TELLEGEN'S THEOREM AND THERMODYNAMIC INEQUALITIES

by

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ABSTRACT

Electrical networks are special types of irreversible thermodynamic systems. The underlying mathematical unity of the two fields allows many of the techniques of network analysis to be generalized, thus permitting a wide class of nonlinear, nonsteady-state irreversible processes to be formulated in a network theoretic framework.

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.

In the following presentation we will derive several thermodynamic inequalities as well as explicit conditions guaranteeing the stability or the unstability of an equilibrium point, or a steady state.

1. INTRODUCTION

Network analogs have been constructed for a wide variety of physical systems, and have proven extremely useful in analyzing their dynamic behavior.

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. This structural isomorphism between discrete and continuous descriptions gives new insight into the structure of dynamical systems, and allows many of the powerful techniques of graph theory and network theory to be brought to bear on the thermodynamic analysis of complex biological structures. By exploiting this connection, the essential assumptions are revealed, permitting a more intuitive and systematic derivation of thermodynamic relations heretofore arrived at by a more circuitous and less illuminating route.[1] The resulting mathematical formalism extends the thermodynamic model to include nonlinear, nonsteady phenomena.

We derive below several known thermodynamic inequalities and in doing so clearly exhibit the minimal assumptions required for their validity. We also derive conditions guaranteeing the stability and the unstability of a steady state.

2. THERMODYNAMICS AND NETWORK THEORY

2.1 Irreversible thermodynamics, as presently constituted, is not a true dynamical theory in the usual sense. Equilibrium thermodynamics deals only

with the initial and final states of a process. Conventional irreversible thermodynamics is also a "static" theory yielding only the nonequilibrium steady states, not the entire dynamical trajectory.

In view of the extreme complexity of the systems encountered in biology, it would seem desirable to extend the thermodynamic phenomenological model so as to facilitate the complete time dependent analysis of complex, nonlinear nonequilibrium systems. The most straightforward approach to such a generalization is to bring thermodynamics into conformity with the other dynamical theories of physics.

The concept of a dynamical system is extremely important and extremely general: with appropriate selection of the system state, it includes the basic models of physics (classical and quantum mechanics, hydrodynamics, elasticity, electromagnetism), of network and control theory, and of computer science (Turing machines, automata, sequential machines).[2]

It would be out of place here to develop the notion of dynamical systems in complete generality. The reader is referred to the following references for a more complete treatment. (Desoer, 1970, p. 42, Zadeh and Desoer, 1964, Jurdjevic, 1970.) It will suffice here to restrict our attention to that class of systems which may be adequately represented by differential equations of the general form

$$\dot{\underline{x}} = \underline{F}(\underline{x}); \quad \underline{x}(0) = \underline{x}_0$$

That is, the system state $\underline{x}$ (whose velocity vector is $\dot{\underline{x}}$) is propelled by the vector field $\underline{F}(\underline{x})$ such that the knowledge of $\underline{x}_0$, the state at any initial time t_0, uniquely determines the trajectory for all times thereafter.

We may frequently place an additional restriction on the dynamical system: the vector field $\underline{F}$ is irrotational and therefore may be expressed as a gradient field.

The detailed procedure for constructing network representations for general thermodynamic systems is given elsewhere (Oster and Auslander, 1970; Oster, Perelson, Katchalsky, 1970). In this communication we will give only a brief discussion to motivate the subsequent derivations and focus our attention on the formal structure of the dynamical equations.

2.2 We must first ask what, if anything, electrical networks have in common with other physical systems that thermodynamics seeks to describe. For whatever else an electrical network may be, it is certainly a non-equilibrium thermodynamic system. However, one does not ordinarily consider network theory as an application of irreversible thermodynamics; this is because electrical engineers have developed a set of specialized techniques which seem quite foreign to the classical methods of thermodynamics. In fact, the network approach is quite general and with modifications can be applied to other thermodynamic systems.

One thing that immediately comes to mind is the remarkable ability of electrical networks to imitate the dynamical behavior of non-electrical systems. The success of such network analogs may seem surprising considering the apparent basic dissimilarity between the network and the process whose dynamic behavior it imitates. Network "analogs" of electrophysiological processes are well-known; indeed, Kron and others have devised network representations for practically all of the equations of

physics, from the Navier-Stokes equations to Schröedinger's equation (Kron, 1943, 1944, 1945, 1946, 1948).

The ubiquity of the network concept is no accident. If we examine the essential mathematical assumptions underlying the various dynamical theories of physics we find a great number of common features. There are two mathematical structures underlying most physical models; one topological or "kinematic," and one "dynamic." The first deals with the connectivity properties of the state <u>space</u> in which the physical processes are described, and the other has to do with the defined relationships between the state <u>variables</u> that one chooses to characterize the system.

2.3 With regard to the topological properties of the state space, there are dual mathematical structures available. On the one hand, point-set topology gives rise to the operational structure of (vector) calculus which continuum theories employ to generate partial differential field equations. On the other hand, combinatorial or algebraic topology provides a discrete, or reticulated view of the state space and gives rise to ordinary differential equations. The network representation employs combinatorial topology to construct a discrete operational structure completely paralleling that of the continuum theory. That is, 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).

For example, imagine that we wish to describe the distribution of current j and potential ϕ, on a smooth conducting surface. On the one

hand, we could attempt a description in terms of continuous functions giving the values of $\underset{\sim}{j}$ and ϕ at each point. This could prove rather cumbersome for complex geometries, boundary conditions and material properties. Alternatively, we could obtain a reticulated description by imagining a "grid," or network overlaying the conducting surface. We could then measure the current, j_i, through each branch and the voltage across each branch, $v_i = \Delta\phi_i$. These measurements could then be arranged in matrix form. Intuitively, it seems clear that, as the network mesh is made finer and finer, we may approach the continuum distributions as closely as desired. The tabulation matrices described above will then approach the continuum differential operators of vector calculus.

