BC}C_A$). The resulting matrix, which obeys rules 1 and 2 (a fact that is evident for $k_{AA} = k_{AD} = k_{BB} = k_{BC} = k_1$ and $k_{CB} = k_{CC} = k_{DA} = k_{DD} =$

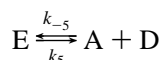
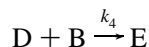
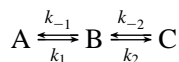
k_{-1}) will then be patterned in the following way

$$\begin{bmatrix} -k_{AA}C_B & 0 & 0 & k_{DA}C_C \\ 0 & -k_{BB}C_A & k_{CB}C_D & 0 \\ 0 & k_{BC}C_A & -k_{CC}C_D & 0 \\ k_{AD}C_B & 0 & 0 & -k_{DD}C_C \end{bmatrix} = \mathbf{K} \quad (\text{M6})$$

DISCUSSION

Kinetic systems composed by unimolecular steps only as well as second order kinetic systems of the type, $A + B \rightarrow C$ whose rate matrices do not exceed 3×3 dimension are amenable to a rather easily closed form solution by the aid of the matrix eigenvalue method.^{11,16,17} The solution, instead of more complex kinetic problems can be rather formidable, and approximations, such as the steady-state or pre-equilibrium approximations, or numerical methods, such as Euler's or the Runge-Kutta's methods, have then to be invoked^{17,18} (and references therein).

Now, the given rules for the construction of rate matrices will be applied to construct the rate matrices of more complicated kinetic reaction schemes. With the given rules (especially with the main rule) to construct second and consequently first order matrices it is possible, i.e., to construct rate matrices of complex kinetic mechanisms composed of first and second order reaction steps, like



After elimination of redundancies (fifth row: first column, $k_{-5}C_D$ term, and fourth column, k_4C_B term) we obtain^{15,17}

$$\begin{bmatrix} -(k_1+k_3+k_5C_D) & k_{-1} & 0 & 0 & k_5 \\ k_1 & -(k_{-1}+k_2+k_4C_D) & k_{-2} & 0 & 0 \\ 0 & k_2 & -k_{-2} & 0 & 0 \\ k_3 & 0 & 0 & -(k_4C_B+k_{-5}C_A) & k_5 \\ 0 & k_4C_D & 0 & k_{-5}C_A & -k_5 \end{bmatrix} = \mathbf{K} \quad (\text{M7})$$

Clearly such mixed-order matrices do not obey neither rule 1 nor rule 2. The concentration vector here is $\mathbf{C} = (C_A, C_B, C_C, C_D, C_E)$.

The second-order matrix (matrix 5 or 6) can be used as the starting point for the construction of other type of matrices such as matrices of second-order steps with stoichiometric coefficients $\nu_i \neq 1$ or matrices of autocatalytic steps and the corresponding matrices of mixed reaction steps. Substituting in matrix 6 subscripts D with C we obtain

$$\begin{bmatrix} -k_{AA}C_B & 0 & 0 & k_{CA}C_C \\ 0 & -k_{BB}C_A & k_{CB}C_C & 0 \\ 0 & k_{BC}C_A & -k_{CC}C_C & 0 \\ k_{AC}C_B & 0 & 0 & -k_{CC}C_C \end{bmatrix} = \mathbf{K} \quad (\text{M8})$$

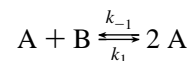
Now, (i) adding the fourth column into the third one and eliminating the fourth column, (ii) adding the fourth row into

the third one and eliminating the fourth row, and (iii) eliminating, successively, the redundant term in the third row (there is a redundancy between first and second term of this row) we obtain the rate matrix of the following elementary step with stoichiometric coefficient $\nu_C = 2$, and with $k_{AA} = k_{AC} = k_{BB} = k_1$ and $k_{CA} = k_{CB} = k_{CC} = k_{-1}$,

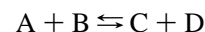


$$\begin{bmatrix} -k_1C_B & 0 & k_{-1}C_C \\ 0 & -k_1C_A & k_{-1}C_C \\ k_1C_B & 0 & -2k_{-1}C_C \end{bmatrix} = \mathbf{K} \quad (\text{M9})$$

