SYSTEMS, CIRCUITS AND THERMODYNAMICS

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ABSTRACT
The fundamentals of equilibrium and nonequilibrium thermodynamics are reviewed in
the context of dynamical systems and network theory. The resulting mathematical
structure forms an appropriate framework in which to discuss complex nonlinear
phenomena encountered in biophysics and chemistry.

INTRODUCTION

1.1. We had the great privilege of collaborating with Aharon Katzir-Katchalsky on
what was to be his last research endeavor, a generalization of thermodynamics that, he
hoped, would shed some new light on the puzzle of biological complexity, a problem
that fascinated him throughout his career. The task was far from completed when he
was killed and, indeed, if ever completed will be the result of many minds and many
years of patient trial and error. However, the spirit and wisdom he brought to this
work will surely have a lasting effect on those of us who worked with him. Aharon's
love for thermodynamics sprang from its great generality, although he was all too
aware of its frail powers in the biological realm. However, one is reluctant to abandon
an old and trusted friend such as thermodynamics without careful examination of its
virtues. Such an examination of the methods of thermodynamics led several workers,
most notably J. Meixner, to see some deeper relations with another formalism, electrical
circuit theory. If such a connection could be made precise, would not circuit theory
provide an admirable tool for analyzing many biological phenomena, since it is made
to order for treating complex systems? Since nothing was dearer to Aharon's intellec-
tual heart than unifying notions in science, we thought it particularly appropriate in
this memorial issue to retrace some of the steps that led us to formulate what Aharon
christened "Network Thermodynamics" and to suggest in part the broader framework
within which thermodynamics may be viewed.

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Under the pressure of modern technology, circuit theory has evolved into a rather complex and abstract mathematical subject. It is perhaps not so obvious that its methods have any relevance to biology given its rather specialized origins. However, the unifying notions that we sought were essentially mathematical and did not reside in the particular physical properties of any system.

In the following disquisition we shall attempt to show how we were led to view thermodynamics in the light of modern dynamical systems and control theory. Although the paper is frankly tutorial in nature, we hope to show that many of the concepts of system theory are related to and, in many ways, generalizations of, familiar but vaguely conceived notions in classical thermodynamics. For example, considerations of passivity and stability in general dynamical systems are not unrelated to notions involving the second law of thermodynamics.

The basic methodology in system theory today is mathematization, which has short patience with fuzzy descriptions. Thus it is first necessary to recast some old ideas in slightly different garb. The object is simply to put old wine in new bottles, hoping not only to enhance its mathematical flavor but also to increase its versatility.

Our principal emphasis will be to stress geometric formulations, since the methods of differential geometry as developed in the past several years show the brightest promise of providing a window through which to view the nonlinear world. Historically, however, geometric notions have played a prominent part in thermodynamic thinking since the time of Gibbs. The language of modern geometrists, however, would probably be unrecognizable to most scientists, so we shall attempt to use conventional vector notations in the following treatment.*

1.2. First let us state more clearly what we mean by a "dynamical systems" model of a physical system. (We trust that the reader will not confuse the physical system, the model, and the particular mathematical representation of that model. This distinction is fundamental, though not often given the emphasis it deserves [5: 42, 6].) In what follows, we shall concern ourselves exclusively with finite dimensional systems. The theory of infinite dimensional systems is far more complex and still in its infancy.

1.3. Fundamental to a dynamical system model are the notions of input, output, and state. The concept of an equilibrium state is a familiar one to thermodynamicists. However, we shall require a broadened definition to include dynamic as well as static states. Roughly, the state of a system is the totality of information that is needed to predict the future behavior of the system, assuming knowledge of future stimuli. The set of all states is called the state space, Σ, and is usually given a vector space structure. More general mathematical objects are frequently employed [7, 8] but for simplicity we shall consider only the case where Σ = R^n (Euclidean n-space). The coordinate functions on Σ are the state variables. A point x = (x_1, ..., x_n) in R^n is precisely what we mean by the state of the system.

It is important to notice that there is no a priori way to decide on what $\Sigma$ should be. This comes only from an intimate physical acquaintance with the experimental facts.

Associated with a dynamical system are an *input space* (i.e., the set of all inputs) and an *output space* (i.e., the set of all outputs). These are the filters through which one can influence and observe the system state. Call the input space $U$ (say, the set of all continuous functions from $R^m$ to $R^n$) and the output space $Y$ (say, the set of all continuous functions from $R^m$ to $R^p$). An input $u$ in $U$ is then a vector function of time, $t \mapsto u(t) \in R^n$. An output $y$ in $Y$ is a function $t \mapsto y(t) \in R^p$. The output at time $t$, when the system is in state $x(t)$ and the input is $u(t)$ is given by the value of the response (or "read-out") function, $r: \Sigma \times U \rightarrow Y$, $(x(t), u(t)) \mapsto r[x(t), u(t)] = y(t)$. (We must allow for the possibility that the output is contaminated by the input.) Note that the response function is memoryless, i.e., it is an instantaneous read-out that depends only on the present value of the state and input. The components of a dynamical system are summarized in Fig. 1.

![Diagram](image)

**FIG. 1.** The relationship between input, state and output spaces.

The basic defining property of a dynamical system is that given the state $x_0$ at some initial time $t_0$, and the input to the system from time $t_0$ to some future time $t$, denoted $u_{[t_0, t]}$, then both the state and the output at time $t$ are uniquely determined. Thus we take as a fundamental postulate the property of determinism. Knowledge of the stage $x_0$, at time $t_0$, must summarize all past effects, in the sense that all future behavior does not depend upon how the system was brought into the state $x_0$. Thus we may consider all trajectories leading to $x_0$ as "equivalent histories".

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* This requirement does not preclude treating systems with memory effects (e.g. time delays). We need only replace the state space $R^n$ by an appropriate infinite dimensional space $[9, 10]$. 
The last component of a dynamical system representation is the prescription for the internal dynamics, that is, the motion of the state point in $\Sigma$. By the axiom of determinism, the state at time $t_0$ determines the future motion. However, inputs also affect the system dynamics allowing the experimenter to steer the motion of the state point, at least to some degree. Mathematically, the equations of the motion for the system are contained in the state transition function, $\varphi$, which acts on the state $x_0$ at time $t_0$, and the future inputs from time $t_0$ to time $t$, i.e.

$$ x(t) = \varphi(t, t_0, x_0, u_{[t_0, t]}). $$

For consistency we require $\varphi(t_0, t_0, x_0, u_{[t_0, t_0]}) = x_0$. The function $\varphi(t, t_0): \Sigma \times U \to \Sigma$ "pushes" the state point in $\Sigma$ from its initial position at $x_0$ to its position at $x(t)$. An important property of $\varphi$ (called the semi-group property) is the following. To compute the state at time $t_2 > t_0$, we can first compute the state at any intermediate time $t_1$, $t_0 \leq t_1 \leq t_2$ by $\varphi(t_1, t_0)$, then go from $t_1$ to $t_2$ by $\varphi(t_2, t_1)$. In other words, $\varphi(t_2, t_0) = \varphi(t_1, t_0) \varphi(t_2, t_1)$ (where $\circ$ indicates composition of maps).

So system outputs are generated from initial conditions and inputs via the intermediate state variables.

The influence of the input on the state and the state on the output can be clarified by introducing the notions of reachability, controllability, and observability. These ideas are not new in thermodynamics. In fact Caratheodory's statement of the second law of thermodynamics concerns itself with reachability. Roughly, the state space of a dynamical system is said to be reachable from a given state, say $x_0$, if there exists an input which will transfer the system from $x_0$ to any state in $\Sigma$. The idea of controllability is similar, but instead of starting at a given initial state and going to any point in $\Sigma$, one is interested in steering the system from any initial state in $\Sigma$ to a given final state. Thus a dynamical system is said to be controllable to a state $x_1$, if for any $x_0 \in \Sigma$ there exists an input, $u(t)$, which will drive the system to $x_1$ at some time $t_1 \geq t_0$ i.e.

$$ x_1 = \varphi(t_1, t_0, x_0, u_{[t_0, t_1]}). $$

In studying chemical systems considerations of controllability may be important. For example, Winfree [11] in studying glycolytic oscillations has shown that there exists an input which drives the system to a state in which the oscillations disappear (the singular point for the limit cycle oscillation). In drug therapy and pharmacokinetics the primary goal is finding the appropriate input (drug dosage) to drive the system to some desired final state. In such instances it is important to know if the dynamical system under study is controllable. The property of observability refers to the possibility of determining the state from output measurements. This is, of course, the goal of many biophysical experiments and it is important to know if it is attainable. For a large class of dynamical systems conditions exist for determining reachability, controllability, and observability [7, 12-14]. We will illustrate these concepts more fully by a thermodynamic example in Section 2.

A complete and precise definition of a dynamical system may be found in, say, Ref. 5 where additional properties of the dynamical system $\{U, Y, \Sigma, \varphi, t\}$ are discussed.

