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TELLEGEN'S THEOREM AND THERMODYNAMIC INEQUALITIES

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Summary

Once it is recognized that irreversible thermodynamics is essentially a field theory in its definition of flux and force variables, the way is clear to construct discrete, or network, representations of a wide class of irreversible phenomena. In this construction, many of the powerful techniques and results of graph theory and network analysis may be applied intact to derive thermodynamic relations heretofore arrived at by a more circuitous and less illuminating route. The network approach reveals the essential physical and mathematical assumptions, permitting a more intuitive and systematic analysis of quite complicated systems.

One of the most powerful of the network theorems is Tellegen's Theorem. Most, if not all, of the energy distribution theorems and extremum principles can be derived from it.

To illustrate the versatility and power of this approach, we derive several well-known inequalities in irreversible thermodynamics from Tellegen's Theorem.

1. Introduction

Network analogs of dynamical systems can be constructed for a wide variety of physical systems. The success of such dynamical modeling is surprising considering the apparent basic dissimilarity between the network and the process whose dynamic behavior it imitates (Kron, 1943, 1944, 1945, 1946, 1948; Olson, 1958).

Recently Roth (1955) and Branin (1962, 1966) have pointed out that the topological foundations of network theory are identical to those of the vector calculus. Thus most of the equations of classical field theory may be modeled to arbitrary accuracy by networks.

This structural isomorphism between discrete and continuous descriptions gives new insight into the structure of dynamical systems and allows many of the results of network analysis to be applied in other areas. Meixner (1963, 1966) has also noted the strong formal similarity between electrical network theory and irreversible thermodynamics, and has shown how the entropy concept in nonequilibrium states may be dispensed with in favor of free energy loss. In this paper we wish to emphasize the generality of the network approach and illustrate the advantages it offers in analyzing irreversible processes by deriving several well-known inequalities in a new and unified way.

2. The Steady-State Criterion

Prigogine (1968) and Prigogine and Glansdorff (1954) have demonstrated that, for a wide class of dynamical systems, the quantity $d_x P \equiv \sum J_i \dot{X}_i \leq 0$ in the natural evolution of a nonequilibrium system toward a steady state; the equality holds only at the stationary state.

For simplicity, the proof of the inequality is given for the case of one-dimensional diffusion of a single species (Degroot and Mazur, 1962).

Consider a volume, V, in contact through semipermeable membranes with two large reservoirs maintained at constant chemical potentials.

Prigogine's theorem says that for time-independent boundary conditions, the quantity $d_x P \equiv \int_V \underset{\sim}{J} \cdot \dot{\underset{\sim}{X}} \leq 0$, equality holding only at steady state. Here $\underset{\sim}{J}$ is the flux across a cross section of V and $\underset{\sim}{X}$ = grad μ is the driving force for diffusion, being the gradient of the chemical potential of the diffusing species.

Then, $d_x P = \int_V \underset{\sim}{J} \cdot \frac{\partial}{\partial t} (\nabla \mu) = \int_V \underset{\sim}{J} \cdot \nabla \frac{\partial \mu}{\partial t}$

$$= \int_V \nabla \cdot \left(J \frac{\partial \mu}{\partial t}\right) - \int_V \frac{\partial \mu}{\partial t} \nabla \cdot J = \int_{\partial V} \underset{\sim}{J} \frac{\partial \mu}{\partial t} - \int_V \frac{\partial \mu}{\partial t} \nabla \cdot \underset{\sim}{J}$$

By the assumption of constant boundary conditions the first integral vanishes. Since, by conservation, $\nabla \cdot \underset{\sim}{J} = \frac{\partial n}{\partial t}$

$$d_x P = - \int_V \frac{\partial \mu}{\partial t} \frac{\partial n}{\partial t} = - \int_V \frac{\partial \mu}{\partial n} \left(\frac{\partial n}{\partial t}\right)^2 .$$

The condition that the constitutive relation $\mu = \mu(n)$ be monotonically increasing is a thermostatic stability condition, and is assumed to hold throughout the dynamical process. We then have

$$d_x P = - \int_V \frac{\partial \mu}{\partial n} \left(\frac{\partial n}{\partial t}\right)^2 \leq 0.$$

The above inequality may be demonstrated in similar fashion for any process whose energy rate may be expressed as a product of a solenoidal and an irrotational vector field (Branin, 1966; Penfield, in press). That is, the potential, μ, and the flow, $\underset{\sim}{J}$, may be replaced by

any quantities obeying Kirchhoff's Laws: $\underset{\sim}{X}$ is the gradient of a scalar function and J satisfies a conservation condition $\nabla \cdot \underset{\sim}{J} = \dot{q}$.