To see how this works, we must introduce a method for describing the network topology, the so-called "connection matrices." These are easily constructed by merely labelling each node, branch and mesh in the networks, and assigning an arbitrary reference direction to each branch and an arbitrary orientation (clockwise, say) to each mesh. We then construct the connection matrices according to the following algorithm (Desoer and Kuh, 1969, p. 417 and p. 458):

(i) Node-branch matrix

$$(A)_{ij} \equiv \begin{cases} +1 & \text{if branch i is directed out of node j} \\ -1 & \text{if branch i is directed into node j} \\ 0 & \text{if branch i is not incident on node j} \end{cases}$$

(ii) Branch-mesh matrix

$$(M)_{ik} \equiv \begin{cases} +1 & \text{if branch i bounds mesh k in the + direction} \\ -1 & \text{if branch i bounds mesh k in the - direction} \\ 0 & \text{if branch i does not belong to mesh k.} \end{cases}$$

If we now construct the vector of all branch currents, $\underset{\sim}{j} = (j_1, \ldots, j_b)$, and the vector of all branch voltages $\underset{\sim}{v} = (v_1, \ldots, v_b)$, we can easily verify that $\underset{\sim}{j}$ lies in the nullspace of $\underset{\sim}{A}$ and $\underset{\sim}{v}$ lies in the nullspace of $\underset{\sim}{M}$:

$$\underset{\sim}{A}\underset{\sim}{j} = \underset{\sim}{0} \tag{1}$$

$$\underset{\sim}{M}\underset{\sim}{v} = \underset{\sim}{0} \tag{2}$$

This, of course, merely expresses the conservation of current flows (Kirchhoff's Current Law, KCL) and the uniqueness of potential (Kirchhoff's Voltage Law, KVL). Furthermore, one can also verify that the following purely topological identity is always valid

$$\underset{\sim}{A}\underset{\sim}{M}^T = \underset{\sim}{0} \tag{3}$$

$$\text{or} \quad \underset{\sim}{M}^T\underset{\sim}{A} = \underset{\sim}{0} \tag{4}$$

By defining a "mesh current vector" $\underset{\sim}{i}$ and a "node to datum" potential vector $\underset{\sim}{e} \equiv (\phi_1 - \phi_0, \ldots, \phi_n - \phi_0)$, where $\phi_i - \phi_0$ is the potential of the ith node with respect to an arbitrarily chosen reference node, the commutative diagram of Fig. 1a results (Branin, 1962, 1966).

The meaning of Fig. 1a is as follows: we are given a topological structure, the linear graph of the network. We associate with the elements of the graph (nodes, branches, meshes) two independent algebraic structures: (a) a set of "flows" obeying a local conservation condition, KCL (1); (b) a set of "efforts" (forces) obeying a uniqueness condition (i.e. state functions), KVL (2).[4] Figure 1 then represents the constraints imposed on the flow and force variables due to the network topology. In the limit of infinitesimal mesh size the topological identities (3) and (4) become

the familiar vector identities, valid for <u>any</u> differentiable fields j, $\phi' \equiv \phi - \phi_0$:

$$\text{div·curl } (j) = 0 \tag{5}$$

$$\text{curl·grad } (\phi') = 0 \tag{6}$$

2.4　In addition to the topological constraints imposed by conservation (KCL) and/or uniqueness (KVL), there are 3 additional "dynamic" constraints on the dynamical variables: the constitutive relations. From the basic branch quantities j and v, we may define two further state variables by integration: a generalized displacement $q(t) = q(0) + \int_0^t j \, dt$ and a generalized momentum, or flux, $\phi(t) = \phi(0) + \int_0^t v \, dt$ (Paynter, 1961, p. 136). These state variables are connected by 3 constitutive relations representing energy storage and dissipation as in Fig. 1b (Oster, Auslander, 1970, Oster, Perelsen and Katchalsky, 1970). More explicitely we have, respectively, for capacitive, resistive and inductive elements the following constitutive relation

$$\text{(a)} \quad v = f_c(q) \; ; \quad \text{(b)} \quad f_R(v,j) = 0 \; ; \quad \text{(c)} \quad j = f_L(\phi) \tag{5}$$

Figure 1a and Fig. 1b represent the complete operational structure of the dynamical systems dealt with here. Furthermore, as we shall see in the case of chemical reactions, not every network arises via reticulation of the continuum.

2.5　We emphasize that we are not dealing with "network analogs" in the

usual sense. We are concerned only with the formal mathematical struc-
ture common to both network theory and thermodynamics (Sudarshan, 1962;
Trautman, 1966, p. 166). In this respect, we regard a network as merely
another, more explicit, way of writing the topological and dynamical con-
straints of the system. Indeed, the differential equations may be obtained
more or less algorithmically from the network. The network representation
and the differential equation representation are, however, not completely
equivalent. While the network contains the dynamical equations as well
as the system topology, the network cannot usually be reconstructed from
the differential equations: information regarding system topology has
been lost in going from the network representation to the differential
equation representation (see Appendix A).

We shall demonstrate below that by using the network representation
of the dynamical system we will be able to clearly separate the topologi-
cal and dynamical aspects of thermodynamic systems. We emphasize that
the separation of reversible and irreversible processes takes concrete
form only for electrical networks. In more general thermodynamic processes,
this separation is a purely conceptual device, serving only to clarify the
formal structure, and enabling us to construct an "equivalent network"
representation of the dynamical system.

3. THE STEADY-STATE CRITERION

3.1 Prigogine (1968) and Prigogine and Glansdorff (1954) have demon-
strated that, for a wide class of dynamical systems, the quantity

$d_x P = \Sigma J_i \dot{X}_i \leq 0$ 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 $d_x P \equiv \int_V J \cdot \dot{X} \leq 0$, equality holding only at steady state. Here J is the flux through a cross section of V and $X = \text{grad } \mu$ is the driving force for diffusion, being the gradient of the chemical potential of the diffusing species.