Thus, a way to construct rate matrices of reactions with nonunitary stoichiometric steps is (i) to expand, by the aid of dummy species, the dimension space of the reaction into a space where no equal species are present and (ii) to reduce it back into the normal dimension of the reaction operating on the columns and rows of the dummy species. Other types of matrices can be obtained with other types of reactions with $\nu_i \neq 1$, i.e., for $A \rightarrow 2B$ (k_1) the matrix for $A \rightarrow B + C$ is first derived, that is, a 3×3 matrix whose first column is, $(-k_1, k_1, k_1)$, the remaining columns being zero, then, steps i and ii are applied and a 2×2 matrix is obtained whose first column is $(-k_1, 2k_1)$, the second column being $(0,0)$. This process can also be used to construct rate matrices of reactions with autocatalytic steps,¹⁴ in fact, the construction of the rate matrix for the following autocatalytic step



starts with the following dummy reaction scheme



whose rate matrix, inserting k_1 and k_{-1} for k_{ij} in matrix 6, is

$$\begin{bmatrix} -k_1C_B & 0 & 0 & k_{-1}C_C \\ 0 & -k_1C_A & k_{-1}C_D & 0 \\ 0 & k_1C_A & -k_{-1}C_D & 0 \\ k_1C_B & 0 & 0 & -k_{-1}C_C \end{bmatrix} = \mathbf{K} \quad (\text{M10})$$

Now, (i) subscripts C and D are replaced by subscript A, (ii) third and fourth columns are added into the first column and are eliminated, (iii) third and fourth rows are added into the first row and are eliminated, and the unexpected result is

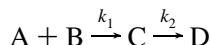
$$\begin{bmatrix} -k_{-1}C_A & k_1C_A \\ k_{-1}C_A & -k_1C_A \end{bmatrix} = \mathbf{K} \quad (\text{M11})$$

that is, a rate matrix with no redundant terms, that obeys rules 1 and 2. The concentration vector associated with this matrix is $\mathbf{C} = (C_A, C_B)$.

The considered rules, which allow one to start with a general second order \mathbf{K} matrix and derive specific \mathbf{K} matrices of the same or lower order, can be applied to an n th order \mathbf{K} matrix to derive any matrices of lower order, rendering, thus, the construction method quite general.

The same matrix formalism, with minor changes, can also be applied to derive kinetic \mathbf{K} matrices in open systems (in

continuous flow stirred tank reactor: CSTR).^{15,18} For example, consider the given reaction in a CSTR

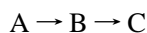


The rate matrix for this scheme with $k_{AA} = k_{BB} = k_{AC} = k_{BC} = k_1$, and $k_{CC} = k_{CD} = k_2$, after elimination of redundancies (k_{AC} or k_{BC}) is given by

$$\begin{bmatrix} (\Phi\Delta + D_A\nabla^2 - k_1B) & 0 & 0 & 0 \\ 0 & (\Phi\Delta + D_B\nabla^2 - k_1A) & 0 & 0 \\ k_1B & 0 & (\Phi\Delta + D_C\nabla^2 - k_2) & 0 \\ 0 & 0 & k_2 & (\Phi\Delta + D_D\nabla^2) \end{bmatrix} = \mathbf{K} \quad (\text{M12})$$

where Φ is the flow rate, Δ is a subtracting operator, that is, $\Delta A = A_0 - A$, A_0 being the concentration of the input flow (the same being valid for the other terms of the concentration vector), $\nabla^2 = \delta^2/\delta x^2 + \delta^2/\delta y^2 + \delta^2/\delta z^2$, is the Laplacian operator, and $D_{A,B,C,D}$ are the diffusion coefficients.

The Principle of Microscopic Reversibility. Let us consider the triangular reaction



which reach equilibrium through a triangular mechanism (with rate constants k_1 , k_2 , and k_3) and let us derive the corresponding \mathbf{K} matrix. As it is a consecutive reaction scheme we can use matrix 3 inserting k_3 into the third column,

$$\begin{bmatrix} -k_1 & 0 & k_3 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & -k_3 \end{bmatrix} = \mathbf{K} \quad (\text{M13})$$

Due to irreversibility of each step only rule 1 is obeyed, and no further regularities can be observed. But as the reaction is in some way reaching equilibrium through the triangular scheme, the fact of nonobeying rule 2 is in some way rather odd.