The role of Kirchhoff's Laws is not accidental in this context. It turns out that KCL (Kirchhoff's Current Law) and KVL (Kirchhoff's Voltage Law) are physical restatements of the topological notions of homology and cohomology sequences (Hocking and Young, 1961). Topology deals with the fundamental connectivity properties of the space in which dynamical events occur. The very same topological considerations arise in the derivation of the vector calculus and network theory, the former being the limiting case of the latter (Branin, 1962; Branin, 1966). From a practical viewpoint, KCL and KVL variables represent physical quantities measured in completely different ways (Trent, 1955; Koenig, 1969).

The engineering terminology of "through" and "across" variables arose from the recognition that two types of measurements may be performed on dynamic systems: a conserved quantity "through" a flow meter, and a force quantity measured as a potential drop "across" two terminal locations (Koenig, 1960; Shearer et al., 1967; Martens and Allen, 1969). The flow variable is always contravariant and the potential covariant (Maclane, 1968; LeCorbeiller, 1950), corresponding physically to their extensive and intensive characters, respectively (Paynter, 1961), and topologically to their identification with the homology and cohomology sequences, respectively, of the linear graph representing the system connections.

The structural diagram in Fig. 1 illustrates clearly the relationship of the variables (Branin 1962; Branin, 1966; Desoer and Kuh, 1969).

The identities $\underset{\sim}{M}^T\underset{\sim}{A}=\underset{\sim}{0}$ and $\underset{\sim}{A}^T\underset{\sim}{M}=\underset{\sim}{0}$ are the discrete counterparts of the continuum identities curl $\circ$ grad=0, div $\circ$ curl=0 which, in turn, are the topological equivalents of $\partial \circ \partial = 0$ and $d \circ d = 0$, where ∂ is the boundary operator of a domain D and d the coboundary operator, or exterior derivative.

Now, consider how measurements are performed on V to determine its state. A discrete number of readings must be made along its length, which may be considered as port variables. That is, to any specified degree of accuracy, the dynamics may be modeled by an R-C chain as shown in Fig. 2.

Since the network represents the actual topology, any statement concerning the network that invokes only the network topology, KCL and KVL, should imply an equivalent statement about the continuum case, or at least its behavior as measured from a finite number of terminals. Such a statement is Tellegen's Theorem (Tellegen, 1952; Desoer and Kuh, 1968; Penfield, in press), which says that the "through" and "across" branch variables lie in orthogonal subspaces specified by the topology of the network only. Consequently, $\underset{\sim}{v}^T\underset{\sim}{j} = \underset{\sim}{0} = \sum_b v_b j_b$ where n = number of branches.

The proof is straightforward. If $\underset{\sim}{B}$ is the loop matrix (containing all the network topology), KCL may be written: $\underset{\sim}{j}=\underset{\sim}{B}^T\underset{\sim}{i}$. Therefore

$$\underset{\sim}{v}^T\underset{\sim}{j} = \underset{\sim}{v}^T\underset{\sim}{B}^T\underset{\sim}{i} = (\underset{\sim}{B}\underset{\sim}{v})^T\underset{\sim}{i}.$$

But KVL is $\underset{\sim}{B}\underset{\sim}{v}=\underset{\sim}{0}$, therefore, $\underset{\sim}{y}^T\underset{\sim}{j} = \underset{\sim}{0}$. Q.E.D.

Since, for each t, $\underset{\sim}{v}$ and $\underset{\sim}{j}$ are in fixed orthogonal subspaces, their time derivatives $\underset{\sim}{v}$ and $\frac{d\underset{\sim}{j}}{dt}$ must also remain in the same orthogonal

subspaces. Therefore, $\dot{\underset{\sim}{v}}^T \underset{\sim}{j} = 0$.

For any network of resistors and capacitors (say, as in Fig. 2),

$$\underset{\text{resis.}}{\sum_R j_k \dot{v}_k} + \underset{\text{cap.}}{\sum_c j_k \dot{v}_k,} + \underset{\text{ports}}{\sum_P j_k \dot{v}_k,} = 0.$$

The third sum vanishes by assumption of constant boundary conditions.