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

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

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

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

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

$$d_x P = -\int_V \frac{\partial \mu}{\partial n} \left(\frac{\partial n}{\partial t}\right)^2 \le 0. \tag{7}$$

3.2 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. That is, the potential, μ, and the flow, $\underset{\sim}{J}$, may be replaced by <u>any</u> quantities obeying Kirchhoff's Laws: $\underset{\sim}{X}$ is the gradient of a scalar function and $\underset{\sim}{J}$ satisfies a conservation condition $\nabla \cdot \underset{\sim}{J} = \dot{q}$.

In most thermodynamic systems the free energy rate (or power) is given as the product of a solenoidal and an irrotational vector field. That is, one dynamical variable is a potential function and the conjugate dynamical variable represents the flow of a locally conserved quantity. That this is generally so can be seen by examining the Gibbs Equation, or its appropriate Legendre Transforms[5]

$$dU = TdS - pdV + \sum_i \mu_i dn_i + HdB + \ldots \tag{8}$$

Electrical network theory concerns itself exclusively with the last two terms representing electronic capacitive and inductive energy storage, respectively.

The role of Kirchhoff's Laws is not accidental in this context. As we have discussed in Section 2 KCL (Kirchhoff's Current Law) and KVL (Kirchhoff's Voltage Law) are physical restatements of the topological properties of the dynamical space. From a practical viewpoint, KCL and KVL variables represent physical quantities measured in completely different

ways (Trent, 1955): the engineering terminology of "through" and "across" variables arose from the recognition that two types of measurements may be performed on dynamical systems: a conserved quantity "through a flow meter," and a force quantity measured as a potential drop "across two terminal locations" (Koenig, 1960, p. 9; Shearer et al., 1967, Chap. 4; Martens and Allen, 1969, p. 19).

3.3 Now, consider how measurements are performed on the volume 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 speci-fied degree of accuracy, the dynamical equations may be represented by a network of resistors and capacitors as shown in Fig. 3.

The network topology via the Kirchhoff laws impose very important constraints on the "through" variables (j) and the "across" variables (v). One of their most important consequences is the Tellegen Theorem (Tellegen, 1952; Desoer and Kuh, 1969; Penfield, et al., 1970).

Tellegen's Theorem: Let v = vector of branch potentials (KVL variables: voltage, chemical potential, pressure, etc.), and j = vector of branch flows (KCL variables: current, chemical reaction flux, etc.), then

$$v^T j = 0 \tag{9}$$

i.e. the KCL and KVL variables lie in fixed orthogonal subspaces, the null-spaces of A and M, respectively.

Proof: The proof follows directly from Fig. 1a, substituting in (9)

either the homology (KCL) or cohomology (KVL) sequences for $\underset{\sim}{j}$ or $\underset{\sim}{v}$, respectively, we observe that (9) is equivalent to the identities:

$$\underset{\sim\sim}{M}\underset{\sim}{A}^T = \underset{\sim}{0} \tag{3}$$

$$\underset{\sim\sim}{A}\underset{\sim}{M}^T = \underset{\sim}{0} \tag{4}$$

which we have earlier identified with their continuum counterparts (5) and (6). Q.E.D.

The reason for the generality of Tellegen's theorem is clear: it is a purely topological result, independent of any assumption on constitutive relations, steady states, etc. The only assumptions are the conservation of flows (KCL), and uniqueness of potentials (KVL).

Stated in thermodynamic terms, Tellegen's Theorem implies the following transparent statement (Oster, Perelson, Katchalsky, 1970):

> "In a closed thermodynamic system,
> the free energy dissipated by the
> irreversible processes is equal to
> the reversible changes in free energy."

e.g., for an isothermal, isobaric system

$$\left(\frac{dG}{dt}\right)_{rev} + \phi = 0 \tag{10}$$

where G is the Gibbs Free Energy and $\phi = T \frac{d_i S}{dt}$ is the dissipation function.

It is important to realize, however, that the scope of Tellegen's Theorem transcends its interpretation in terms of energy. For instance,

consider the following situation: given two thermodynamic systems S_1 and S_2 (say, electrical networks) with <u>different</u> processes and constitutive relations but with the <u>same topology</u>. Tellegen's Theorem assures us that at each instant of time, not only

$$v_1^T \, j_1 = 0 \tag{11}$$

and

$$v_2^T \, j_2 = 0 \tag{12}$$

but also

$$v_1^T \, j_2 = 0 \tag{13}$$

and

$$v_2^T \, j_1 = 0 \ ! \tag{14}$$

This holds even though S_1 and S_2 may represent completely different thermodynamic processes. Furthermore, if $v_1(t)$ represents the potentials for S_1 at time t and $j_2(\tau)$ is the flows in S_2 at any other time τ, then

$$v_1(t)^T \, j_2(\tau) = 0. \tag{15}$$

It is clear that these identities cannot be interpreted in terms of energy conservation. Such relations, while not amenable to any simple physical interpretation, are useful in proving many other theorems (see Penfield, 1970).

3.4   We now return to the steady state criterion. The proof parallels that given in Section 3.1, but now we begin with Tellegen's Theorem.

<u>Theorem</u>:

Given a nonequilibrium thermodynamic system obeying the following

conditions:

(i) constant potentials on the boundaries

(ii) the thermodynamic stability condition

$$\underset{\sim}{f}'_C(\underset{\sim}{q}) > 0$$

holds (i.e. $\underset{\sim}{x} \neq \underset{\sim}{0}$ implies $\underset{\sim}{x}^T \underset{\sim}{f}'(\underset{\sim}{q})\underset{\sim}{x} > 0$), where

$$\underset{\sim}{v} = \underset{\sim}{f}_C(\underset{\sim}{q})$$

is the capacitive constitutive relation and

$$\underset{\sim}{q}(t) \equiv \underset{\sim}{q}(0) + \int_0^t \underset{\sim}{j} \, dt.$$

Then the following inequality holds along any dynamical trajectory

$$\sum_R \dot{v}_i \, j_i \leq 0,$$

equality holding only at the steady state, and where the sum is taken over

all dissipative processes (resistors).

