1.1 INTRODUCTION

Michel Boudart concludes his fine book *Kinetics of Chemical Processes* (1968) with a chapter called "The Analysis of Reaction Networks" in which he touches upon two rather broad areas. The first of these has to do with interpretation of dynamic experiments for situations in which the underlying chemistry is complex. The second has to do with recent theoretical and experimental observations that, with sufficiently complex chemistry, reactors can exhibit dynamics of exotic character. The last sentence of Boudart's book is this: "In any case, the analysis of reaction networks remains the most elaborate problem facing the chemical kineticist in pure and applied work."

In one sense, this chapter may be taken as a partial exposition of progress made in both areas discussed by Boudart since publication of his book. In another sense, it may be taken as something more: The reader will find that certain new ideas (e.g., mechanism deficiency) inexorably and repeatedly force their way to the forefront in seemingly disjoint sectors of the theoretical landscape Boudart took as part of reaction network analysis. It is this recurrence of themes, this interplay of apparently skew lines of study, which suggests that the "elaborate problem" to which Boudart refers will perhaps give rise to a theory of breadth and maturity appropriate to the complexities it will help resolve. Hence, this review of recent work might be taken as a suggestion, however premature, of what coloration that theory might ultimately take.

However it evolves, the theory begun in the early 1960s by men such as Rutherford Aris and James Wei will, in the final analysis, draw
heavily upon modern mathematics. There will be those of us who will complain that anything so mathematical cannot be of much practical use, and there will be those of us who will, in fact, do theoretical work of little worth. In the end, however, something of value will emerge if only because we shall be compelled to solve problems of increasing complexity. In the meantime we might gain perspective by looking past our own provincial boundaries: we need only look to work of modern economic theorists (social scientists!) to find that chemical engineers are not quite so mathematical after all.

All the work discussed here in detail has been published since 1970. No attempt has been made to survey all or even a good part of recent research on mathematical aspects of chemical dynamics. In particular, all systems discussed are isothermal and homogeneous. Focus is primarily upon the two principal areas touched upon in Boudart's final chapter, and these have been treated in such a manner as to highlight common threads which run through both.

Section 1.2 is intended to be a guide to mathematics required for the balance of the chapter. The terseness of style in that section was dictated by considerations of space; the reader will probably find the style in all other sections to be somewhat more congenial. In Section 1.3 some very basic ideas are reviewed, some new ideas are introduced, and the framework for Sections 1.4 and 1.5 is constructed. Section 1.4 is devoted to a discussion of theoretical aspects of rate constant determination in the context of complex chemistry. Section 1.5 takes up questions related to stability of open isothermal reactors endowed with intricate reaction networks, and conditions are presented which serve to distinguish between those systems which might exhibit pathology and those which cannot. In Section 1.6 there are offered some brief concluding remarks.

In his preface, Boudart writes of his book: "All it tries to do is explain the concepts associated with the kinetic study of the chemical process 'A goes to B goes to C.' It may seem unfortunate that compounds A, B, and C have neither odor nor taste nor color. But if they did, the subject matter of this book would be chemistry and not chemical kinetics. It is hoped that this ascetic presentation of the subject will help in forging a more generally usable tool for pure and applied research." We adopt a similar view here.

In fact, the reader will find scattered about this chapter hypothetical mechanisms which almost certainly do not reflect real chemistry. That these were chosen for illustrative purposes should not be attributed to lack of concern for applications or, worse still, contempt for the real world. It should be clearly understood that theorems presented here apply to all mechanisms which satisfy their hypotheses, whether these be "real" or contrived. The apparently artificial mechanisms which are explored were chosen for the sake of pedagogy, and, more often then not, these are cited as examples of mechanisms which fail to satisfy the hypothesis of a particular theorem under consideration. Clearly, examples of this sort in no way detract from the truth of the theorem under scrutiny. On the contrary, the more one is compelled to indulge in chemical fantasy to construct systems not embraced by the hypothesis of a theorem, the more likely is the applicability of that theorem to systems we might encounter in practice.
1.2 MATHEMATICAL PRELIMINARIES

Chemical reactor analysis confronts us with problems involving concentrations of several species, each varying with time by virtue of occurrence of perhaps several chemical reactions. We know that the temporal evolution of each species concentration is related to the evolution of other species concentrations in at least two ways: through the stoichiometry of the underlying set of reactions and through the dependence of instantaneous rates of individual reactions on mixture composition. With this in mind even the most intuitive among us might ultimately be led to the conclusion that, at least for those reactors endowed with complex chemistry, some mathematical framework is required so that order and clarity might be imposed upon otherwise perplexing problems.