The constitutive relation for the storage elements, C_k, are assumed to be thermodynamically stable (Callen, 1960):

$$v_k = f_k(q_k),$$

$$f'_k(q_k) > 0.$$

Then, since

$$\dot{v}_k = f'_k(q_k)\,\dot{q}_k = f'_k(q_k)\,j_k,$$

$$\sum_R \dot{v}_k j_k = -\sum_c f'_k(q_k) j_k^2 \leq 0.$$

Aside from the restriction of monotonicity on the capacitor constitutive relations, nothing but the network topology and Kirchhoff's Laws (which are equivalent to conservation of charge and uniqueness of potential) has been employed. In particular, no statement concerning the nature of the other elements need be made.

Note that the dual statement $\Sigma v_k \frac{d}{dt} j_k < 0$ is not true for the above network, since $\frac{d}{dt} j_k = \ddot{q}_k$, whose sign is indeterminate in general.[2]

Prigogine's Theorem therefore emerges as a direct consequence of Tellegen's Theorem and thermodynamic stability.

3. Generalization

Since the derivation employs only the topological character of the flow and force variables in the form of Kirchhoff's Laws, we may

generalize the above inequality to arbitrary vector spaces. Any dynamical system with m degrees of freedom may be modeled by a network with m independent meshes.[3] The mesh currents, $\underset{\sim}{i}$, correspond to generalized velocities, and the mesh charges $\underset{\sim}{q} \equiv \int \underset{\sim}{i} dt$ are generalized coordinates.

The purpose here is not primarily to construct equivalent networks, although once this can be done algorithmically the way is clear to simulate arbitrary nonlinear dynamical processes quite easily (Oster and Auslander). More important, in our view, is the insight obtained from graphical representations. In addition to the intuitive advantages, much of the symbolic manipulation and mathematical simplification may be performed <u>before</u> the differential equations are written (Karnopp and Rosenberg, 1968). Once the differential equations have been written, all topological information is generally obscured. In addition, the large body of existing knowledge concerning networks may be employed to simplify analysis and obtain new results.

4. Chemical Reactions

By this approach we can deal with the phenomenological aspects of chemical reaction dynamics. It is evident that the flux and force variables employed to describe chemical reactions may be chosen to be "through" (conserved) and "across" (potential) quantities (Katchalsky and Curran, 1965; Haase, 1969). Therefore, the loose notion of reaction "network" can be made precise by the appropriate interpretation of the thermodynamic quantities.

Each reaction comprises a single degree of freedom in the dynamical sense (Duinker, 1968; Crandall et al., 1968), so that a reaction corresponds to a mesh, where the reaction flux $J_r \equiv \frac{1}{\nu_{rk}} \frac{dn_k}{dt}$ is the mesh current i_r, the mesh charge $q_r \equiv \int_0^t i_r dt$ is the degree of advancement of the reaction, ξ; and ν_{rk} is the stoichiometric coefficient of species k in reaction r (Katchalsky and Curran, 1965; Haase, 1969).

Since a chemical reaction is a dissipative process, a dissipative element must be included in each mesh. It is this branch that thermodynamically characterizes the reaction in the sense that the free energy loss accompanying the progress of the reaction is equivalent to the energy dissipated in the resistive branch.

Now the topology of a reaction network is completely contained in the stoichiometric matrix, $\underset{\sim}{\nu}$, which is obtained by writing the kinetics in matrix form, as illustrated in the following example. Note that the usual sign convention in chemical kinetics (reactants -, products +) is identical to the usual sign convention for the loop matrix (Desoer and Kuh, 1969). The substances may represent irreducible subunits of the reaction,

$$\left.\begin{array}{l} A + B \longrightarrow C \\ C \longrightarrow D \\ D + E \longrightarrow F + B \end{array}\right\} \quad \text{or} \sum_{b=1}^{6} \nu_{mb} n_b = 0 \quad \text{or} \ \underset{\sim}{\nu}\,\underset{\sim}{n} = 0$$

$$\text{where } \nu = \left[\begin{array}{cccccc} -1 & -1 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 1 & 0 & 0 \\ 0 & 1 & 0 & -1 & -1 & 1 \end{array}\right] \left.\begin{array}{l}\text{Three} \\ \text{reac-} \\ \text{tions.}\end{array}\right\}$$

$$\underbrace{\qquad\qquad\qquad}_{\text{6 species}}$$

The topological graph of this scheme is shown in Fig. 3, which may be constructed algorithmically in the following way.