<u>Proof</u>: Since, for each t, $\underset{\sim}{v}$ and $\underset{\sim}{j}$ lie in <u>fixed</u> orthogonal subspaces, their

time derivatives $\dot{\underset{\sim}{v}}$ and $\frac{d}{dt}\underset{\sim}{j}$ must also remain in the same orthogonal sub-

spaces. Therefore,

$$\dot{\underset{\sim}{v}}^T \underset{\sim}{j} = 0. \tag{17}$$

For any network of resistors (dissipation) and capacitors (storage)

(say, as in Fig. 2),

-14-

$$\sum_{\substack{R \\ \text{resis.}}} j_k \dot{v}_k + \sum_{\substack{c \\ \text{cap.}}} j_k \dot{v}_{k,} + \sum_{\substack{P \\ \text{ports}}} j_k \dot{v}_{k,} = 0$$

The third sum vanishes by assumption of constant excitation at the ports, or bounderies.

The constitutive relation for the capacitive storage elements (see (5.a)) are assumed to be thermodynamically stable (Callen, 1960):

$$f_k'(q_k) > 0. \tag{18}$$

Then, since

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

$$\sum_R \dot{v}_k j_k = - \sum_c f_k'(q_k) \ j_k^2 \leq 0. \qquad \text{Q.E.D.}$$

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.[7]

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

Comment: Since the derivation employs 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.[9] 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.
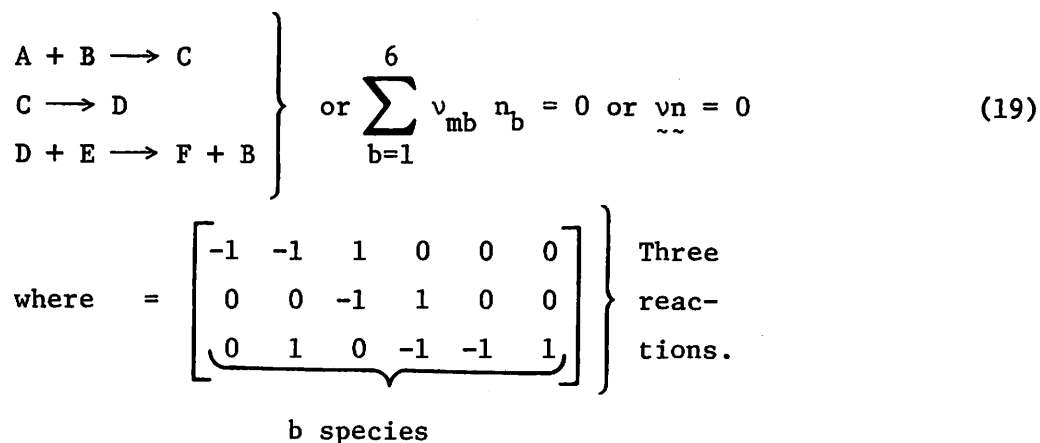
4. CHEMICAL REACTIONS

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" and "across" quantities (Katchalsky and Curran, 1965). 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), so that a reaction corresponds to a loop (mesh)[8] where the reaction flux of the rth reaction $J_r \equiv \dfrac{1}{\nu_{rk}} \dfrac{dn_k}{dt}$ is the loop current i_r, the loop 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 loop. It is this branch that thermodynamically characterizes the reaction in the sense that the free energy loss accompanying the progress of the reaction is represented by the energy dissipated in the resistive branch.

Now the topology of a reaction network is completely contained in the stoichiometric matrix, ν, 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,

$$
\left.\begin{array}{l}
A + B \longrightarrow C \\
C \longrightarrow D \\
D + E \longrightarrow F + B
\end{array}\right\} \quad \text{or} \quad \sum_{b=1}^{6} \nu_{mb}\, n_b = 0 \quad \text{or} \quad \nu n = 0 \tag{19}
$$

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

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

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

To each specie we associate a capacitive branch (labelled A, B, C, D, E and F in Fig. 3); to each reaction we associate a loop. Now the definition of affinity is $a = -\nu\mu$, where μ_b is the chemical potential of specie b. Since affinity is a KVL variable, $a + \nu \cdot \mu = 0$ is the expression of KVL for the associated network. The affinity of reaction r will be the voltage across the resistor inserted in loop r to represent the dissipative process. Thus in general, the resistor branch current j and branch voltage v completely characterize the dynamic behavior of the reaction loop. In

analyzing the system, the loop matrix $\underset{\sim}{B}$ has a natural decomposition obtained

by taking the resistors R_i as links and the remaining capacitive branches

as tree branches (Desoer and Kuh, 1969, p. 481). 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 reaction loop,

the loop matrix may be written immediately as

$$\underset{\sim}{B} = \left[\begin{array}{c|c} \mathcal{I} & \mathcal{V} \end{array} \right] \tag{20}$$

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

$$\underset{\sim}{j}_R^T \, \underset{\sim}{\dot{v}}_R = - \underset{\sim}{j}_c^T \, \underset{\sim}{\dot{v}}_c = - \underset{\sim}{j}_c^T \, \underset{\sim}{Df}_c(q) \underset{\sim}{\dot{q}}_c = - \underset{\sim}{j}_c^T \, \underset{\sim}{Df}_c(q) \underset{\sim}{j}_c \le \underset{\sim}{0}. \tag{21}$$

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

Again, once the topological structure is recognized, the proof pro-

ceeds independently of the physical nature of the variables, so long as

they are "Kirchhoff Law variables."

This network representation of chemical reactions offers several

advantages over conventional representations. The topological relation-

ships and dependencies are immediately apparent. It is clear, for example

that to maintain a steady state, at least one loop must not contain any

capacitor. For example, branches A, E and F must be source branches (voltage sources), i.e., the corresponding species must hold constant by external reservoirs. Note that a voltage source is a limiting case of a capacitor whose voltage is independent of q. 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 (Desoer and Kuh, 1979). 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 $\sum_{mesh} A_i = 0$ 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 driven by 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 conclusions may be generalized to arbitrary thermodynamic systems described by Kirchhoff Law variables.