The principle of microscopic reversibility (also known in chemical kinetics as the detailed balance principle) states that for a system at equilibrium, any elementary reaction and the exactly reverse reaction must occur at the same rate.²⁵ This principle forbids triangular mechanisms of the given type, allowing at equilibrium only opposing triangular mechanisms, which give rise to matrices that obey both rules 1 and 2 and which show a high regular pattern. In fact, for a triangular opposing scheme the following \mathbf{K} matrix (with k_3 and k_{-3} controlling the closure of the reaction scheme) is obtained

$$\begin{array}{c} \begin{array}{ccccc} & & \xrightarrow{k_1} & & \\ A & \xleftarrow{k_1} & B & \xleftarrow{k_2} & C \\ & & \xrightarrow{k_2} & & \end{array} \\ \begin{bmatrix} -(k_1+k_{-3}) & k_{-1} & k_3 \\ k_1 & -(k_2+k_{-1}) & k_2 \\ k_{-3} & k_2 & -(k_3+k_{-2}) \end{bmatrix} = \mathbf{K} \end{array} \quad (\text{M14})$$

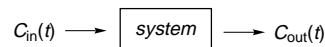
The resulting matrix is not only highly structured, but a further property (property 3) due to the detailed balance principle can be detected, that is, $(k_1k_2)/(k_{-1}k_{-2}) = k_{-3}/k_3$.

For a system of square opposing reactions ($A = B = C = D = A$), this third property can further help to construct the corresponding rate matrix, as, put it in another way, forward rate constants stay on the lower secondary diagonal, reverse rate constants stay on the upper secondary diagonal, and rate constants for the closure step $D \leftrightarrow A$ stay on the antidiagonal, in a reverse order (k_i in the lower corner and k_{-i} in the upper corner). Thus with rules 1, 2, and 3 it is an easy task to construct the following rate matrix for a square opposing system of first-order reactions (notice, now, the interesting structure of this matrix along the main, secondary, and anti diagonals).

$$\begin{bmatrix} -(k_1+k_{-4}) & k_{-1} & 0 & k_4 \\ k_1 & -(k_2+k_{-1}) & k_{-2} & 0 \\ 0 & k_2 & -(k_3+k_{-2}) & k_{-3} \\ k_{-4} & 0 & k_3 & -(k_4+k_{-3}) \end{bmatrix} = \mathbf{K} \quad (\text{M15})$$

CONVOLUTION KINETICS. METHOD

A chemical reaction can be seen as a physical system (a kind of transducer) which transforms an input $C_{in}(t)$ into an output $C_{out}(t)$, like the following schema



The system is completely characterized when it is possible to know the relationship between input (cause) and output (effect). The relationship is a functional transformation of $C_{in}(t)$ into $C_{out}(t)$, like in eq 1 where a mathematical operator O (a kind of transfer function) transforms the input into the output (for the moment being let us forget a strict parallelism with a chemical system)

$$O[C_{in}(t)] = C_{out}(t) \quad (\text{C1})$$

If the operator is linear ($O[\sum a_i C_i(t)] = \sum a_i O[C_i(t)]$), that is, if the system behaves linearly a condition that generally holds for kinetic systems exhibiting strict first-order kinetics, then the output $C_{out}(t)$ signal can be described by a convolution-like integral, and it can be said that $C_{out}(t)$ is the convolution of $C_{in}(t)$ being $S(t)$, the impulse response function

$$C_{out}(t) = \int_0^t C_{in}(\Theta) \cdot S(t - \Theta) d\Theta = C_{in}(t) \otimes S(t) \quad (\text{C2})$$