The definition of the affinity is $\underset{\sim}{a} = \underset{\sim}{\nu}\underset{\sim}{\mu}$, where μ_b is the chemical potential of substance (branch) b. Since the affinity is a KVL variable, $\underset{\sim}{a} + \nu\mu$ is the expression for KVL for the associated circuit. Therefore, the resistor branch current $\underset{\sim}{j}$ and branch voltage $\underset{\sim}{v}$ completely characterize the dynamic behavior of the reaction mesh. In analyzing the system, the loop matrix $\underset{\sim}{B}$ has a natural decomposition obtained by taking the R_i as links and the remaining branches as the tree (Desoer and Kuh, 1969). In this manner the link (or cotree) variables represent the thermodynamics of the reaction. Since with this unique partition there is only one link in each mesh, the loop matrix may be written immediately as

$$\underset{\sim}{B} = \begin{array}{c} \left[\begin{array}{c:c} I & \nu \end{array}\right] \\ \text{r links} \quad \text{b species} \end{array} \quad \begin{array}{l} \text{r loops} \\ \text{(reactions)} \end{array}$$

Therefore, the graph may be drawn directly from the stoichiometric matrix.

The proof of the steady-state criterion follows exactly as before. Let R = link (resistor) index and c = tree (capacitor) index. From Tellegen's theorem we have

$$\underset{\sim}{j}_R^T \dot{\underset{\sim}{v}}_R = \underset{\sim}{j}_c^T \dot{\underset{\sim}{v}}_c = - \underset{\sim}{j}_c^T \underset{\sim}{Df}_c(\underset{\sim}{q})\dot{\underset{\sim}{q}}_c = - \underset{\sim}{j}_c^T \underset{\sim}{Df}_c(\underset{\sim}{q})\underset{\sim}{j}_c \leq \underset{\sim}{0}.$$

where $\underset{\sim}{Df}_c(\underset{\sim}{q})$ is the Jacobian matrix of $\underset{\sim}{f}(\underset{\sim}{g})$.

Again, once the topological structure is recognized, the proof proceeds independently of the physical nature of the variables, so long as they are "Kirchhoff Law variables."

This structural representation of chemical reactions offers several advantages over conventional representations. The topological relationships and dependencies are immediately apparent. It is clear, for

example, that to maintain a steady state, branches A, E, and F must be source branches, i.e., substances maintained constant by external reservoirs. KCL applied to each node yields immediately the integrals of motion, i.e., linear combinations of substances remaining constant during the reaction. A basic result of graph theory is that the node-incidence matrix, A_{nb}, is of rank n-1 (Seshu and Reed, 1968; Desoer and Kuh, 1969). Therefore the node-incidence matrix automatically generates a complete and nonredundant set of integrals. Reaction loops, or feedback, appear as dependent meshes, as in the classical Onsager triangle scheme shown in Fig. 4 (Katchalsky and Curran, 1965).

It can be easily verified that $\sum_{\theta} A_i = 0$ merely expresses the fact that mesh abc is the sum of meshes (reactions) 1, 2, and 3, which is evident from the graph.

If any substance participates in more than two reactions, the graph must be nonplanar. This has no effect on any of the above statements.

5. Minimum Entropy Production

In 1891 Maxwell formulated the "minimum heat theorem" (Maxwell, 1892), which states that, for <u>linear</u> resistive circuits with constant sources, the flows distribute themselves in such a way that the power dissipated (i.e., heat generated), P, is a minimum. Since the circuit is assumed isothermal, dividing the heat, Q, dissipated in the resistors by the ambient temperature, T, we find that $\frac{Q}{T} = \frac{dS}{dt}$, the entropy production, is also minimum (Prigogine, 1947).

An examination of this theorem reveals once again that the only requirements are the Kirchhoff Law properties of the variables. Thus the conclusions generalize to arbitrary thermodynamic systems whose variables are similiarly defined.

We first drop the requirement that the resistors be linear. We then define two new quantities (Millar, 1951; Duffin, 1946, 1947, 1948) for each branch, the "content," G, and its Legendre Transform, the "cocontent," G:

$$G_k = \int_0^{j_k} v_k dj_k \qquad G = \sum_k G_k$$

and

$$G^*_k = \int_0^{v_k} j_k dv_k \qquad G^* = \sum_k G^*_k.$$

Note that $G + G^* = P$, the total dissipation. For linear constitutive relations, $G = G^* = (1/2)P$.