We first drop the requirement that the resistors be linear. We then define two new quantities (Millar, 1951; Duffin, 1956, 1947, 1948) for each branch, the "content," G, and its Legendre Transform, the "cocontent," G:

$$G_k = \int_0^{j_k} v_k dj_k \qquad\qquad G = \sum_k G_k \qquad (22)$$

and

$$G_k^* = \int_0^{v_k} j_k dv_k \qquad\qquad G^* = \sum_k G_k^*. \qquad (23)$$

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

Consider first the case of systems driven by constant current sources. 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

$$(\underset{\sim}{j} + \underset{\sim}{\delta j})^T \underset{\sim}{v} = 0. \qquad (24)$$

By subtraction $\underset{\sim}{\delta j}^T \underset{\sim}{v} = 0$, i.e., the variations are also perpendicular to the voltage subspace. And so, $\delta G = \underset{\sim}{v}^T \underset{\sim}{\delta J} = 0$. Therefore, at the 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, 1956, 1957, 1948); hence the stationary point is the unique absolute minimum.

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

$$\delta G^* = j^T \delta v = 0. \qquad (25)$$

for systems driven by constant force (voltage) sources.

For the special case of linear resistors, the extremum is exactly the minimum power theorem of Maxwell, $\delta P = \delta(j^T R_b j) = 0$.

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, provided that the nonlinear coupled resistors are reciprocal (so that the content can be well defined) (Brayton and Moser, 1964).

6. STABILITY OF STEADY STATES

Prigogine has also proposed the "excess entropy production"

$\delta_x P = \sum \delta j_i \delta X_i$ as a stability criterion for thermodynamic systems (Prigogine and Glansdorff, 1965). Intuitively, it would seem that

variations about a stable steady state that effect a <u>net</u> 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 dynamical equations (Coppel, 1965, Chap. 3, Sec. 3),

$$R\dot{q} + Sq = 0, \tag{26}$$

$$\dot{q} = (-R^{-1}S)q, \tag{27}$$

where R, 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: λ is an eigenvalue of $R^{-1}S$ if and only if $1/\lambda$ is an eigenvalue of $(R^{-1}S)^{-1} = S^{-1}R$. The matrix S is

positive-definite by thermodynamic stability, therefore $\underset{\sim}{S}^{1/2}$ is a well

defined, real symmetric, positive-definite matrix. Now $\underset{\sim}{S}^{-1}\underset{\sim}{R}$ is equiva-

lent to $\underset{\sim}{S}^{-1/2}\underset{\sim}{R}\underset{\sim}{S}^{-1/2}$ by the similarity transformations $\underset{\sim}{S}^{1/2}(\underset{\sim}{S}^{-1}\underset{\sim}{R})\underset{\sim}{S}^{-1/2}$; 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. Observe that $\underset{\sim}{S}^{-1/2}\underset{\sim}{R}\underset{\sim}{S}^{-1/2}$

is congruent to $\underset{\sim}{R}$, and therefore has the same index, i.e., the same

number of negative eigenvalues (Martin and Mizel, 1966). From these facts

we draw the following important conclusions:

(1) If the matrix R has all its eigenvalues positive, then the

steady state is (locally) asymptotically stable;

(2) If R has one or more negative eigenvalues, then the steady

state is unstable (Coppel, 1965, p. 69 and 75).[10]

The rate of free energy loss in the resistors is

$$P = \underset{\sim}{j}^{T}\underset{\sim}{R}_{b}\underset{\sim}{j} \ , \qquad \underset{\sim}{R}_{b} = \text{resistor branch matrix.} \tag{28}$$

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

$$P = \underset{\sim}{i}^{T}\underset{\sim}{M}\underset{\sim}{R}_{b}\underset{\sim}{M}^{T}\underset{\sim}{i}$$
$$\tag{29}$$
$$= \underset{\sim}{\dot{q}}^{T}\underset{\sim}{R}\underset{\sim}{\dot{q}},$$

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

$\underset{\sim}{i}$ = mesh currents.

Consider any perturbation of branch currents and voltages about the

steady state, conforming to KCL, KVL, and the local (linearized) constitu-

tive relations. If for some such perturbation and considering only

resistor currents and voltages,

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

then R has at least one negative eigenvalue; hence the steady state is unstable.

We have proven the following:

<u>Theorem</u>

(i) If, for <u>any</u> perturbation of branch voltages and branch currents about the steady state, and conforming to KVL, KCL and the constitutive relations,

$$\sum_{\text{resis.}} \delta j_k \, \delta v_k > 0, \tag{30}$$

then the steady state is locally stable.

(ii) If, for <u>some</u> such perturbation,

$$\sum_{\text{resis.}} \delta j_k \, \delta v_k < 0, \tag{31}$$

then the steady state is locally unstable.

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

$$\delta \underset{\sim}{v}^T \, \delta \underset{\sim}{j} = 0 \tag{32}$$

we obtain

$$\sum_{\text{resis.}} \delta j_k \delta v_k + \sum_{\text{cap.}} \delta j_k \delta v_k + \sum_{\text{ports}} \delta j_k \delta v_k = 0.$$

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

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

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

$$\delta \dot{\underset{\sim}{q}}^T \underset{\sim b}{R} \delta \dot{\underset{\sim}{q}} = - \frac{d}{dt} \mathcal{E}_c, \tag{33}$$

where $\mathcal{E}_c(q; \delta q) \equiv (1/2) \delta \underset{\sim}{q}^T S \delta \underset{\sim}{q}$ is the "small-signal energy" about the steady state.[11]

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

$$\delta \underset{\sim}{q}^T R \delta \underset{\sim}{q} < 0 \tag{34}$$

or

$$\sum_{\text{resis.}} \delta v_k \, \delta j_k < 0. \tag{35}$$

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 conceptual separation of processes actually occurring within the same volume element, the

state variables (q,v) will enter into the resistor characteristics in a parametric fashion. For example, the phenomenological diffusion resistance in part 2 is concentration dependent $(L_D = \frac{CD}{RT})$, i.e. 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 multivibrators. In thermistors (Chua, 1969) the thermal state of the resistor (i.e. the heat capacitance) modulates the constitutive relation of device. 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).