In general we shall be concerned with systems represented by ordinary differential equations of the general form (see Fig. 2)

$$ \dot{x} = f(x(t), u(t)) $$

(1a)
y = g(x(t), u(t)) \tag{1b}

However, we emphasize that, with appropriate choice of input space, output space, state space, state transition function and readout function, the above framework encompasses all of the deterministic models of engineering and physics (classical and quantum mechanics, thermodynamics, electromagnetism, circuit and control theory, hydrodynamics, etc.) For the system represented by Eq. (1) the state transition function is determined by the solution to the differential equation (1a), g is the readout function,

\[ U = Y = \mathbb{R}^m, \text{ and } \Sigma = \mathbb{R}^n. \]

**FIG. 2.** Block diagram of the dynamical system representation:

\[
\dot{x}(t) = f(x(t), u(t)) \\
y(t) = g(x(t), u(t))
\]

1.4. One can see from Figs. 1 or 2 that there are two basic ways to view a dynamical system. On the one hand we can view a dynamical system as a black box which generates outputs \( y(t) \) from inputs \( u(t) \) and initial conditions \( x_0 \). This is the input-output viewpoint, which ignores explicit consideration of the intermediate state variables \( x(t) \). On the other hand, the state viewpoint focuses attention on the state trajectory itself and attempts to follow the detailed motion of the state point by constructing \( \varphi \) (i.e. by solving the differential equation (1a)). The transition from a state ("internal") to an input-output ("external") description is relatively straightforward for the system described by Eq. (1): solve the differential equation (1a) for \( x = \eta(u) \) and substitute the solution into Eq. (1b) to obtain \( y = g(\eta(u), u) \oplus h(u) \). The converse procedure, the "realization" problem, that is, deducing a state model from an input-output description, is an unresolved question for all but linear systems.

1.5. In Sections 2 and 3 we recast first equilibrium and then non-equilibrium thermodynamics within the framework of dynamical systems theory. Our primary concern will be directed at coming to grips with complex systems. To do this we shall employ a certain subclass of dynamical system models, so-called "interconnected systems". That is, systems which can be considered as being assembled from simpler subsystems. In this fashion we can approach modelling complex systems by assembling a nested sequence of black boxes, much as one would construct a complicated piece of electronic
apparatus. The study of interconnections between dynamical subsystems leads naturally to the introduction of certain notions from topology which greatly simplifies the business.

2. EQUILIBRIUM THERMODYNAMICS REVISITED

2.1. In this section we shall reconsider certain notions from equilibrium thermodynamics from a somewhat different point of view. The experienced thermodynamicist will find little fundamentally new here, but he is warned that there are deep mathematical waters lurking beneath the surface [15, 16].

![Diagram of a thermodynamic 3-port](image)

FIG. 3. A simple thermodynamic 3-port.

2.2. First, consider the familiar system shown in Fig. 3 consisting of a fluid-filled piston and cylinder arrangement equipped with diathermal and semipermeable walls. According to the classical thermodynamic viewpoint the system (i.e. the gas in the cylinder) is viewed as a "black box" whose properties must be deduced from external measurements only. Borrowing some terminology from circuit theory, we will call the diathermal, semipermeable and moveable walls the thermal, chemical and mechanical ports respectively, while the system itself is called a 3-port; each port represents a possible interaction mode between the system and its surroundings. From this external viewpoint we may attempt to characterize the system's behavior by certain input-output experiments, such as varying the piston force $\vec{F}$ and measuring the resulting equilibrium piston displacement, $\vec{X}$, while maintaining the temperature, $\vec{T}$, and the chemical potential, $\vec{\mu}$, at the diathermal and semipermeable walls constant.* The totality of such measurements completely specifies the behavior of the system with regard to its mechanical, chemical and thermal responses to external stimuli. A way of summarizing all this information is to say that the system acts as an "input-output" device which assigns to a set of port variables, say $\vec{x} = (\vec{X}, \vec{N}, \vec{S})$, their conjugate port variables $\vec{y} = (\vec{F}, \vec{\mu}, \vec{T})$. More succinctly, we can say this device is characterized by a vector map

* A superscript tilde denotes externally measured quantities.
G : \mathbb{R}^3 \to \mathbb{R}^3

(\tilde{X}, \tilde{N}, \tilde{S}) \mapsto (\tilde{F}, \tilde{\mu}, \tilde{T}) \tag{2.1}

called the constitutive relation for the 3-port. The choice of which port variables completely characterizes the system naturally depends upon the system's properties.

We can generalize the above discussion to arbitrary equilibrium systems and define the constitutive relation to be a map \( G : \mathbb{R}^n \to \mathbb{R}^n \). An equilibrium system may be regarded as an "n-port capacitor," since it is a generalization of a "1-port capacitor," with only an electrical charge-voltage port [16].

According to the usual terminology, the "thermostatic state" of the system refers to an independent set of port quantities \( \tilde{X} \) in \( \mathbb{R}^3 \). This is assumed to reflect the internal properties of the system. Later, when we represent the piston-cylinder as a dynamical system, \( \tilde{X} \) will play the role of the state point \( x \in \mathbb{R}^3 = \Sigma \). To simplify the notation we will drop the tilde in our discussion of n-ports, and reintroduce it when needed in discussing dynamical systems.

2.3. It is convenient to view the constitutive map \( G \) as defining a vector field on \( \mathbb{R}^3 \); for example, if \( x = (X, N, S) \) are the inputs, then the output variables \( y = (F, \mu, T) = (G_1(x), G_2(x), G_3(x)) = G(x) \) can be viewed as shown in Fig. 4.

![Diagram](image)

FIG. 4. The constitutive relation for a thermodynamic system viewed as a vector field.

Now, notice that the vector field*

\[ N \mapsto \nabla N(x) = \left( \frac{\partial N}{\partial X}(x), \frac{\partial N}{\partial N}(x), \frac{\partial N}{\partial S}(x) \right) \]

is just the unit vector \((0, 1, 0)\) located at \( x = (X, N, S) \). Similarly, \( \nabla X(x) \) and \( \nabla S(x) \) are the unit vectors \((1, 0, 0)\) and \((0, 0, 1)\), respectively. Therefore, we can expand the vector field \( G \) in this basis set, as shown in Fig. 4.

\[ G(\cdot) = F(\cdot) \nabla X(\cdot) + \mu(\cdot) \nabla N(\cdot) + T(\cdot) \nabla S(\cdot) \tag{2.2} \]

* Due to typographic limitations, the symbol \( \nabla \) is not set in boldface type. It does, however, denote a vector operator.
So far no specific property has been ascribed to the constitutive vector field \( \mathbf{G}(\cdot) \). However, if we manipulate the port variables such that the point \( \mathbf{x} \) traces out a closed curve in \( \mathbb{R}^3 \) and then compute the circulation the vector field \( \mathbf{G}(\cdot) \) inducens around this curve, we have

\[
\oint \mathbf{G} \cdot d\mathbf{l} = \sum_{\text{ports}} \oint y_i \nabla x_i \cdot d\mathbf{l}
\]  

or, by Stoke's Theorem

\[
\iint \nabla \times \mathbf{G} \cdot d\mathbf{a} = \sum_{\text{ports}} \iint (\nabla y_i \times \nabla x_j) \cdot d\mathbf{a} = \sum_{\text{ports}} \iint (\nabla \times \mathbf{G}) \cdot d\mathbf{a} = 0
\]

The integrand on the right is just the area enclosed on the \( j^{th} \) constitutive plane during the cyclic process. (The areas enclosed by cycles traced clockwise on the constitutive planes correspond to work delivered to the port, while the areas enclosed by cycles traced counterclockwise represent work obtained from the port.)** Carrying out the required manipulation on an actual system invariably produces the result that:

\[
\sum_{\text{ports}} \iiint (\nabla y_i \times \nabla x_j) \cdot d\mathbf{a} = 0
\]

i.e., the sum of the oriented areas on the constitutive planes vanishes in a cyclic process. Since \( d\mathbf{a} \) is arbitrary, \( \nabla \times \mathbf{G} = 0 = \sum_j \nabla y_j \times \nabla x_j \). This result tells us that the constitutive vector field \( \mathbf{G}(\cdot) \) is the gradient of some scalar potential function (see Fig. 5).

\[
\mathbf{G}(\cdot) = \nabla \Psi(\cdot), \quad \Psi : \mathbb{R}^3 \to \mathbb{R}
\]

This indeed puts a severe restriction on the constitutive relation, \( \mathbf{G}(\cdot) \), since \( \nabla \times \mathbf{G} = \nabla \times \nabla \Psi = 0 \), i.e., \( \mathbf{G} \) is irrotational; or, in components,

\[
0 = (\nabla \times \mathbf{G})_k = \left( \frac{\partial G_i}{\partial x_j} - \frac{\partial G_j}{\partial x_i} \right)_k \quad \text{i.e.} \quad \frac{\partial G_i}{\partial x_j} = \frac{\partial G_j}{\partial x_i}
\]

Physically this tells us that all equilibrium systems are reciprocal under small-signal port excitations since \( \delta \mathbf{y} = \nabla \mathbf{G}(\mathbf{x}) \cdot \delta \mathbf{x} \) and \( \nabla \mathbf{G} = \nabla \mathbf{G}^T \). That is, if we perturb, say, port variable \( x_j \) by \( \delta x_k \) and observe the system response at port \( k \), and then perturb \( x_k \) by \( \delta x_j \) and observe the response at port \( j \), we find the responses to be the same: the system is symmetric under exchange of input and output. The condition that the constitutive relation \( \mathbf{G}(\cdot) \) be irrotational (which in coordinates is just the Maxwell reciprocity rela-

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* We assume as usual that the manipulation of the port variables is carried out slowly enough so as not to disturb the internal equilibrium of the device. Thus \( \mathbf{G}(\cdot) \) uniquely characterizes the port behavior throughout the whole process.