From Tellegen's Theorem, $\underset{\sim}{j}^T \underset{\sim}{v} = 0$. Consider now a virtual change in the j's: $j_k \longrightarrow j_k + \delta j_k$, subject only to the constraint that the variations also obey KCL. Therefore

$$(\underset{\sim}{j} + \delta \underset{\sim}{j})^T \underset{\sim}{v} = 0.$$

By subtraction $\delta \underset{\sim}{j}^T \underset{\sim}{v} = 0$, i.e., the variations are also perpendicular to the voltage subspace. And so, $G = \underset{\sim}{v}^T \delta \underset{\sim}{J} = 0$. Therefore, at steady state, the content is stationary. If, in addition, all the resistor characteristics are strictly monotonically increasing, then G can be shown to be strictly convex (Duffin, 1946, 1947, 1948); hence the stationary point is an absolute minimum.

Alternatively, we could have considered variations in the forces, $\underset{\sim}{v} + \delta \underset{\sim}{v}$, subject to KVL, and arrived at

$$\delta G^* = \underset{\sim}{j}^T \delta \underset{\sim}{V} = 0.$$

For the special case of linear resistors, the extremum is exactly the minimum power theorem of Maxwell, $\delta P = \delta(\underset{\sim}{j}^T \underset{\sim}{R}_b \underset{\sim}{j}) = 0$.

A resistive network with constant sources is always in the steady state, since it has no dynamic elements. A network with dynamic (energy storage) elements and with constant sources will be purely resistive in the steady state only. Hence, again, the steady state is characterized by the stationarity (or the minimum) of the content. As far as stationarity is concerned, no assumption as to the nature of the branch relations has been assumed, so the theorem holds for arbitrary nonlinear, coupled systems.

6. Stability of Steady States

Prigogine has also proposed the "excess entropy production" $\delta_x P \equiv \sum \delta j_i \delta X_i$ as a stability criterion for thermodynamic systems (Prigogine and Glansdorff, to be published). Intuitively, it would seem that variations about a stable steady state that effect a net entropy reduction of the system are not favored in a thermodynamically stable system. Conversely, $\delta_x P < 0$ should be some indicator of system instability. We can make this notion clearer and more precise by examining the nonequilibrium system par excellence, the electrical network. For example, consider the chemical reaction network operating at a steady state.

In order to study the stability of the steady state, we may linearize about the steady state and obtain the small-signal dynamic equations,

$$\underset{\sim}{R}\dot{\underset{\sim}{q}} + \underset{\sim}{S}\underset{\sim}{q} = \underset{\sim}{0},$$

$$\dot{\underset{\sim}{q}} = (-\underset{\sim}{R}^{-1}\underset{\sim}{S})\underset{\sim}{q},$$

where $\underset{\sim}{R}$, $\underset{\sim}{S}$ are real, symmetric, nonsingular matrices. If the resistor and capacitor characteristics are strictly monotonically increasing, it can be shown that there is a unique steady state which occurs at the unique minimum of the total content of the network (Duffin, 1946, 1947, 1948; Desoer and Katzenelson, 1965). Furthermore, a simple Liapunov-type reasoning (see pp. 816-820 of Desoer and Kuh, 1969) shows that given <u>any</u> initial state, the circuit will asymptotically reach the unique steady state. It follows, therefore, that whenever the steady state is <u>unstable</u>, at least one resistor (dissipative process) must have a characteristic with a negative slope at the steady-state operating point.

Now, consider the following facts:

(i) λ is an eigenvalue of $\underset{\sim}{R}^{-1}\underset{\sim}{S}$ if and only if $1/\lambda$ is an eigenvalue of $(\underset{\sim}{R}^{-1}\underset{\sim}{S})^{-1} = \underset{\sim}{S}^{-1}\underset{\sim}{R}$.

(ii) $S > 0$ by thermodynamic stability. Therefore $\underset{\sim}{S}^{1/2}$ is a well defined, real symmetric, positive-definite matrix.

(iii) Then $\underset{\sim}{S}^{-1}\underset{\sim}{R}$ is equivalent to $\underset{\sim}{S}^{1/2}\underset{\sim}{R}\underset{\sim}{S}^{-1/2}$ by the similarity transformation $S^{1/2}(S^{-1}R)S^{-1/2}$. So $\underset{\sim}{S}^{-1}\underset{\sim}{R}$ and $\underset{\sim}{S}^{-1/2}\underset{\sim}{R}\underset{\sim}{S}^{-1/2}$ have the same eigenvalues.

(iv) $\underset{\sim}{S}^{-1/2}\underset{\sim}{R}\underset{\sim}{S}^{-1/2}$ is congruent to $\underset{\sim}{R}$, and therefore has the same index, i.e., the same number of negative eigenvalues (Martin and Mizel, 1966).