Clearly, the resulting value of this convolution integral is a function of t . The term $(t - \Theta)$ appears because the time-resolved evolution must be relative to the starting time (i.e., the time lapse since the creation time), which is Θ ; for $t < \Theta$ it is understood that $C_{out}(t) = 0$. It can be shown that $C_{out}(t) = S(t) \otimes C_{in}(t) = C_{in}(t) \otimes S(t)$.^{31,32} An interesting result of this method being that the final result of a consecutive scheme, $C_{in} \rightarrow \square \rightarrow C_1 \rightarrow \square \rightarrow C_2 \rightarrow \square \rightarrow C_{out}$ through three systems, a, b, and c, can easily be written in the following way: $C_{out} = C_{in} \otimes S_a(t) \otimes S_b(t) \otimes S_c(t)$.³³

The $S(t)$ function characterizes the system, and once known it allows one to determine the response to every kind of input. The object of measuring the time-resolved evolutions is to determine the impulse response function $S(t)$. This is the

time evolution which would be observed with an infinitely sharp excitation pulse. Now, a procedure will be followed that is mathematically not excessively correct but that gives a straightforward view of the result. Considering, then, this function being the response of the system to an ideal unitary rectangular pulse with small pulse-width ϵ at time Θ (a pulse whose width is much shorter than the evolution time of the sample), substitution of $C_{in}(\Theta) = 1/\epsilon$ into eq 2, and in the limit of ϵ approaching zero, $\epsilon \rightarrow 0$, when $C_{in}(t) = \delta(t)$ [$\delta(t)$ is the Dirac's delta function: $\delta(t) = 0$, and ∞ for $t \neq 0$, and $t = 0$, respectively, and $\int \delta(t)dt = 1$] we obtain, if $S(t)$ is a continuous function

$$C_{out}(t) = \frac{1}{\epsilon} \int_0^\epsilon S(t - \Theta) d\Theta = \frac{1}{\epsilon} [\epsilon \cdot S(t - \epsilon')] = S(t - \epsilon')$$

$$C_{out}(t) = \lim_{\epsilon \rightarrow 0} S(t - \epsilon') = S_\delta(t) \quad (C3)$$

where $S(t - \epsilon')$ is the mean $S(t)$ value in the $[0 - \epsilon]$ range ($0 < \epsilon' < \epsilon$).

Coming back to a normal chemical kinetic problem, function $S_\delta(t)$, a kind of specific output, can be considered the evolution of a reactive chemical species that can instantaneously be produced at unit concentration time. It is the response to a unit input of C_{in} at time zero, that is to a Dirac's function, and reflects all possible disappearance routes for C_{in} . From now on this function will be known as the instantaneous $C_\delta(t)$ unit production function, which for a chemical species i becomes $C_{i\delta}(t)$. This function will be weighted by the respective initial amount produced, that is, by the production rate $P(t) = C_{in}(t)$ function which normally controls the initial conditions. Under first-order or pseudo-first-order conditions $C_{i\delta}(t)$ is independent of all concentrations and is given by¹⁸ $C_{i\delta}(t) = \exp(-\sum_j k_{ij}t)$, where k_{ij} are first- or pseudo-first-order rate constants of the elementary steps by which C_i is consumed. The final convolution equation for a chemical system for a species i will, then, be

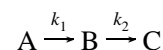
$$C_i(t) = \int_0^t P_i(\Theta) C_{i\delta}(t - \Theta) d\Theta = P_i(t) \otimes C_{i\delta}(t) \quad (C4)$$

Following this method, an isolated chemical species A can be imagined as the output of an unitary Dirac-like pulse with $P(t) = N \cdot \delta(t)$, and $C_{A\delta}(t) = 1$, and given by the following convolution equation: $C_A(t) = P(t) \otimes C_{A\delta}(t) = N \cdot \delta(t) \otimes 1 = N$, where the normalization constant N is the concentration of A at $t = 0$, that is, $N = A_0$.