** Note that \( \nabla y_j \times \nabla x_i \) is a unit normal on the \( j^{th} \) constitutive plane, if \( \mathbf{V} \) and \( \mathbf{W} \) are any two vectors in the \( j^{th} \) plane, then \( (\nabla y_j \times \nabla x_i) \cdot (\mathbf{V} \times \mathbf{W}) = \text{area spanned by } \mathbf{V} \text{ and } \mathbf{W} \). Therefore, \( \Sigma_j (\nabla y_j \times \nabla x_i) \cdot (\cdot, \cdot) \) measures the sum of areas on the constitutive planes.
tions) could in fact be taken as the defining property for equilibrium multiport systems. Another approach would be to postulate the existence of $\Psi$ for all equilibrium multiports (c.f. [17]). What one chooses as one's basic postulates is largely a question of personal prejudice and taste; we have chosen the present approach to permit an easy generalization to nonreciprocal systems.

Notice that the integrability condition for vector fields, $G \cdot \nabla \times G = 0$, is satisfied identically by any gradient vector field. For a multiport this property of the constitutive relation can be determined by testing the system for the reciprocity condition at all its ports.* Early in the history of thermodynamics, before the "heat port" was "discovered," systems such as Fig. 3 could not be characterized by a potential function, since an $n$-port will generally not appear reciprocal if only $n-1$ of its ports are subject to experimental manipulation, i.e., $\sum_{i=1}^{n-1} \nabla Y_i \times \nabla X_i \neq 0$ in general. The inclusion of the thermal port, if the system was to be reciprocal, necessitated the introduction of a "displacement" variable, $S$, conjugate to the "force", $T$. (Hindsight can always be made to look elegant!)

The reason for describing an $n$-port by the vector field $G$ rather than the potential function $\Psi$, as is customary, will become clear when we encounter systems which are not reciprocal.

2.4. In order to consider equilibrium multiports as elements of a dynamical system, in the sense of Section 1, we must reintroduce the distinction between state variables, $x$, and port variables, $\tilde{x}$.

By applying inputs, i.e., manipulating the port variables, the location of the state point can be altered. The inputs to the system that we shall consider fall into two categories. First, we can apply various "generalized forces"; for example, we can vary the

* Note, however, that an $n$-port can be integrable without being reciprocal.
force on the piston with respect to time, or vary the chemical potential of the gas externally in contact with the semi-permeable wall.

Alternatively, we can input \( "\text{generalized flows}" \); that is, we can pump in gas through the semi-permeable wall at a rate \( \tilde{x}_N(t) \), allow heat or entropy to enter the system through the diathermal wall at rates \( \tilde{x}_Q(t) \) or \( \tilde{x}_S(t) \), respectively, or change the volume of the system by moving the piston at a rate \( \tilde{x}_V(t) \). We shall choose to use the entropy flow, \( \tilde{x}_S \), instead of the heat flow \( \tilde{x}_Q \), in order that the product of the generalized force and generalized flow variables have the dimensions of energy rate or power.* Although this is not a requirement of the theory it is sometimes a convenience [18]. In Section 4 we shall be more precise about the distinction between \"forces\" and \"flows\"; here we use the terms in their conventional sense.

One final, and obvious, remark is in order. Although we have written the inputs as functions of time, they can of course be constant inputs. However, if the inputs are time-varying we shall require that they vary much slower than the internal relaxation time of the system, so that the properties of gas inside the cylinder remain uniform (c.f., footnote p. 452). Otherwise, our finite dimensional state description will break down, and we must employ an infinite-dimensional state space with a state transition function generated by partial rather than ordinary differential equations.** Thus, if we input \( \tilde{f}(t) \) we can assume that the temperature of the gas \( T(t) = \tilde{T}(t) \). Similarly, we assume \( \mu(t) = \tilde{\mu}(t) \), and \( p(t) = \tilde{p}(t)/A \), where \( A \) is the area of the piston, and \( p \) and \( \mu \) are the gas pressure and chemical potential, respectively. (For simplicity one can assume \( A = 1 \) cm², so that \( p = \tilde{F} \).

The possible outputs from this system are of the same form as the inputs (i.e. \( U = Y \)). That is, one can measure \( \tilde{F}(t), \tilde{T}(t), \tilde{\mu}(t), \tilde{x}_N(t), \tilde{x}_S(t), \) or \( \tilde{x}_V(t) \).

Since in the case of both inputs and outputs \( \mu = \tilde{\mu}, T = \tilde{T}, p = \tilde{F} \), we shall occasionally drop the tilde superscript. However, we emphasize that state variables are internal variables and, as we shall see in Section 2.6, are not always available to external measurements.

By making particular choices of state variables, inputs and outputs, we can view, in a precise manner, the piston-cylinder arrangement as a dynamical system. For example, consider \( x = (V, N, S) \), \( u(t) = (\tilde{x}_V, \tilde{x}_N, \tilde{x}_S) \) and \( y(t) = (F, \mu, T) \). Then we can represent this system by the equations

\[
\dot{x}(t) = u(t) \tag{2.7a}
\]

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* Notice that we have not chosen \"generalized displacements\" as inputs. For example, if one wishes to input 10 moles of gas, this can be accomplished, say, by letting gas flow into the system at a rate of \( \tilde{x}_N = 10 \) mole/sec for 1 sec. This is, of course, how one does it experimentally.

** Another way of saying the same thing is that the shortest wavelength in the input must be larger than the dimensions of the system, so that no significant internal gradients are generated within the system. This limitation depends on the physical properties of the system itself; usually thermal processes are the slowest to propagate and so are \"rate limiting\" for the finite dimensional model.
\[ y(t) = g(x(t)) \]  
\[ (2.7b) \]
where the function \( g(\cdot) \) is determined by the read-out function. For the piston-cylinder system \( x(t) = x_0 + \int_0^t u(t) \, dt \) and \( g(\cdot) \) is just the equation of state for the gas, \( G(\cdot) \) since it maps \( (V, N, S) \mapsto (p, \mu, T) \).

This example is a rather trivial dynamical system since the internal state is totally constrained to track the input, and the output is not dependent upon the input. For example, Eq. (2.7a) implies that
\[ N(t) = N(0) + \int_{t_0}^t u(t) \, dt \]
and Eq. (2.7b) that
\[ \mu(t) = g_2(V(t), N(t), S(t)) \]
where \( g = (g_1, g_2, g_3) \).

We see that this system can be viewed in network theoretic terms as a "multiport capacitor". If one differentiates Eq. (2.7b) with respect to time and then combines it with Eq. (2.7a) one finds
\[ \dot{y}(t) = \nabla g \cdot \dot{x}(t) \overset{\Delta}{=} C^{-1} u(t) \]
\[ (2.8) \]
where \( C^{-1} \overset{\Delta}{=} \nabla g \) is a "susceptance matrix". The equation \( C \dot{y} = u \) then resembles the circuit equation \( CV = i \).

2.5. Although it is not necessary, the inputs and outputs to a system are frequently defined so that their product has the units of energy/time. In such cases, we can define the power supplied to the system as
\[ P(t) \overset{\Delta}{=} u(t) \cdot y(t) = u(t) \cdot g(x(t), u(t)) \]
\[ (2.9) \]
and the energy supplied to the system from time \( t_0 \) to \( t \) as
\[ W(t_0, t) \overset{\Delta}{=} \int_{t_0}^t P(t) \, dt. \]
\[ (2.10) \]
Both of these quantities are defined by external measurements only.

Now, suppose that inside the system, we can find a non-negative function \( \Psi: \Sigma \to \mathbb{R}_+ \) such that
\[ \frac{d\Psi}{dt} \leq P \]
\[ (2.11) \]
or
\[ \nabla \Psi \cdot f(x, u) \leq g(x, u) \cdot u \]
\[ (2.12) \]
Then we say that the dynamical system is passive.* That is, a system is passive if the rate at which the state point crosses $\Psi = \text{constant}$ surfaces is always less than or equal to the power supplied to the system through the ports.