(v) The steady state is unstable if and only if the matrix $= \underset{\sim}{R}^{-1}\underset{\sim}{S}$ has at least one positive eigenvalue (Lefschetz, 1963).

From these facts it follows that the steady state is locally unstable if and only if R has at least one negative eigenvalue.[4]

The rate of free energy loss in the resistors is

$$P = \underset{\sim}{j}^T \underset{\sim}{R}_b \underset{\sim}{j} \quad , \qquad \underset{\sim}{R}_b = \text{resistor branch matrix.}$$

Using KCL in the form $\underset{\sim}{j} = \underset{\sim}{M}^T \underset{\sim}{i}$, we have

$$P = \underset{\sim}{i}^T \underset{\sim}{M} \underset{\sim}{R}_b \underset{\sim}{M}^T \underset{\sim}{i}$$

$$= \dot{\underset{\sim}{q}}^T \underset{\sim}{R} \dot{\underset{\sim}{q}} ,$$

where $\underset{\sim}{R} \equiv \underset{\sim}{M} \underset{\sim}{R}_b \underset{\sim}{M}^T$ is the resistor mesh matrix (Desoer and Kuh, 1969) and i = mesh currents.

Consider any perturbation of branch currents and voltages about the steady state, conforming to KCL, KVL, and the local (linearized) constitutive relations. If for some such perturbation

$$\delta \underset{\sim}{j}^T \delta \underset{\sim}{v} = \delta \underset{\sim}{j}^T \underset{\sim}{R}_b \delta \underset{\sim}{j} = \delta \underset{\sim}{i}^T \underset{\sim}{R} \delta \underset{\sim}{i} < 0,$$

then R has a negative eigenvalue; hence the steady state is unstable.

We have proven the following <u>Theorem</u>:

(i) The steady state is locally stable if and only if for <u>any</u> perturbation of branch voltages and branch currents about the steady state conforming to KVL, KCL, and the constitutive relations,

$$\delta \underset{\sim}{j}^T \delta \underset{\sim}{v} > 0.$$

(ii) The steady state is locally unstable if and only if for <u>some</u> such perturbation

$$\delta \underset{\sim}{j}^T \delta \underset{\sim}{v} < 0.$$

This result may be obtained more quickly (but less precisely) by starting from Tellegen's Theorem, $\underset{\sim}{v}^T \underset{\sim}{j} = 0$.

Therefore $\sum_{\text{resis.}} \delta j \; \delta V_k + \sum_{\text{cap.}} \delta j_k \delta V_k + \sum_{\text{ports}} \delta j_k \delta V_k = 0.$

By assumption of constant boundary conditions, the last sum vanishes. Inserting the (linearized) constitutive relations, we obtain the small-signal equations of motion:

$$\delta \underset{\sim}{j}^T \underset{\sim}{R}_b \delta \underset{\sim}{j} + \delta \underset{\sim}{j}^T \underset{\sim}{S} \delta \underset{\sim}{q} = 0,$$

$$\delta \dot{\underset{\sim}{q}}^T \underset{\sim}{R}_b \delta \dot{\underset{\sim}{q}} + \frac{d}{dt} \left[(1/2 \; \delta \underset{\sim}{q}^T \underset{\sim}{S} \delta \underset{\sim}{q} \right] = 0,$$

$$\delta \dot{\underset{\sim}{q}} \underset{\sim}{R}_b \underset{\sim}{S} \dot{\underset{\sim}{q}} = - \frac{d}{dt} \mathcal{E}_c,$$

where $\mathcal{E}_c \left[\underset{\sim}{q}(t) \right] \equiv (1/2) \delta \underset{\sim}{q}^T \underset{\sim}{S} \delta \underset{\sim}{q}$ is the "small-signal energy" about the steady state.

If the system is unstable, the trajectory initially moves away from the origin, $\delta \underset{\sim}{q} = 0$. Therefore $\mathcal{E}_c \left[\delta \underset{\sim}{q}(t) \right]$ is increasing, at least initially. Therefore

$$\delta \underset{\sim}{q}^T \underset{\sim}{R} \delta \underset{\sim}{q} < 0$$

$$\text{or} \sum_{\text{resis.}} \delta v_k \; \delta j_k < 0.$$

This reasoning, however, does not indicate what kinds of perturbations, δv_k and δj_k, are allowed in the search for a negative sum.