To solve the convolution integral use of the Laplace transform is normally required.^{31,32} Laplace transform is a linear operator L , ($L[\sum a_i f_i] = \sum a_i L[f_i]$), which transforms a differential equation into an algebraic one, changing the space in which the function is defined, and has the interesting property to transform a convolution product into the product of the individual transforms ($L[f \otimes g] = L[f] \cdot L[g]$). Both properties (linearity and convolution handling) are shared by the respective anti-Laplacian L^{-1} operator, which transforms $F(s)$ back to $f(t)$, $f(t) = L^{-1}[F(s)]$. For a detailed discussion of the properties and handling of the convolution in chemical kinetics see ref 20. A rather easy convolution problem is represented by the case, $P(t) = \exp(-at)$ and $C_{i\delta}(t) = \exp(-bt)$, in fact, here, the convolution integral can directly be solved (see consecutive reaction scheme, eq 14), the final solution being $[\exp(-at) - \exp(-bt)]/(b-a)$.

DISCUSSION

In the following lines we will analyze in greater detail the internal structure of the convolution method. Some different types of reactions will be considered here, these reactions have a rather easy convolute pattern, whose structure can be seen as a rule. The three kind of reactions considered here, consecutive, reversible, and CSTR reactions, have in common a similar convolute pattern for species A and B, namely, $A = P_A \otimes A_\delta$, and $B = P_B \otimes B_\delta$. Clearly, they differ each other in their production rates, and in their response to δ -production. Species C of the consecutive scheme has an analogous convolutive pattern, namely, $C = P_C \otimes C_\delta$, and, as there are no disappearance routes for C, its response to δ -production is $C_\delta = 1$. Generally the solution of a convolution equations is done in four steps: (1) identification of the delta responses $I_\delta(t)$ with $I = A, B, C, \dots$, (2) identification of the production terms, $P_i(t)$, (3) derivation of the full integral equations, $I = P_i \otimes I_\delta$, and (4) solution of the system of coupled equations, e.g., by the use of Laplace and anti-Laplace transforms. In the following lines use of I , and I_δ instead of $C_i(t)$ and $C_{i\delta}(t)$, respectively, is done. Consider the following consecutive first-order reaction scheme



For this reaction scheme the following elementary convolution equation can be written

$$I_i = P_i \otimes I_\delta \quad (C5)$$

Equation 5 condenses three different equations for $I = A, B$, and C . Let the initial concentrations of A, B, and C be A_0 , 0, and 0, respectively. The production rates and the time evolution of A, B, and C in response to each δ -production, which are dictated by their routes of disappearance, are

$$P_A = A_0 \delta(t); \quad A_\delta(t) = \exp(-k_1 t) \quad (C6)$$

$$P_B = k_1 A; \quad B_\delta(t) = \exp(-k_2 t) \quad (C7)$$

$$P_C = k_2 B; \quad C_\delta(t) = 1 \quad (C8)$$

Now, eq 5 for $I = A, B$, and C yields

$$A = P_A \otimes A_\delta(t) = A_0 \delta(t) \otimes \exp(-k_1 t) = A_0 \exp(-k_1 t) \quad (C9)$$

$$B = k_1 A \otimes B_\delta(t) = k_1 A_0 \exp(-k_1 t) \otimes \exp(-k_2 t) \quad (C10)$$

$$C = k_2 B \otimes C_\delta(t) = k_1 k_2 A_0 \exp(-k_1 t) \otimes \exp(-k_2 t) \otimes 1 \quad (C11)$$

To notice here is the final pattern $C = k_2 k_1 P_A \otimes A_\delta \otimes B_\delta(t) \otimes C_\delta(t)$, which is the classical pattern which defines relations describing reaction schemes with consecutive steps. Performing the convolution integrals one obtains, with $\Delta k = k_2 - k_1$

$$\exp(-k_1 t) \otimes \exp(-k_2 t) = \frac{\{\exp(-k_1 t) - \exp(-k_2 t)\}}{\Delta k} \quad (C12)$$

With $k_1 = 0$ together with the commutative property of the

convolution eq 13 can be derived

$$\exp(-k_2 t) \otimes 1 = \frac{1 - \exp(-k_2 t)}{k_2} \quad (\text{C13})$$

A result which could directly be obtained performing the integral or indirectly through Laplace transforms. The convolution pattern of eq 11 can thus be rewritten in the following way

$$\exp(-k_1 t) \otimes \exp(-k_2 t) \otimes 1 = \frac{1}{k_2} \{ \exp(-k_1 t) \otimes 1 - \exp(-k_1 t) \otimes \exp(-k_2 t) \} \quad (\text{C14})$$

The final result, which can easily be obtained by the aid of eqs 12 and 13,¹⁸ can thus be obtained without solving any differential equation.