In general, the energy supplied to the system may be either stored or dissipated. We say that a dynamical system is lossless if

$$\frac{d\dot{\Psi}}{dt} = P$$ (2.13)

For capacitive systems described by Eqs. (2.7) the passivity condition is

$$\frac{d\dot{\Psi}}{dt} = \nabla \dot{\Psi} \cdot u \leq g(x) \cdot u$$ (2.14)

On the other hand, the definition of passivity for an $n$-port is:

$$W(t_0, t) + \epsilon(t_0) \geq 0,$$

where $\epsilon(t_0)$ is a positive quantity (the initial stored energy) [20]. By integrating (2.14) the two definitions are seen to be equivalent.

It can be shown that, for capacitive dynamical systems, passivity implies losslessness and reciprocity [18]. In general, however, passivity and reciprocity are independent properties.

Many of the stability results for general dynamical systems are intimately related to the notion of passivity, since, in a sense, all Liapunov functions for the dynamical system above are topologically equivalent. It is no accident that the passivity inequality bears a strong resemblance to Second Law inequalities [21].

2.6. It is clear that for the piston-cylinder example we can, by appropriate inputs, steer the state point $x(t)$ to any desired position in $\mathbb{R}^n$ (the positive orthant, that is!). However, for a more complicated system, it is frequently the case that there exist some internal states which are not reachable. An obvious case would be to replace the diathermal wall with an adiabatic one; this clearly partitions the state space into reachable and unreachable regions. This is true even for irreversible processes, a fact which Caratheodory used to formulate the Second Law.

We can also use a variation of this piston-cylinder arrangement to illustrate the idea of observability. If inside the cylinder (system 1) we place an adiabatic, impermeable bag containing a second gas (system 2), there is no way of ascertaining the state of the composite system from external measurements (i.e., outputs of the composite system). We can abstract this condition as shown in Fig. 6.

Conversely, if even the bag were diathermal and permeable (so that there were no internal "open circuits") its state would not be observable from the composite system.

* This definition is from Ref. 19.
outputs over the range of any phase transition. This can be seen from our simple dynamical system formulation roughly as follows: examine the linearized system about some operating point $\bar{x}$:

$$\delta \dot{x} = \delta u$$

$$\delta y = \nabla g(\bar{x}) \cdot \delta x$$

But, if there is an internal phase transition, then some terms of the matrix $\nabla g(\bar{x})$ will vanish (e.g. during a liquid-vapor transition $(\partial p/\partial V)_T = 0$). Therefore, some components of the output vector will be zero, and variations in the corresponding state will not show up at the external ports.

Questions of controllability and observability are clearly germane to any discussion of complex systems. However, even though such notions are familiar to most thermodynamicists, a rigorous treatment quickly involves rather deep mathematical questions [5, 12].

2.7. Next, let us reexamine the notion of thermostatic equilibrium using the vector field characterization of multiports. To do this we must introduce some internal degrees of freedom, since if all port quantities are clamped at specified values, the input $u$ is fixed and the system has no latitude to seek its own equilibrium. The easiest way to supply some internal degrees of freedom is to interconnect two systems, i.e., allow them to interact...
through their ports and ask when they are in equilibrium. (It is clear that only ports of the same type can be connected!) For example, consider two identical copies of our piston-cylinder system, and allow them to interact through their chemical ports as shown in Fig. 7. For simplicity, we will “clamp” the remaining ports by temporarily maintaining $S$ and $X$ constant.

![Diagram of internal interconnection of chemical ports.](image)

**Fig. 7.** Internal interconnection of chemical ports.

By interconnecting the two 3-ports as shown, the resulting system is a 4-port with one internal constraint. (In general, connecting $p$ ports of an $n$-port to $p$ ports of an $m$-port results in an $(n + m - 2p)$-port with $p$ internal connections; we shall consider the general interconnection problem in Section 5.) The internal port variables are free to adjust themselves so that the composite system reaches its equilibrium configuration. Since the external ports are fixed, we need only examine the internal port variables $(\mu_1, N_1, \mu_2, N_2)$ and the constitutive vector field $G(\cdot)$ restricted to the coordinate plane $(N_1, N_2); (N_1, N_2) \mapsto (\mu_1, \mu_2).$ The interconnection imposes the equation of constraint, $N_1 + N_2 = \text{constant}.$ System displacements are then confined to the 1-dimensional submanifold, $K,$ defined by the equation: $K \triangleq \{ x \in \mathbb{R}^2 \mid N_1 + N_2 = \text{constant} \}.$ The equilibrium configuration of the system is located at the point where the projection of the vector field $G(\cdot)$ on $K$ vanishes. That is, if we imagine a point $x = (N_1, N_2)$ whose motion is restricted to $K,$ being driven by the vector field $G(\cdot),$ then this point will come to rest at $x$ such that $G(x) \cdot r(x) = 0,$ where $r(\cdot)$ is any vector field tangent to $K.$ (This is, of course, just the “virtual work” principle from mechanics.) If we let $\tau = (a, -a),$ then the equilibrium point is characterized by

$$0 = G(x) \cdot r(x) = (G_1(x), G_2(x))^T (a, -a)$$

or $\mu_1(x) = \mu_2(x).$ That is, if we denote by $G_K(\cdot)$ the projection of $G(\cdot)$ onto $K$ (i.e. $G_K(\cdot) = \Sigma_i (G(\cdot) \cdot r_i(\cdot)),$ where the $r_i(\cdot)$ are unit vector fields forming a basis for the tangent space to $K),$ then the zero of $G_K(\cdot)$ defines the equilibrium point, see Fig. 8. However, since our system is reciprocal, $G = \nabla \Psi,$ and there is an easier way to locate $x,$ i.e. at the level surface of $\Psi(\cdot)$ tangent to $K.$ So the internal equilibrium of the $(n + m - 2)$-port can be characterized by a constrained extremum principle:
FIG. 8. (a) Locating the equilibrium configurations of a constrained system. (b) The potential function for a reciprocal homogeneous system is a generalized "cone."

\[ \nabla \Psi(x) = \lambda \nabla (N_1 + N_2 - \text{constant}) \]

where \( \lambda \) is a Lagrange multiplier.

Expanding \( \nabla \Psi(x) \) in the natural basis:

\[ \mu_1(\bar{x}) \nabla N_1 + \mu_2(\bar{x}) \nabla N_2 = \lambda \nabla N_1 + \lambda \nabla N_2 \]

and, equating components

\[ \mu_1(\bar{x}) = \mu_2(\bar{x}). \]

Remark: To enable us to visualize things concretely, we can restrict the form of the vector field \( G(\cdot) \) by considering only homogeneous fluid systems which can be characterized as follows: let

\[ \rho(x) \Theta \mathbf{x} \cdot \mathbf{G}(\mathbf{x}) = \mathbf{x} \cdot \nabla \Psi(\mathbf{x}) \]

be the real valued function on \( R^n \) which measures the radial component of the constitutive vector field (not to be confused with \( P = \mathbf{x} \cdot \mathbf{G}(\mathbf{x}) \) which measures the component of \( G(\cdot) \) parallel to the input \( \mathbf{x} = u \)). An \( n \)-port capacitor is said to be homogeneous (of first order) if \( \rho(\cdot) = \Psi(\cdot) \), i.e., \( \Psi(x) = x \cdot \nabla \Psi \). Then, for any real number, \( \lambda \),

\[ \Psi(\lambda x) = \lambda x \cdot \nabla \Psi = \lambda \Psi(x) \]

and so the graph of \( \Psi(\cdot) \) looks like a "cone" over the \( N_1 - N_2 \) plane, Fig. 8b. The potential lines are equally spaced on the plane and the determination of the equilib-
rium point may be clearly envisioned. (Note that, since we have taken the vector field characterization of constitutive relations as primitive, logic compels us to define the homogeneity property as we have done here. The usual development begins with the assumption: \( \Psi(\lambda x) = \lambda \Psi(x) \) and proceeds via Euler's Theorem [17].)

If the \( n \)-port were non-reciprocal (that is, if \( G \) were not derivable from a scalar potential, as will be the case for some irreversible processes), then we could not use the extremum principle, but instead would have to solve the equations \( G(x) = 0 \). This is a harder computation and perhaps a less esthetic criterion for equilibrium, but it has the virtue of being more general (not tied to reciprocity). Moreover, it is just the usual criterion for equilibrium employed in differential equation theory.