Fortunately, the tools routinely provided to students of science and engineering in today's undergraduate mathematics courses are of considerable help. Unfortunately, those same tools, particularly modern linear algebra coupled to multivariable calculus, were probably not provided on any large scale to engineering undergraduates of even 15 years ago. This section is intended as a cursory guide to the mathematics required for a comfortable reading of this chapter.

Most of this survey is devoted to linear algebra, a subject which requires of the student both patience and trust. Unlike elementary calculus, which affords applications at almost every step of the way, the strength of linear algebra as a subject resides not in its various parts but rather in its structure as a whole. For this reason the teaching of linear algebra to students interested in applications is hampered by pedagogical problems of unusual severity. Patience is required because nontrivial applications can come only after a substantial amount of structure has been erected. In turn, that patience must be rooted in trust that the study of axioms, definitions, and minor propositions which, at the outset, seem barren will, in the long run, place in the hands of the student tools of considerable power.

Although the brief survey contained in this section is hardly a course in linear algebra, these same remarks apply here as well. Those students unfamiliar with the rudiments of modern linear algebra are encouraged to approach this modest introduction patiently. It is incomplete and all too terse. On the other hand, it is reasonably self-contained, and a careful reading of this section should provide the basis for a decent understanding of the applications to follow.

A good deal of the material presented here is available at greater length in Lang's Introduction to Linear Algebra (1970), a short readable text intended for college freshmen. The first eight chapters of Advanced Calculus by Nickerson et al. (1959) are difficult in places but are highly rewarding. Students interested in an elegant treatise on linear algebra might try the book by Greub (1967).

1.2.1 Vector Spaces

Some very good textbooks on linear algebra are devoted exclusively to study of column vectors, row vectors, matrices, and operations among them. However, in recent years a somewhat different approach has taken root in many classrooms. Behind the more modern view lies the idea that
matrices, column vectors, and the like are merely aspects of something more basic; to overemphasize matrix manipulation is perhaps to confuse shadow and substance. We shall follow the modern line here not because modernity is to be valued in itself but because there are advantages in so doing.

We shall begin by defining what is meant by a vector space. If we view linear algebra as a game to be played in accordance with certain rules, then it is the definition of a vector space which specifies the most essential of those rules.

A vector space* is a set of objects (called vectors) taken together with two operations. The first operation, called addition, assigns to each pair of vectors in the set, say $x$ and $y$, a vector of the set denoted $x + y$. The second operation, called multiplication by a real number, assigns to each vector $x$ in the set and each real number $\alpha$ a vector of the set denoted $\alpha x$. These operations are required to conform to the following rules:

V1. If $x$, $y$, and $z$ are elements of $V$, then 
   $(x + y) + z = x + (y + z)$.
V2. There is an element of $V$, called the zero vector and denoted by 0, such that $x + 0 = x$ for every $x$ in $V$.
V3. To every element $x$ in $V$ there corresponds an element ($-x$) such that $x + (-x) = 0$.
V4. For every $x$ in $V$ and every $y$ in $V$, $x + y = y + x$.
V5. If $\alpha$ is a real number and $x$ and $y$ are elements of $V$, then $\alpha(x + y) = \alpha x + \alpha y$.
V6. If $\alpha$ and $\beta$ are two real numbers and $x$ is an element of $V$, then $(\alpha + \beta)x = \alpha x + \beta x$.
V7. If $\alpha$ and $\beta$ are two real numbers and $x$ is an element of $V$, then $(\alpha\beta)x = \alpha(\beta x)$.
V8. For every $x$ in $V$, $0x = 0$, $1x = x$, and $(-1)x = -x$.

The operation $x + (-y)$ is usually written $x - y$.

The reader will notice that, although the rules of the game are specified, nothing is said about the nature of the "pieces" (vectors) with which the game is played. They are not described in detail apart from a vague statement to the effect that we are dealing with "a set of objects." It is precisely this vagueness which affords breadth to the modern theory. The fact of the matter is that the nature of the pieces may vary from one application to another, while the essential rules of the game stay the same. Thus, if we can make deductions from study of only the rules of the game, then these same deductions will hold true regardless of the nature of the pieces with which we play. Such a deduction is the very simple Theorem 1.2.a, which we shall present shortly and which, in the course of this chapter, we shall apply in two vector spaces of very different character.