Let us consider now the following opposing first-order reaction schema



The two convolution equations can be derived from the formally very simple equation

$$I = P_1 \otimes I_\delta \quad (\text{C15})$$

where $I = A$ and B . The production rates, which have to take into account the production due to the reversibility of the reaction, and δ -production responses (same as before) are

$$P_A = A_0 \delta(t) + k_2 B; \quad A_\delta(t) = \exp(-k_1 t) \quad (\text{C16})$$

$$P_B = B_0 \delta(t) + k_1 A; \quad B_\delta(t) = \exp(-k_2 t) \quad (\text{C17})$$

Combining eqs 16 and 17 with eq 15 two coupled equations are obtained with a characteristic pattern given in equation 18, where $I = A, B$ and $J = B, A$ and $f =$ forward and $r =$ reverse (it should be remembered that for $I = A$ $k_f = k_1$, and for $I = B$ $k_f = k_2$)

$$I = I_o \exp(-k_f t) + k_r J \otimes \exp(-k_f t) \quad (\text{C18})$$

The two coupled equations can be solved using Laplace and anti-Laplace transforms (for a detailed handling of this system of equations see ref 18, and references therein).

It should just here be noticed the particular symmetric structure of the rate matrix for this kind of reaction, which obeys both rules 1 and 2

$$\begin{bmatrix} -k_1 & k_2 \\ k_1 & -k_2 \end{bmatrix} = \mathbf{K} \quad (\text{C19})$$

Kinetics in Open Systems. The previous reasoning applies equally well to open systems. In fact, input flow of reactants from the outside is incorporated in the production terms whereas output flow of both reactants and products affects only the δ -responses. Consider a constant volume ideal continuous flow stirred tank reactor (CSTR) where reaction



occurs, no A being initially present in the reactor. A flow of A solution, with concentration A_0 , enters the reactor (which has constant volume V), at a constant volume rate Φ . The output flow also has the same volume rate, Φ . The two general convolution equations can again be derived from the following general equation, with $I = A$ and B

$$I = P_1 \otimes I_\delta \quad (\text{C20})$$

Then assuming also instantaneous mixing

$$P_A = A_0 \Phi / V; \quad A_\delta(t) = \exp\{-(k + \Phi/V)t\} \quad (\text{C21})$$

$$P_B = kA; \quad B_\delta(t) = \exp(-\Phi t / V) \quad (\text{C22})$$

and, again, a well-known patterned relation is obtained: $B = kA \otimes B_\delta = kP_A \otimes A_\delta \otimes B_\delta$ (a detailed solution for this system can also be seen in ref 18).

The convolution approach can sometimes be used even for complex kinetic mechanisms which contain bimolecular steps¹⁸ such as $A + B \rightarrow C$ (k_1), $A \rightarrow D \rightarrow E$ (k_2 , and k_3). While species A and B cannot in general be handled by the present approach, as they participate in a bimolecular step, species C, D, and E can still be related with A and B by the convolution approach. In fact, an easy task to write, with the given pattern for consecutive reactions, are the following relations:

$$C = (k_1 AB) \otimes 1; \quad D = (k_2 A) \otimes \exp(-k_3 t); \\ E = (k_3 D) \otimes 1 = k_2 k_3 A \otimes \exp(-k_3 t) \otimes 1 \quad (\text{C23})$$

In these cases (mixture of unimolecular and bimolecular steps) all species disappearing through first-order processes can still be handled by the convolution mechanism, and this may allow the direct estimation of rate constants or the comparison between experimental and calculated time evolutions. More complex cases, where the rate coefficients are time-dependent, including excimer formation and radiationless energy transfer can also be treated by the same formalism, nontrivial results being then obtained.²¹

CONCLUSION

The real subject of this work is pattern recognition in physical chemistry topics. In fact, all along this study, patterns are detected and discussed. This is rather evident for the thermodynamic part, less evident but nonetheless detectable in the second chemical kinetic part, where rate matrices and convolution equations can be mechanically constructed taking into consideration their particular structure, which in some cases gives rise to well defined rules. Pattern formalism can, thus, be further regarded as a formalism which describes the intrinsic structure of equations, allowing their construction in a mechanical way.