The above computation tells us that we may characterize the equilibrium point \( x \) by (1) the constraint \( N_1 + N_2 = \text{constant} \), (2) \( \psi(\cdot) \) extremal, resulting in (3) \( \mu_1 = \mu_2 \) (equality of forces at the interconnection boundary). It should be clear that, of the above three conditions, any two imply the third. In particular, we can take as our primitive criterion for internal equilibrium the two interconnection constraints, (1) and (3), rather than (1) and (2). This has the virtue of eliminating the potential function from consideration, (but at the expense of some elegance and perhaps increased computational labor). This idea is not new. Brönsted recognized in the 1930's that one could do all of thermodynamics using just interconnection constraints: there is no need to ever mention anything of free energies or such.* The utility, yea necessity, of such an approach was not recognized until irreversible thermodynamics made its debut.

Summarizing, the constitutive relation for a capacitive \( n \)-port is a map \( G: \mathbb{R}^n \to \mathbb{R}^n \), \( x \to y \) with the properties (i) reciprocity, \( \sum_{\text{ports}} \nabla y_j \times \nabla x_j = 0 \), (or \( G(\cdot) = \nabla \Psi(\cdot) \)), and for fluid systems (ii) homogeneity, \( G(x) \cdot x = \Psi(x) \) (or \( \Psi(\lambda x) = \lambda \Psi(x) \)). Viewed as a dynamical system, its governing equations are \( \dot{x} = u, y = g(x) \) where \( g(\cdot) = G(\cdot) \).

3. IRREVERSIBLE THERMODYNAMICS

The connection between irreversible thermodynamics and circuit theoretic concepts has been exploited for some time in various contexts [21, 23-26]. At the most primitive level the similarity between the flow of electrical current through a resistor, \( i = LV \), and the flow of a permeable substance through a membrane, \( J = LDu \) is obvious. Mathematically, they are indistinguishable. From the multiport view we have adopted, we regard both the resistor and the membrane as black boxes with port variables (\( i, v \)) and (\( J, Du \)), respectively. This is schematized in Fig. 9.

In general the constitutive relation characterizing the input-output properties of the membrane "resistive \( l \) -port" need not be linear. we only require that there be a unique relation between \( J \) and \( Du \), say \( h(J, Du) = 0 \).

The generalization to coupled membrane flows is also obvious: we need only switch to vector notation. Figure 10 shows a membrane with two coupled solute flows repre-

* The Brönsted approach to thermodynamics is summarized in Ref. 22.
The particular choices $J = L(X)$, $X = R(J)$ and $(J_2, X_2) = T(J_1, X_1)$ are called the admittance, impedance and transmission representations, respectively.

* Since many more pathological phenomena can arise in multiport resistors than in capacitive systems, a much more general notion of resistive constitutive relation is required in practice [27]. In our discussion the above definition will suffice.
Another more abstract example of a resistive multiport is a set of chemical reactions, whose inputs are a set of reaction affinities, $A_k = -\Sigma \nu_{ik} \mu_i$, ($\nu_{ik}$ = stoichiometric coefficients of species $i$ in reaction $k$) and whose outputs are reaction flows $J_k^f$. We shall return to this important case in Section 5.

Resistive constitutive relations are capable of more pathological behavior than capacitive constitutive relations. Therefore, instead of viewing the constitutive relation as a vector field on $\mathbb{R}^n$ as we did for capacitors, it is advantageous to take an alternate approach and view the constitutive relation as a surface in $\mathbb{R}^n \times \mathbb{R}^n$ via its graph: $\{(x, \Lambda(x)) | \forall k \Lambda_k \}$. The constitutive relations for equilibrium systems displayed the universal properties of reciprocity (and for fluid systems, homogeneity). No such general properties can be asserted for resistive constitutive relations. For example, let us test a multiport resistor for the reciprocity property. Recall that a multiport is reciprocal if

$$\sum_{\text{ports}} \nabla y_i \times \nabla x_i = \sum_i \sum_{k > i} \frac{\partial \Lambda_i}{\partial x_k} - \frac{\partial \Lambda_k}{\partial x_i} \nabla x_j \times \nabla x_k = 0.$$  

This condition imposes a restriction of the orientation of the constitutive manifold $(x, \Lambda(x))$ in $\mathbb{R}^n \times \mathbb{R}^n$. To see this, we proceed as follows, referring to Fig. 11.
The tangent plane to $\Lambda_\delta$ at the point $(x, \Lambda(x))$ is $\{(x, y) \in \mathbb{R}^{2n} | y = \nabla \Lambda(x) \cdot x\}$. Let $S = (\delta V, \nabla \Lambda(x) \cdot \delta v)$ and $t = (\delta w, \nabla \Lambda(x) \cdot \delta w)$ be two tangent vectors to $\Lambda_\delta$ at $(x, \Lambda(x))$.

We interpret $\sum_{i=1}^{n} \Delta y_i \times \Delta x_i$ as a unit normal on the tangent plane to $\Lambda_\delta$, so that in order for the resistive $n$-port to be reciprocal we must have

$$0 = (\sum_i \nabla y_i \times \nabla x_i) \cdot (s \times t)$$

$$= \sum_i [((\nabla y_i \cdot s)(\nabla x_i \cdot t) - (\nabla y_i \cdot t)(\nabla x_i \cdot s)]$$

$$= \sum_i [((\nabla \Lambda(x) \cdot \delta v_i) \delta w_i - (\nabla \Lambda(x) \cdot \delta w_i) \delta v_i)]$$

$$= \nabla \Lambda(x) \delta v \cdot \delta w - \nabla \Lambda(x) \delta w \cdot \delta v$$

This can be written as

$$s \cdot Jt = 0 \quad (3.2)$$

where $J$ is the matrix $\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$, $I$ being the $n \times n$ identity matrix. So one can see that, in order for the projections on the constitutive planes $(x_i, y_i)$ of the area spanned by the tangent vectors $s$ and $t$ to vanish, the graph of the constitutive relation must be sitting “just right” in $\mathbb{R}^{2n}$. This is obviously a rather delicate situation, as the slightest change in material properties of the $n$-port may cause the surface to rotate slightly, destroying the reciprocity property.* Nevertheless, this constitutive assumption has been employed quite commonly for linear, near-equilibrium systems, even though the theoretical basis for such an assumption seems to be in doubt [29]. When an $n$-port resistor does exhibit the reciprocity property, however, two consequences can be shown to accrue:

---

* Surfaces with the property $S^T J S = 0$ are called "Langrangian" in differential geometry jargon, since the quantity $\sum_j \nabla y_j \times \nabla x_j$ is equivalent to the Lagrange Bracket operation in mechanics [28].
(i) there is, as for capacitive $n$-ports, a potential function, whose extremal set is just the constitutive manifold $\Lambda_\mathbf{x}$ [15] and (ii) a dynamical system constructed from such objects will exhibit the property of global asymptotic stability, a fact of considerable importance for dynamical systems [16].

If we are looking to model interesting biological phenomena such as oscillatory chemical processes [30, 31] or dissipative instabilities [32] we should certainly expect that nonreciprocity will be required. Even a single chemical reaction is generally not a reciprocal system except in the vicinity of chemical equilibrium [16]. In any event, reciprocity does not play as central a role in irreversible processes as had been imagined, so although its passing has left us bereft of the potential functions so dear to the hearts of thermodynamicists, the admission of nonreciprocal processes has opened the door to a much richer universe of behavior. (A transistor is a nonreciprocal 2-port: its usefulness springs in large part from its nonreciprocity!) In Section 4 we shall show that any assembly of reciprocal systems results in an overall system which is also reciprocal; therefore, one cannot create nonreciprocal systems from reciprocal ones. Nonreciprocity must be built in at the level of a single multiport process. Finally, we note that reciprocity is not an invariant property of an $n$-port, but is strongly dependent on the coordinate system chosen to describe the constitutive relation. For example, it is common in many circuit theoretic applications to employ the "scattering port variables" $\tilde{s}_i = \frac{x_i + y_i}{2}, \tilde{\eta}_i = \frac{x_i - y_i}{2}$. In these coordinates, $\Sigma_i \nabla \tilde{s}_i \times \Delta \tilde{\eta}_i \neq 0$, so the system does not look reciprocal in this coordinate system, even though it does in those coordinates $(x_i, y_i)$ where $\Sigma_i \nabla y_i \times \nabla x_i = 0$ [15]. In particular only "canonical" (symplectic) coordinate changes $S$ of the form $S^T I S = J$ will preserve the property of reciprocity for an $n$-port. Reciprocity is an experimental property; there is no a priori way of determining which, if any, coordinate system to choose so that the system appears reciprocal.

The resistive $n$-port (or an interconnection of them, as we shall see) can also be cast in the form of a dynamical system in the formal sense. We simply write

$$o = x(t) - u(t) \tag{3.3}$$

$$y(t) = \Lambda(x(t)) \tag{3.4}$$

In general, a purely resistive (dissipative) system has the dynamical equations

$$o = f(x, u) \tag{3.5}$$

$$y = g(x, u) \tag{3.6}$$

Finally, the passivity criterion for resistive multiports is just

$$\nabla \tilde{y} \cdot \dot{x} = 0 \leq u \cdot g(x, u) \tag{3.7}$$
Or, in the present case,

\[ P = u \cdot y = x \cdot A(x) \geq 0. \]  

(3.8)

As remarked previously, passivity and reciprocity have nothing to do with each other, although each is an important property of a dynamical system for investigating stability.