The question naturally arises: What sorts of physical phenomena can generate dissipative instabilities, i. e., locally active constitutive relations? Roughly speaking, it corresponds to the existence of "state-controlled resistors." Since the network represents a <u>conceptual</u> separation of processes actually occurring within the <u>same</u> volume element, the state variables $(\underset{\sim}{q}, \underset{\sim}{v})$ will enter into the resistor characteristics in a parametric fashion. For example, the phenomenological diffusion

resistance in part 2 is concentration dependent $\left(L_D = \frac{CD}{RT}, \text{ i.e.,}\right)$ the state variable of the capacitance feeds back to modulate the resistor characteristic (Katchalsky and Curran, 1965; Othmer and Scriven, 1969). This is a familiar effect in many nonlinear circuit devices such as thermistors (Chua, 1969), where the thermal state of the resistor (heat capacitance) alters the operating point of the electrical resistance.

The identical phenomenon arises in membrane oscillators (Mauro, 1961; Teorell, 1962), stirred tank reactors (Aris, 1969), and auto- and cross-catalytic chemical reactions (Prigogine and Nicholis, 1967; Lefever and Prigogine, 1968; Lefever, 1968). This generalization will be dealt with in a further publication.

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Footnotes

[1] B is the mesh matrix $\underset{\sim}{M}$ above, partition in a special way to be discussed later.

[2] By duality, $\Sigma v_k \frac{d}{dt} j_K \leq 0$ is true for RL networks, i.e., systems with inertial elements and dissipation, but not capacitive energy storage.

[3] With certain geometrical and dimensional restrictions to be dealt with elsewhere (Oster and Auslander, to be published).

[4] Remarks: (1) One negative resistor does <u>not</u> imply $\underset{\sim}{R}$ has one negative eigenvalue. For the chemical reaction network, however, $\underset{\sim}{R}$ is always diagonal; hence one negative resistor does imply a negative eigenvalue. (2) The above argument shows that if R has negative eigenvalue(s), the steady state cannot be stabilized by adjustment of the energy storage elements. (3) The critical case ($\lambda = 0$) is ruled out by the fact that, for our networks, $\underset{\sim}{R}$ is nonsingular. (4) Since $\underset{\sim}{R}$ and $\underset{\sim}{S}$ are real and symmetric, λ is necessarily real.

[5] $\mathcal{E}_c$ is <u>not</u> the "perturbation energy" about the steady state $\bar{\underset{\sim}{v}}^T \bar{\underset{\sim}{j}}$:

$$(\bar{\underset{\sim}{v}} + \delta \underset{\sim}{v})^T (\bar{\underset{\sim}{j}} + \delta \underset{\sim}{j}) = \bar{\underset{\sim}{v}}^T \bar{\underset{\sim}{j}} + \delta \underset{\sim}{v}^T \delta \underset{\sim}{j} + \delta \underset{\sim}{v}^T \bar{\underset{\sim}{j}} + \bar{\underset{\sim}{v}} \delta \underset{\sim}{j} ,$$

so $\mathcal{E}_c$ includes the "correlation" terms, since power is a nonlinear function.

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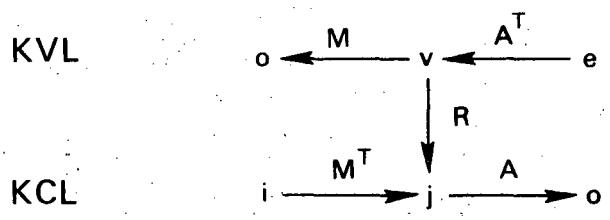
List of Symbols*

$\underset{\sim}{A}$	defined on fig. 2
$\underset{\sim}{\mathcal{A}}$	affinity $\equiv - \underset{\sim}{\nu}\ \underset{\sim}{\mu}$
B	= partitioned mesh matrix
$\underset{\sim}{C}$	branch capacitance matrix
d	coboundary operator
D	diffusion coefficient
$D\underset{\sim}{f}(\underset{\sim}{x})$	Jacobian matrix of $\underset{\sim}{f}(\underset{\sim}{x})$
$\underset{\sim}{e}$	defined on fig. 2
c	small signal energy
G	content
G^*	cocontent
$\underset{\sim}{i}$	defined on fig. 2
$\underset{\sim}{I}$	identity matrix
$\underset{\sim}{j}$	defined on fig. 2
J_i	thermodynamic flux
$\underset{\sim}{J}_r$	reaction flux of reaction r
L_D	Onsager phenomenological diffusion conductance
M	defined on fig. 2
$\underset{\sim}{N}$	particle vector
P	dissipation
$\underset{\sim}{q}$	branch charge vector
$\underset{\sim}{q}_r$	mesh charge vector
Q	= heat
R	gas constant
$\underset{\sim}{R}$	resistor mesh matrix