7. COUPLED PHENOMENA

So far, for the sake of simplicity, we have restricted ourselves to single mode energetic processes. However, the real interest in irreversible thermodynamics, insofar as biological systems are concerned, lies in multiple energy couplings and transductions; e.g. coupled diffusion, diffusion-reaction, mechanochemical and electrochemical processes. The central device employed in network thermodynamics is the conceptual separation of reversible and irreversible processes. As we have stressed, such a reticulation is a purely formal device; but it permits a graphical representation of the system equations for complex processes. The representation of nonelectrical dynamical systems by linear graphs is a well

established technique in engineering (Shearer, et al., 1967; Koenig, et al., 1969; Martens and Allen, 1969).

In principle, it is possible to represent by network graphs the more general thermodynamic processes mentioned above, in which many types of energy are involved. However, for such phenomena, network graphs are unwieldy and confusing. A more satisfactory graphical notation, called "bond graphs" has been developed which is particularly well suited for irreversible thermodynamics. A detailed account of bond graph representations is available elsewhere (Oster and Auslander, 1970; Oster, Perelson and Katchalsky, 1970; Karnopp and Rosenberg, 1968). Here we indicate how the notion of reciprocity may be extended to nonlinear thermodynamic systems via the network representation.

In the "near-equilibrium" range, where the constitutive relations may be taken as linear, the Onsager condition on the dissipative processes in a steady state is expressed as

$$\underset{\sim}{L} = \underset{\sim}{L}^{T} \tag{36}$$

where

$$\underset{\sim}{j} = \underset{\sim}{L}\underset{\sim}{v}. \tag{37}$$

In general, however, the constitutive relations are nonlinear:

$$\underset{\sim}{j} = \underset{\sim R}{g}(\underset{\sim}{v}) \text{ for irreversible processes} \tag{38}$$

$$\left.\begin{array}{l} \underset{\sim}{q} = \underset{\sim C}{g}(\underset{\sim}{v}) \\[2ex] \underset{\sim}{\phi} = \underset{\sim L}{g}(\underset{\sim}{y}) \end{array}\right\} \text{ for reversible processes.} \tag{39}$$

For the capacitive, or reversible constitutive relations, the symmetry

of the derivative, or Jacobian matrix of g_c is equivalent to the familiar Maxwell Relations:

$$[Dg] = [Dg]^T \qquad (40)$$

The corresponding equation for the dissipative constitutive relation is

$$[Dg_R] = [Dg_R]^T \qquad (41)$$

which reduces to (36) in the linear case. A large class of systems are amenable to a bond graph description that employs only reciprocal "elements" of 3 types; energy storage, dissipation, and transduction. For this class of system we may invoke a Theorem due to Brayton:

Theorem:

Any interconnection of reciprocal elements is reciprocal (Brayton, 1969).

Reciprocity emerges as an integrability condition on the respective constitutive relations, and with the above theorem, extends to nonlinear, nonsteady thermodynamic systems of large complexity.

APPENDIX

The purpose of this appendix is to elaborate on the remark (see Section   ) that a network diagram representation contains more information than a differential equation representation.

Modern dynamical system theory recognizes that theories are invented, not discovered. Therefore, a clear distinction is maintained between (1) the physical system under study, (2) any one of the possible models chosen to describe it, and (3) the mathematical representation of the model (Fig. A-1).

The model is specified by a set of axioms summarizing what we judge to be the minimal assumptions required to describe the physical behavior of the system. (The axioms, of course come from the ingenuity of the model-builder, and are usually valid over a more or less restricted range of behavior.)

Once the axioms are listed, however, there are usually available several ways of translating these assumptions into mathematics, e.g. ordinary differential equations, partial differential equations, integro-differential equations, integral equations, operator equations, etc. A choice of mathematical description for the model is called a mathematical representation.[12]

In the case of electrical networks, several representations are available: state equations, mesh equations, loop equations, node equations, mixed equations, etc. That is, the model generates an equivalence class of mathematical representations.

Frequently, many of the representations are interchangeable, in the sense that one may be derived from another, e.g. Lagrangian, Hamiltonian and Hamilton-Jacobi formalisms in classical mechanics. This is not always the case, however. For example, the mesh equations are not always a special case of loop analysis: it is possible to have a mesh completely embedded in surrounding meshes. Such a mesh cannot be described by (fundamental) loop equations, since it cannot contain a link.

A network diagram is a very convenient method of representing a dynamical system, since different algorithms lead to all of the other mathematical representations. However, it is generally not possible to uniquely reconstruct the network that originally generated a set of dynamical equations, (e.g. dual networks, Desoer and Kuh, p. 454). In going from the network the diagram to the dynamical equations the topological information is lost. That is, a set of state, loop, node, etc. equations do not uniquely determine a network, but only an equivalence class of "dynamically similar" networks.

As a closing comment, let us emphasize that, in our view, insofar as possible, all consequences of the model must be derived mathematically from the various mathematical representations. No intermixing of "physical reasoning" is permitted below the level of the original model axioms (Fig. 5). Otherwise, once conclusions are reached and have to be tested against experiment, one is never sure whether it was the model assumptions that went awry, or one of the "intuitive" steps inserted in the analysis.

Of course a good model leads to verifiable and disprovable conclusions which determine the range of validity of the model. Thermodynamics

is a fairly general model whose principal restriction is the assumption of "local equilibrium;" this enables one to uniquely define the various state parameters and constitutive relations.

The best of all possible worlds is when several models lead to similar conclusions, e.g. the wave and particle models of light. A collection of such model-independent results, or "robust theorems," is entitled to be called a theory.

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LIST OF SYMBOLS

$\underset{\sim}{A}$	defined on Fig. 2
$\underset{\sim}{}$	affinity $\equiv - \underset{\sim}{\nu} \underset{\sim}{\mu}$
B	= partitioned mesh matrix
$\underset{\sim}{C}$	branch capacitance matrix
d	coboundary operator
D	diffusion coefficient
$\underset{\sim}{D}\underset{\sim}{f}(\underset{\sim}{x})$	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
$\underset{\sim}{J}_{i}$	thermodynamic flux
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 flux
∂	boundary operator
$\underset{\sim}{\mu}$	chemical potential vector
$\underset{\sim}{\nu}$	stoichiometrix matrix (reactions x species)
ξ_r	degree of advancement of reaction r

FOOTNOTES

1. Meixner (1963, 1966) has also employed the formal similarity between electrical network theory and irreversible thermodynamics in the context of linear passive systems.