It is important to notice that, unlike capacitive systems (Eq. (2.7)), the dynamical system defined by resistive \( n \)-ports is purely algebraic; that is, resistive \( n \)-ports are characterized by an algebraic relation between the variables \( J \) and \( x \). No derivatives of state variables occur in Eqs. (3.5) and (3.6) and hence a resistive \( n \)-port is presumed to be always in a stationary state. This assumption is not so severe as it looks, since we can always reticulate a real system \textit{mathematically} into dynamic (capacitive) subsystems and static (resistive) subsystems. The details of this procedure are contained in Ref. 16 but the general idea will be sketched in Section 4.

4. INTERCONNECTIONS OF MULTIPORE

4.1. By now it should be clear that we have not added much of substance to conventional thermodynamics (except, perhaps, to make precise some heretofore vague notions. But thermodynamicists have always thrived on vague ideas, so perhaps we will not be thanked for this effort!) However, we have recast our knowledge into a form which will enable us to generalize things considerably. In particular, we will show how complex systems can be built up out of simpler subsystems. The technology is well developed for purely electrical (1-port) systems, but the procedure for general thermodynamic multiports may not be so familiar. In this regard it is important to realize that the properties of the collective system are not simply related to the properties of the subsystems, any more than the characteristics of a television set are deducible from the properties of the component transistors. A complex system is certainly greater than the sum of its parts insofar as dynamic performance is concerned.

The idea behind interconnection constraints is quite simple — a generalization of Kirchhoff's laws familiar from electrical circuit theory.

When several \( n \)-ports are "connected" by constraining their port variables in some fashion (e.g., placing membranes in series or parallel) the state variables for the resulting composite system are constrained to remain in a manifold of dimension lower than the product of the individual state space dimensions. In this sense, interconnections are very much like "kinematic constraints" in mechanics. We wish to abstract the essentials of this procedure by examining the character of the interconnection constraint submanifold. Then we shall see, for example, that a complex reaction network can be viewed as an interconnection of simpler subsystems, the reaction stoichiometry entering in as the connection constraint.

Before discussing interconnection constraints, however, we digress for a moment to discuss some operational definitions and their mathematical meaning.

4.2. The notion of "conjugate variables" is an intimate part of thermodynamics and is no less important in network thermodynamics. However, we shall require a precise
mathematical definition in order to discuss interconnection constraints. Fortunately, the mathematical definition parallels the physical notion. Consider the state space $\Sigma$ for some dynamical system. It is well known that we can define two different kinds of vector fields on $\Sigma$: (1) If $t \mapsto \mathbf{r}(t)$ is a curve in $\Sigma$, then the velocity of the curve is just $\dot{\mathbf{r}}(t)$, a tangent vector to the curve $\mathbf{r}(t)$. In fact, any vector $\mathbf{v}(\mathbf{x})$ at $\mathbf{x}$ can be realized as the velocity vector of some (appropriately parameterized) curve (Fig. 12a). (2) On the other hand, if we have a real-valued function on $\Sigma$, $f : \Sigma \to \mathbb{R}$, we can define a different kind of vector field on $\Sigma$ by constructing the gradients to the level surfaces of $f$. (Just as the length of $\dot{\mathbf{r}}(t)$ can be adjusted by changing the parameterization of the curve, so can the length of $\nabla f$ be altered by changing the spacing of the level surfaces.) Although they are often confused, the two types of vector fields are not at all similar. For example, under a mapping $\mathbf{F} : \mathbb{R}^n \to \mathbb{R}^m$, $\dot{\mathbf{r}}$ maps “contra-variantly”, i.e., as $\dot{\mathbf{r}} \to \mathbf{F}(\mathbf{x}) \cdot \dot{\mathbf{r}}$, while $\nabla f$ maps backwards (“covariantly”) $\nabla f \to$
\( \nabla F(x)^T \cdot \nabla f \). More importantly, the two kinds of vectors represent two distinct types of physical quantities. A covariant vector, or covector, arising as it does as normals to potential surfaces, is used to represent potential-like quantities such as voltage, temperature, pressure and chemical potential. Engineers call these types of quantities across variables since the meters used to measure them make "2-point measurements", e.g. a voltmeter measures voltage "across" an electrical element and a thermocouple measures temperature differences, etc. It is differences between potential like-quantities, as measured by the spacing of their level surfaces, which generate "driving forces." So force "vectors" are really covectors.

On the other hand, flow quantities are usually measured by "1-point measurements" (e.g. an ammeter) and are called by engineers through variables (since the flow occurs "through" the 1-point meter); the more the flow, the bigger the flow vector. Flow quantities are vectors in the usual sense, i.e., they can be realized as tangent vectors to streamlines, etc.

4.3. In joining two dynamical systems together, we must impose two types of boundary condition on the two types of vectors at the interconnection surfaces. On the one hand, vectors, representing flows, must obey a conservation law across an interconnection boundary, \( \nabla \cdot \mathbf{r} = 0 \) (since the boundary has zero volume to store the flowing quantity). On the other hand, the covector fields must be equal on opposite sides of the boundary (i.e., the potential surfaces must be continuous) lest an infinite gradient field be generated at the connection surface. These ideas were introduced informally in Section 2.7. The conservation and continuity condition of vector and covector fields, respectively, is quite familiar in field theory; however, let us abstract the elements of these boundary conditions and apply them to the interconnection of n-ports. Consider first a situation familiar to membrane biophysicists: the series-parallel array of semipermeable membranes shown in Fig. 13a.

Each membrane element of this system imposes boundary conditions on its neighbors which, based on the above discussion, are of two types: (i) continuity of the covector quantities (chemical potentials), (ii) conservation of the vector quantities (diffusional flow of species i). The relation of these boundary conditions to Kirchhoff's laws is readily apparent by drawing the system as an interconnection of multiports. Figures 13b and 13c show the reticulation for one and two diffusing species, respectively. Although the abstraction required to achieve this representation is minor, considerable benefits accrue to us because of it. As one can easily verify, the conservation and continuity boundary conditions at each membrane interface are now contained identically in Kirchhoff's Current Law (KCL) and Kirchhoff's Voltage Law (KVL), respectively. What is significant about this is that KCL and KVL are purely topological notions, a fact that has some rather far-reaching consequences, of which we shall mention only a few.

* In fact, covariant vectors are not really vectors at all but linear operators on ordinary vectors. Covariant vector fields are called "differential forms" in modern calculus books [3, 33].
First, let us perform a few more mental gymnastics with Fig. 13b. Imagine that we can collect all of the interconnection junctions into one "terminal box" and all of the resistive multiports into a separate composite multiport. This is illustrated in Fig. 14 for the collection of 1-ports in Fig. 13b. For an arbitrarily complicated collection of multiports the corresponding manipulation will produce the structure shown in Fig. 14b. The black box containing only the junctions (i.e., the boundary conditions) is called a connection $n$-port [34], for, indeed, it contains only the interconnection laws of the system.

We can generalize the above conceptual separation to include arbitrarily complex interconnections of multiports of any kind. (Although we have limited our discussion to resistive and capacitive multiports, there are many other kinds.) The only restriction that must be observed is that interconnections be performed only between ports
of a similar nature, e.g. thermal to thermal, mechanical to mechanical, etc. So there is one connection n-port for each energy mode in the system. This idea is schematized in Fig. 15.

Of course, the manipulations we have performed, although conceptually straightforward, would be impractical for systems of high complexity, since the amount of mental gymnastics required to actually effect these reticulations would become prohibitive. Fortunately, there exists a convenient, easily visualized notation called “bond graphs” which handles all of these manipulations automatically. This is a graphical notation specifically designed to treat multiport systems. A detailed exposition in the context of thermodynamic systems can be found in Ref. 16.

The crucial aspect of this construction is that the organization of the system is contained in the connection n-port. As remarked previously, what distinguishes a functioning television set from a bag of resistors, capacitors, and so forth is the nature of its interconnections. Topology is the key to organizational complexity. Nowhere is this more true than in biochemical systems, where the system (the cell) is considerably more than the sum of its constituent chemical species.

4.4. Let us look at the connection n-port more closely and see if we can say anything in general about its nature. First of all we will have to accept a few facts that would
FIG. 15. Assembling of a dynamical system from subunits.

take too much space to completely justify here (see Ref. 16 for details). First of all, the connection \(n\)-port contains only the boundary conditions that the subsystems impose on one another, coded in KCL and KVL. Each interconnection condition is a linear equation relating port variables, e.g. \(\mu_i = \mu_j, J_i = -J_j\), etc. It can be shown that the constitutive relation for the connection \(n\)-port can be written as a hybrid matrix equation

\[
\begin{bmatrix}
X_I \\
J_{II}
\end{bmatrix} =
\begin{bmatrix}
O & -D^T \\
-D^T & O
\end{bmatrix}
\begin{bmatrix}
J_I \\
X_{II}
\end{bmatrix}
\]  \hspace{1cm} (4.1)

where \(X = (X_I, X_{II})\) and \(J = (J_I, J_{II})\) are the port variables, and where \(D\) is a matrix all of whose entries are either (+1, -1, 0). \(D\) is called a connection matrix for obvious reasons.