The diagrammatic method for thermodynamic relationships based on geometric and matrix operations not only represents a stimulating alternative view on a matter which usually leaves no space for imagination but also being based on a minimal set of information is not too unwieldy, computationally and conceptually. The space covered by the thermodynamic diagram can be considered a thermodynamic topological space in which neighborhood relations are important properties, and where combinatorial methods might

be applied, as already done in some other fields.³⁴ In fact the geometry of these neighborhood relations determine the entire formalism which is, unambiguous and straightforward. It should be noticed that while the propagating step of the matrix formalism is self-explanatory, the construction of the less obvious generating step can be generated with the help of diagram 1 and of the rule that allows only *S* and *T* or *P* and *V* combinations of the diamond parameters (orthogonality rule). This space can be used not only for its interesting mnemonic power but also to recognize the particular symmetry that connects the thermodynamic parameters and to derive new relationships of any order and complexity. The wealth of relations that can be found with this diagrammatic method is enormous. In fact, since the work of Gibbs there have been many attempts to divide the most important equations of thermodynamics into families due to their symmetry,^{1,2} and even the alternative work of Bridgman based on a condensed summary of differential coefficients³⁵ can be regarded along such an optic. Some aspects of this last work, together with the work of Callen² on the subject, are the basis of Phillips' work on a three-dimensional extension of the original Born construction. These last constructions, however, are "topologically" rather convoluted, and even if geometrically very accurate they normally assume a good background in theoretical physics.

The matrix and convolution methods find several applications in chemical kinetics of complex systems and in photochemical kinetics. The mechanical method to construct the rate matrices of any order and complexity reduces the task of writing the rate equations, a very tedious and error prone procedure, at the level of a recipe. Furthermore the matrix approach allows a general view of the integration of rate equations and introduces, for first-order and some second-order *K* matrices, the possibility to use the eigenvalue method for the solution of the kinetic equation with a formalism that, being very similar to the one used in quantum chemistry, emphasizes the formal similarity of these two fields. Some rate matrices, especially when opposing reactions are considered, show highly regular patterns, which can help to check the validity of the matrix for a given reaction, and even to control if the principle of microscopic reversibility is respected. The matrix approach can be extended to include open systems (tank reactors) with input and output flows and diffusion of reactive species, and reactions with stoichiometric coefficients $\nu \neq 1$ or with autocatalytic steps, which can be written using a method based on a series of rules, which reminds the simplex method for linear optimization. The convolution approach for chemical kinetics offers an alternative way to derive kinetic equations in a rather straightforward way. This method allows the writing of the mole balance equations directly in the integrated form, whenever the decay of a species is effectively first-order, and in the case of consecutive reaction schemes, the convolution equation itself act as a sort of pattern based on the iteration of consecutive growing terms after the production term like, i.e., $I = KP_A \otimes A_\delta \otimes B_\delta C_\delta \otimes D_\delta \dots$

It has been written that pure mathematics is a box of games³⁶ and that games have four components: objects to play with, an opening arrangement, rules, and a goal. Well, our aim in this paper has been to derive a kind of game for some topics of physical chemistry. The thermodynamic diagrams, the rate matrices, and the convolution equations

can be considered the objects to play with, the opening arrangements are the arrangements of the variables in the diagram, or of the rate constants in the *K* matrix, and of the production and δ -response term in the convolution equation. Patterns, sign rules, the rules for matrix construction and for construction of the sequence of *P*- and δ -terms in the convolution equation can be considered the rules of the game. The goal is the final meaningful relation used to derive the property of the system. Certainly, this game has here and there many flaws, but, nevertheless, it will be interesting to see where this effort will lead, as, "pattern building is a lot more fun than problem solving"³⁶ an assertion which seems to be well-known in the natural world, which, i.e., uses the fundamental pattern of the Fibonacci sequence for several natural phenomena.³⁷

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