2. Not all models used in physics are dynamical systems. Statistical fluctuations are not included: therefore for, say, prediction, filtering and stochastic control the model must be enlarged.

3. Most experimental systems are limited to simple input functions, e.g. constant excitation, step, impulse, sinusoidal, e.g. plane wave, etc.

4. The KCL and KVL variables represent the homology and cohomology groups associated with the linear graph (Branin, 1966, Hocking and Young, 1961).

5. The entropy flow term does not, of course, obey a conservation law except in pure heat conduction, but this causes no problem in the general treatment (Oster, Perelson, Katchalsky, 1970).

6. Tellegen's Theorem is merely the Poincaré Lemma: $d \cdot d = 0$, where d is the exterior derivative (Sternberg, 1964, p. 101). The dual expression is: $\partial \cdot \partial = 0$, where ∂ is the "boundary operator," (Sternberg, 1964, p. 107). This latter identity gives a concrete topological interpretation to all the other identities: "the boundary of the boundary is zero" for any simply connected domain.

7. 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.

8. In Eqn. (20) we will partition M, the mesh matrix in a particular way. The partitioned form we relabel as $\underset{\sim}{B}$, the "loop matrix," to

distinguish it from $\underset{\sim}{M}$.

9. With certain geometrical and dimensional restrictions to be dealt with
    elsewhere (Oster and Auslander, (1970)).

10. 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 $\underset{\sim}{R}$ 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.

11. $\mathcal{E}_c$ is <u>not</u> the "perturbation energy" about the steady state $\overline{\underset{\sim}{v}}^T\overline{\underset{\sim}{j}}$:

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

so $\mathcal{E}_c$ does not include the "correlation" terms.

12. The model we employ in this paper, for instance, assumes conservation
    of energy and conservation of flows as represented in Kirchhoff's
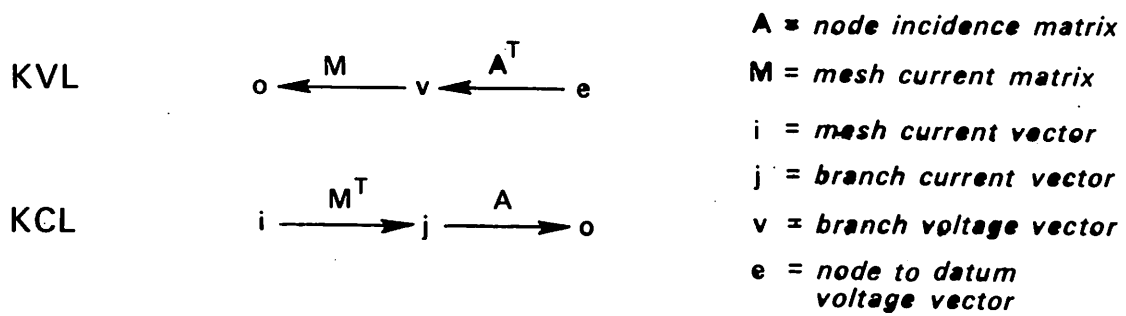   Laws, KVL, and KCL.

KVL   o ←———— v ←———— e
              M   A^T

KCL   i ————→ j ————→ o
              M^T   A

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

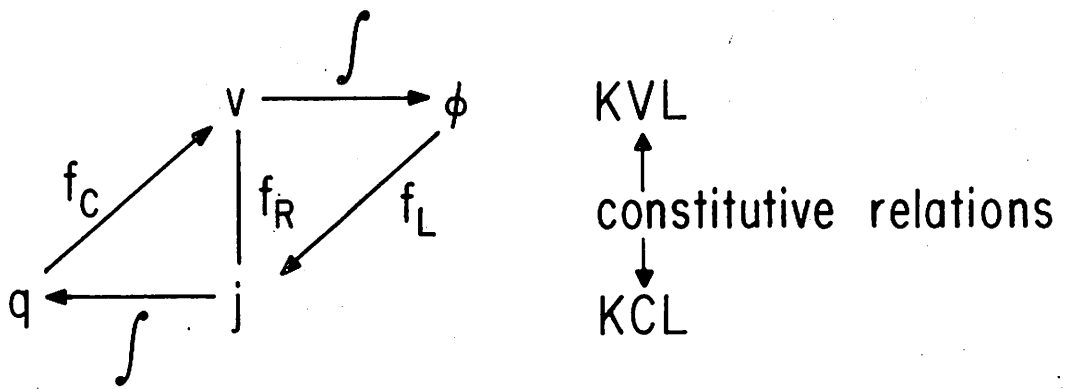Fig. 1a.   Topological relationship between dynamical variables

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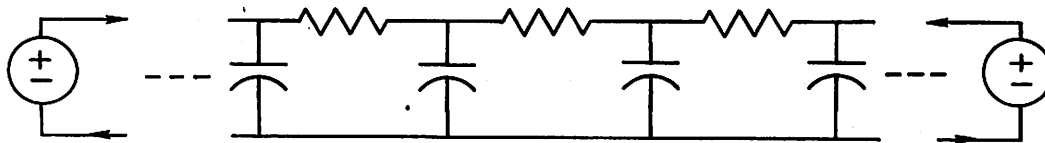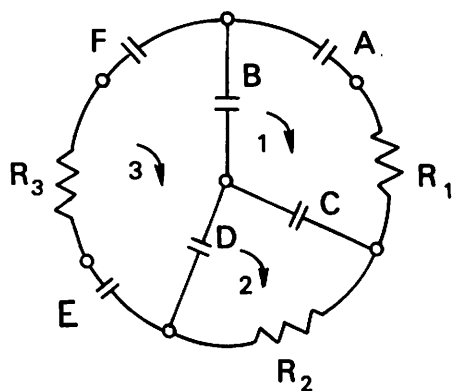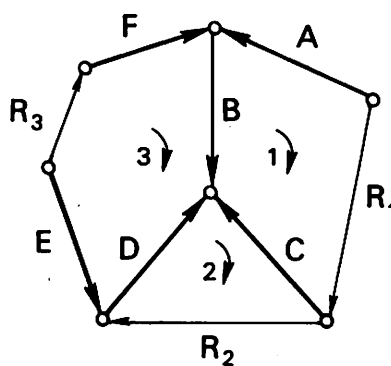Fig. 1b. Constitutive relations between dynamical variables.