An important fact about the constitutive relation of the connection \(n\)-port is that it is reciprocal. This can be proven directly from the antisymmetry of the hybrid constitutive matrix \([15, 34]\), or by computing the reciprocity form \(\Sigma \nabla y_j \times \bigtriangledown x_i = 0\).

The second important fact is that KCL and KVL are neutral interconnections \([18]\); that is, they neither store nor dissipate energy.*

\[
X \cdot J = X_I \cdot J_I + X_{II} \cdot J_{II} = 0.
\]

* The connection \(n\)-port is a resistive multiport whose dynamical equations (3.5) and (3.6) are passive and lossless (c.f. Section 2).
This can be interpreted as an orthogonality condition on the through and across variables. In this form it is known as Tellegen's theorem. The importance of this condition cannot be overemphasized; virtually every theorem concerning energy distribution in circuit theory is derived starting with Tellegen's theorem [35]. Many thermodynamic stability conditions for nonequilibrium systems are a direct consequence of this central result [6]. Moreover, it provides the jump-off point for a general foundation of the nonlinear equations of motion [8, 36].

Using the notion of a connection \( n \)-port one can show that any interconnection of reciprocal \( n \)-ports results in a reciprocal \( n \)-port. The proof of this important result can be found in Ref. 16 or Ref. 34.

4.5. Finally, let us see what the foregoing constructions mean in the context of dynamical systems theory.

Recall that the input-state-output equations of capacitive and resistive multiports are of the form

\[
\dot{x}_C(t) = u_C(t) \tag{4.2}
\]

\[
y_C(t) = g_C(x_C) \tag{4.3}
\]

and

\[
o = f_R(x_R, u_R) \tag{4.4}
\]

\[
y_R = g_R(x_R, u_R) \tag{4.5}
\]

where the subscripts \( C \) and \( R \) refer to capacitive and resistive quantities. In order to interconnect these two systems and derive the equation describing the composite dynamical system, we first partition the resistive and capacitive input and output vectors into components which remain after the interconnection, denoted \( \tilde{u} \) and \( \tilde{y} \) and those that do not, denoted \( \bar{u} \) and \( \bar{y} \) (see Fig. 15). The components of \( \tilde{u} \) and \( \tilde{y} \) refer to external ports of the composite system, while those of \( \bar{u} \) and \( \bar{y} \) refer to the interconnected ports. For simplicity we shall further assume that all of the interconnected ports are of the same energy type, say electrical. If this were not the case we would simply decompose \( u \) into \( (u_\text{electrical}, u_\text{mechanical}, u_\text{thermal}, \ldots) \) and \( y \) into \( (y_\text{electrical}, y_\text{mechanical}, y_\text{thermal}, \ldots) \) and insure that only ports of similar type were interconnected as shown in Fig. 15, where \( K_1 \) and \( K_2 \) are connection \( n \)-ports corresponding to different energy modes. Notice also that, in Fig. 15, we have allowed for the possibility that new ports are created by the interconnection procedure. We shall neglect both of these complications in the subsequent calculations.

The partitioned dynamical systems may now be written as:

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* Tellegen's theorem is related to the well known fact in field theory that the inner product of an irrotational and a solenoidal vector field is always zero (see e.g. [37: 111-112]).
The constitutive relation for the connection \( n \)-port is a linear input-output equation between the hatted quantities, say in the form

\[
\begin{pmatrix}
\dot{\tilde{u}}_R \\
\dot{\tilde{u}}_C
\end{pmatrix} = K \begin{pmatrix}
\dot{\tilde{y}}_R \\
\dot{\tilde{y}}_C
\end{pmatrix} = \begin{pmatrix}
k_{11} & k_{12} \\
k_{21} & k_{22}
\end{pmatrix} \begin{pmatrix}
\dot{\tilde{y}}_R \\
\dot{\tilde{y}}_C
\end{pmatrix}
\]  

(4.12)

Now Eqs. (4.6)-(4.12) may be "solved" to yield the behavior of the composite system. First we may eliminate \( x_R \) by solving the algebraic resistive state equation (4.9) for \( x_R = h_R (\tilde{u}_R, \tilde{u}_R) \). Substituting the result into Eqs. (4.10) and (4.11) yields

\[
\begin{align*}
\dot{\tilde{y}}_R &= \tilde{g}_R (\tilde{h}_R (u), u) \hat{\Delta} \tilde{I}_R (\tilde{u}_R, \tilde{u}_R) \\
\dot{\tilde{y}}_C &= \tilde{g}_C (x_R, \tilde{u}_C, \tilde{u}_C) + k_{22} \dot{\tilde{y}}_C
\end{align*}
\]  

(4.13)  

(4.14)

Next we can utilize the interconnection constraint, Eq. (4.12), to eliminate \( \tilde{u}_R \) and \( \tilde{u}_C \). Thus, for example, the output equations (4.8) and (4.14) become

\[
\begin{align*}
\dot{\tilde{y}}_C &= \tilde{g}_C (x_R, \tilde{u}_C, k_{21} \dot{y}_R + k_{22} \dot{y}_C) \\
\dot{\tilde{y}}_R &= \tilde{I}_R (\tilde{u}_R, k_{11} \dot{y}_R + k_{21} \dot{y}_C)
\end{align*}
\]  

(4.15)

which can then be solved for

\[
\begin{align*}
\dot{\tilde{y}}_C &= m_C (x_R, \tilde{u}_C, \tilde{u}_R) \\
\dot{\tilde{y}}_R &= m_R (x_R, \tilde{u}_C, \tilde{u}_R)
\end{align*}
\]  

(4.16)

Equations (4.16) and (4.12) can then be employed to transform equations (4.6), (4.7) and (4.12) into a set of input-state-output equations for the composite system which have the general form
\[
\dot{x}_C = F (x_C, \tilde{u}_C, \tilde{u}_R)
\]
\[
(\tilde{y}_C, \tilde{y}_R) = G (x_C, \tilde{u}_C, \tilde{u}_R)
\] (4.17)

This final set of dynamic equations contains only external port quantities and unconstrained state variables.

By an exactly analogous method we could extend the above procedure and consider the interconnection of the composite system to form even higher order \(n\)-port structures.

This construction is somewhat of a swindle, since these manipulations may be exceedingly difficult to perform in practice. In fact, given the nonlinearity of the constitutive relations, solutions may be either multiple or non-existent! Therefore, while easy to describe, each of the above steps is contingent on satisfying the requirements of the implicit function theorem, a far from trivial restriction [3, 33].

Before illustrating in the next section how a chemical system can be viewed as an interconnected dynamical system, we would like to record a few observations about the interconnection procedure. First, notice that resistive and interconnection equations, (Eqs. (4.9)-(4.12), are nondynamic (i.e. algebraic), and act as constraints which confine the motion of the composite system’s state point to a submanifold of \(\Sigma_R \times \Sigma_C\), the composite state space. This submanifold will be nonlinear if and only if the resistive constitutive equations, Eqs. (4.13) and (4.14) are nonlinear. The importance of this submanifold lies in the fact that it summarizes the influence of the system’s organization on its dynamic behavior by defining the manifold on which possible motion can occur. Also notice that although both the dissipation and the interconnections appear as algebraic constraints, connection \(n\)-ports are linear, neutral and reciprocal, while resistive \(n\)-ports, in general, have none of these properties.

Although we shall not dwell on the subject at length here, we note in passing that considerations of controllability and observability enter into the interconnection procedure directly when the input and output quantities are partitioned into external and internal ports [38]. It is only through these external ports that we may peer into the system state space. and it is hardly ever trivial to reconstruct the state from input-output measurements alone. Moreover, the most useful state variables may not even be simply related to the external port variables. For example, scattering variables \(\xi = \frac{X_i + J_j}{2}\), \(\eta = \frac{X_i - J_j}{2}\) are extremely useful in many contexts [39]. So interposed between the experimenter and the internal state space are the input and output spaces, which may combine and confound the state so as to be unrecognizable from the outside.