$\underset{\sim}{R}_b$	branch resistance matrix
S	entropy
$\underset{\sim}{S}$	$= \underset{\sim}{C}^{-1}$
t	time
T	= absolute temperature
$\underset{\sim}{v}$	defined on fig. 2
V	volume of system
X_i	thermodynamic force
∂	boundary operator
$\underset{\sim}{\mu}$	chemical potential vector
$\underset{\sim}{\nu}$	stoichiometrix matrix (reactions x species)
ξ_r	degree of advancement of reaction r



A = *node incidence matrix*

M = *mesh current matrix*

i = *mesh current vector*

j = *branch current vector*

v = *branch voltage vector*

e = *node to datum voltage vector*

Topological relationship between dynamical variables

Fig. 1

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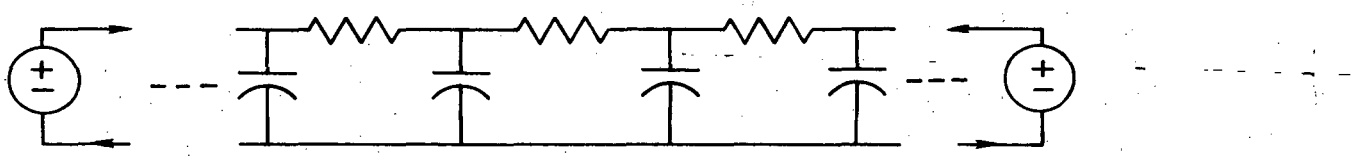

Network realization of 1-dimensional diffusion

Fig. 2

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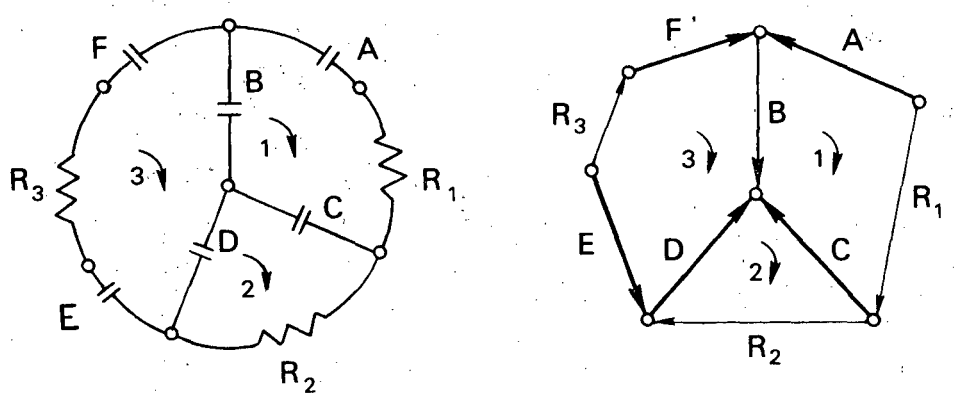

(a) CIRCUIT *(b) TOPOLOGICAL GRAPH*

Graphical representation of reaction network

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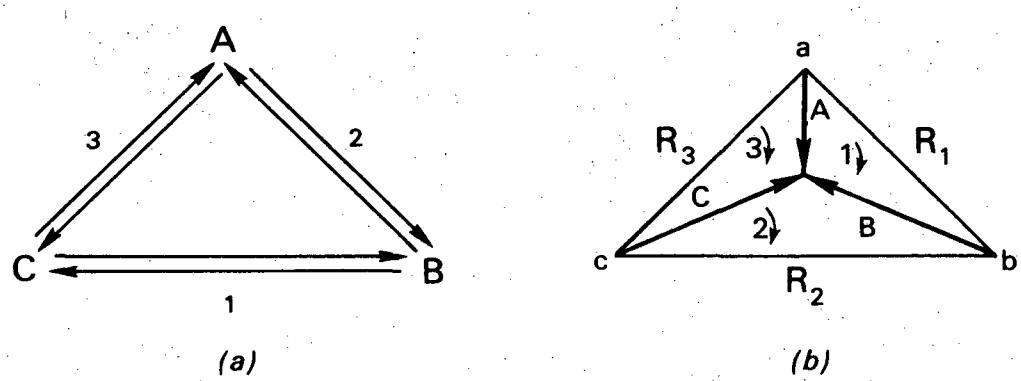
Fig. 3



Onsager scheme

Fig. 4

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