Fig. 2.   *Network realization of 1-dimensional diffusion*

(a) CIRCUIT   (b) TOPOLOGICAL GRAPH

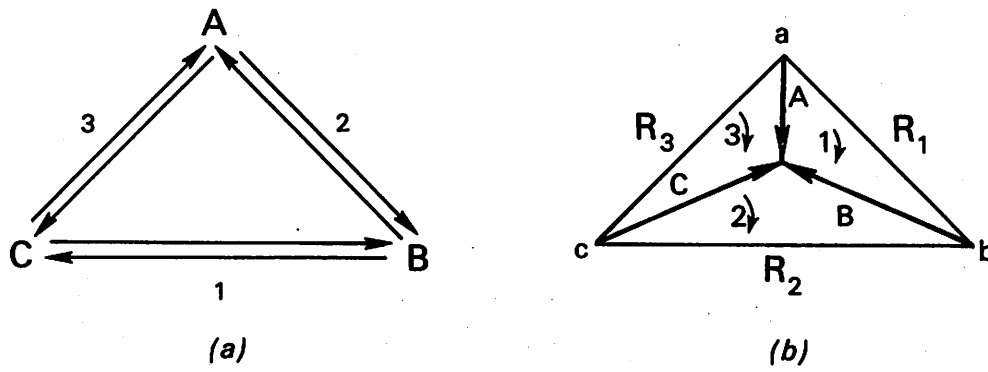Fig. 3. Graphical representation of reaction network
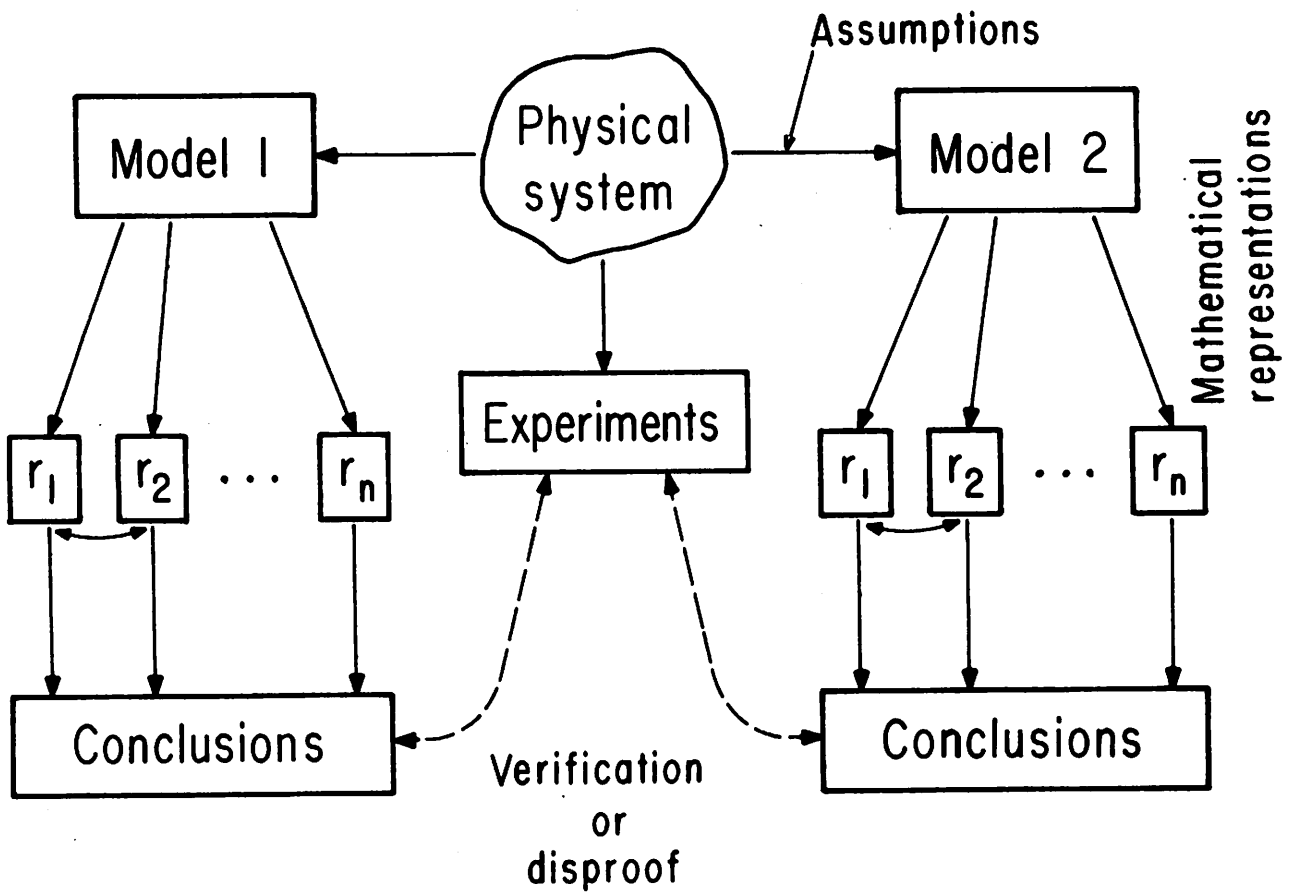
(a)

(b)

Fig. 4. Onsager scheme

Fig. 5.   Systems, models and representations