This whole approach of building up a complex system from simpler subunits to form a “nested sequence of black boxes” is the keystone of modern electronic technology. The principle purpose of network thermodynamics is to make these techniques available for modelling complex biophysical systems. As an aesthetic bonus, we are able to put both classical and irreversible thermodynamics on a much firmer mathematical basis than heretofore.
5. CHEMICAL REACTION SYSTEMS

5.1. Having discussed topology at some length, let us now examine a particular class of dynamical systems in more detail. Network thermodynamics provides a very natural framework with which to treat complex biochemical systems, since it is just these systems which exhibit the complexity and delicacy of control processes for which network methods are suited. Indeed, as remarked previously, topological concepts are implicit in considerations of reaction stoichiometry. Stoichiometry determines how the various chemical species are "connected" by reaction pathways. To make this notion precise let us consider the case of reaction processes close to thermodynamic equilibrium where one usually presumes them to be reciprocal. This is not a good assumption for arbitrary processes, but it will simplify the discussion somewhat; the complete and rigorous mathematical treatment for the general case can be found in Ref. 40.

5.2. The reaction stoichiometry is completely summarized by the \((n \times m)\) stoichiometric matrix \(v\) \((n = \text{number of reacting species}, m = \text{number of independent reactions})\). To further simplify considerations, let us assume that the entries in \(v\) are all \((+1, -1, 0)\) (see Ref. 40 for the general case). Given such a matrix, it is natural to regard it as a connection matrix\(^*\); we need only establish what it connects. This requires a mild abstraction of the foregoing treatment. If we regard \(v\) as a map \(\nu : R^m \to R^n\), then we see that \(\nu\) connects "reaction space", \(R^m\) with "species space" \(R^n\). That is, if we identify \(\nu\) with the circuit matrix \(D\), then we are led to regard a point in \(R^n\) as representing the state of an \(n\)-port capacitor. As we will see below, a point in \(R^m\) represents the state of an \(m\)-port resistor. In this particular case, the species and reaction multiports are interconnections of \(l\)-ports, where \(v\) acts as the connection multiport (Fig. 16).

![FIG. 16. Species and reaction spaces connected by reaction stoichiometry.](image)

Thus we have effected a conceptual (i.e., mathematical) separation of chemical species from the reaction process in which they partake. Unlike the example in Section 4 where the state of interconnected resistive and capacitive multiports was determined by the state of the capacitor restricted to a submanifold of \(\Sigma_C \times \Sigma_R\); here the state of a reaction system at any moment is given by a set of reaction advancements, i.e., a point in \(R^m\).

\(^*\) If the entries of \(v\) have absolute value greater than 1, it can be regarded as a "weighted" connection matrix and the following treatment will remain valid.
which we denote by $\xi^\circ$. However, this state is accessible only via measurements of the chemical concentrations of the various species, which we view as a point $n$ in $\mathbb{R}^n$ (the mole numbers). That is, $\mathbb{R}^n$ is the input-output space for the state space $\mathbb{R}^m$. A point $n$ in $\mathbb{R}^n$ is related to a point $\xi$ in $\mathbb{R}^m$ by the well known relation

$$n = n^\circ + \nu \xi + \int_0^t \xi N dt = g(\xi u).$$

(5.1)

where $n^\circ$ is a vector of initial mole numbers, and $\xi_N$ is the input rate.

5.3. To construct the equations of motion on the state space $\mathbb{R}^m$ we must introduce the constitutive relations for the species capacitors and the reaction resistors. The former are given by the chemical potential covector field defined on $\mathbb{R}^n$:

$$n \mapsto \mu(n)$$

(5.2)

where $\mu(n) = (\mu_1(n), \cdots, \mu_m(n))$ is a vector of chemical potentials.

The constitutive relation for a reaction process would relate a covector field on $\mathbb{R}^m$ to the reaction velocity field $J^R$. (Recall that constitutive relations are always between covariant and contravariant quantities.) The covector field on $\mathbb{R}^m$ is called the reaction affinity, and is obtained by pulling $\mu$ over to $\mathbb{R}^n$ using the map $\nu^T$:

$$\alpha = -\nu^T \mu$$

(5.3)

So the reaction constitutive relation is the map $\Lambda : \mathbb{R}^m \to \mathbb{R}^m, \alpha \mapsto \Lambda(\alpha) = J^R$.

Now we construct the dynamical equations generating the reaction trajectory $\xi(t)$. We shall simplify matters by omitting the input component, i.e. we consider only closed chemical systems. The autonomous equations of motion are then

$$\dot{\xi} = F(\xi)$$

$$= \Lambda(-\nu^T \mu (n^\circ + \nu \xi))$$

(5.4)

Once the equations are solved, the trajectories $\xi(t)$ can be mapped back to species (output) space via $n(t) = n^\circ + \nu \xi(t)$. In fact, in this simple case, the equations may be written in terms of $n(t)$ directly:

$$\dot{n} = \nu \Lambda(-\nu^T \mu(n))$$

(5.5)

This cannot be done in the general case, however; the basic state space is $\mathbb{R}^m$, not $\mathbb{R}^n$.

5.4. We have constructed a set of generic equations of motion for near-equilibrium, autonomous, unit-stoichiometry reactions. They are of limited practical interest, of course.

* The reason for this difference is technical and we refer the reader to page 40.
course, but they have served to introduce the general philosophy of the network approach to chemical systems analysis. By modifying the above procedure somewhat (at the expense of considerable technical difficulty!) one can generate a set of generic equations which govern any reaction process, however complex, with no restrictions whatever. Their form is similar to the above equations in that a separation of the dynamical vector field is effected into (a) equilibrium properties of reactants, \( \mu(n) \); dissipative properties of the reaction process, \( \Lambda(\alpha) \), and topological relationships between reactants and reactions, \( \nu \).

What is the advantage of formulating a generic set of dynamical systems? First, and most importantly, it provides the necessary first step in constructing a general mathematical theory of reaction dynamics. Secondly, it isolates the distinct roles of thermo-static and thermodynamic properties from kinematic constraints in determining dynamic behavior. We can then investigate the consequences of various assumptions as the individual constitutive relations (e.g., passivity, reciprocity, convexity, monotonicity, etc.). For example, if we assume \( \Lambda(\cdot) \) is reciprocal, then it can be shown that the above equations are asymptotically stable with respect to a unique equilibrium set given by the extremals of the resistive potential function \[16\]. Thirdly, having cast reaction dynamics in a circuit theoretic context (it seems almost tailor-made for the purpose!), we can draw on a vast storehouse of design and analysis techniques developed for electronic systems. Although we can hardly hope to resolve the formidable problem of biochemical complexity, we at least have a reliable formalism with which to take the first steps in that direction.

5.5. There is an interesting comparison to be drawn between the generic equations for reactions and the corresponding generic equations from classical mechanics. Let us consider the case where the reaction constitutive relation \( \Lambda(\cdot) \) can be considered linear. Then, recalling that \( \mu = \nabla \Psi \), we can move this potential function over to the reaction space via \( \nu^T \), and write the equations of motion as

\[
\dot{\xi} = \Lambda \cdot \nabla \Psi^*(\xi)
\]  

(5.6)

where \( \Psi^*: \mathbb{R}^m \to \mathbb{R} \) is given by \( \Psi^*(\xi) = \Psi(n_0^\top + \nu \xi) \).

Hamilton's canonical equations can be written in the form

\[
\dot{x} = J \nabla H(x)
\]

(5.7)

where \( H: \mathbb{R}^{2m} \to \mathbb{R} \) is the Hamiltonian, \( x = (q, p) \), the vector of positions and momentums and \( J = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \) is the symplectic matrix encountered in our discussion of reciprocity.

The form of the two sets of equations is superficially similar. They are identical only if (a) \( \xi \in \mathbb{R}^{2m} \), i.e., an even number of independent reactions, and (b)

\[
\Lambda = \begin{bmatrix} 0 & I \\ -I & 0 \end{bmatrix}
\]
i.e. the reaction is a purely antisymmetric neutral constraint.* There is certainly a dramatic difference between the physical properties of a mechanical and a reaction system; here we see the difference explicitly and the contrast is enlightening.

6. CONCLUSION

Our purpose in the above discourse was to present the broad strokes of a modern approach to thermodynamic systems. The motion of a formal dynamical system is at once a profound and trivial concept. It is remarkable that the abstract definition of a dynamical system was not precisely enunciated until quite recently [10, 41], although physicists had been groping toward such a model for some time. The conceptual clarity and unifying force of the systems viewpoint can best be appreciated by one who has struggled with the vagaries and imprecision of traditional thermodynamics. During the course of our research with Katchalsky we all became fervent converts to this mode of thinking. Aharon's enormous intellectual versatility always enabled him to seize a new idea and incorporate it into his own conceptual framework in such an intimate fashion that no scientific apostacy was ever apparent; each new viewpoint seemed a natural and logical consequence of the old order. He frequently paraphrased Newton, saying: "The way to see farther than others is to stand atop the backs of giants." No one was quicker to seize a new concept and turn it to his own ends; the true scientist is intellectually promiscuous, he maintained. The search for order, unity and beauty was his driving passion. We shall forever be in his debt.

REFERENCES


* In circuit theory, a 2m-port with the constitutive relation \( J = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \) is called a "gyrator."