In the meantime we consider as an example of a vector space the one studied almost exclusively in some linear algebra courses. In Section 1.2.8 we shall study yet another example.

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* Here we take the term "vector space" to mean real vector space. The definition offered is redundant in that some of the axioms can be derived from others.
EXAMPLE: Let the set in question be the set of all possible ordered triplets of real numbers (e.g., $[-17, 2.4, 9], \ [1, 1, 2], \ etc.$). We shall take addition to be defined in the following way:

$$[x_1, x_2, x_3] + [y_1, y_2, y_3] = [x_1 + y_1, x_2 + y_2, x_3 + y_3]$$

Multiplication by a real number will be defined as follows:

$$a[x_1, x_2, x_3] = [ax_1, ax_2, ax_3]$$

It is easily verified that these operations conform to the rules outlined above. Hence, the ordered triplets taken together with these rules for addition and multiplication by a real number constitute a vector space.

Of course this example generalizes to sets of sequences of $M$ real numbers ("$M$-tuples" of the type $[x_1, x_2, \ldots, x_M]$) with addition and multiplication by a real number defined similarly. The vector space of $M$-tuples is usually denoted by the symbol $\mathbb{R}^M$. Thus, the example of ordered triplets corresponds to $\mathbb{R}^3$. The vector space $\mathbb{R}^1$ coincides with the set of real numbers and is usually denoted simply by the symbol $\mathbb{R}$.

1.2.2 Linear Independence

Let $V$ be a vector space, and let $\{x_1, x_2, \ldots, x_k\}$ be a set of vectors taken from $V$. If there exists a set of numbers $\{a_1, a_2, \ldots, a_k\}$, not all zero, such that

$$a_1x_1 + a_2x_2 + \ldots + a_kx_k = 0$$

(1.1)

then $\{x_1, x_2, \ldots, x_k\}$ is said to be a linearly dependent set of vectors. Otherwise, $\{x_1, x_2, \ldots, x_k\}$ is said to be a linearly independent set of vectors.

EXAMPLE: In $\mathbb{R}^3$ (for which the zero vector is $[0, 0, 0]$) the set $\{[2, 1, 0], [1, 1, 1], [0, 1, 2]\}$ is linearly dependent since

$$(1)[2, 1, 0] + (-2)[1, 1, 1] + (1)[0, 1, 2] = [0, 0, 0]$$

(1.2)

On the other hand, the set $\{[1, 0, 1], [3, 1, 0]\}$ is linearly independent since the equation

$$a_1[1, 0, 1] + a_2[3, 1, 0] = [0, 0, 0]$$

(1.3)

is satisfied only if $a_1 = 0$ and $a_2 = 0$.

An important theorem of linear algebra is the following:

THEOREM 1.2.a: Let $V$ be a vector space, and let $\{x_1, x_2, \ldots, x_k\}$ be a set of vectors taken from $V$. If $z$ is a vector of $V$ such that the equation

$$z = a_1x_1 + a_2x_2 + \ldots + a_kx_k$$

(1.4)

has a solution [i.e., a set of numbers $\{a_1, a_2, \ldots, a_k\}$ such that Eq. (1.4) holds], then that solution is unique if and only if $\{x_1, x_2, \ldots, x_k\}$ is a linearly independent set.
The proof, which is quite elementary, may be found in Greub, (1967, p. 10). It must be emphasized that the proof draws only upon the axioms for a vector space and the definition of linear independence. Hence, it holds for any vector space, not just those with which the reader might be most familiar.

If $V$ is some vector space, we can ask the following question: Can we find in $V$ a linearly independent set containing an arbitrarily large number of elements? Or is there a maximum number of elements that can reside in a linearly independent set taken from $V$? The answer will depend on the vector space in question. A vector space is said to be finite dimensional if there exists a number $m$ such that one can find in that vector space a linearly independent set of $m$ vectors but no linearly independent set of $m + 1$ vectors. The number $m$ is said to be the dimension of that space. The dimension of $\mathbb{R}^M$ may be shown to be $M$. In this chapter we shall deal only with finite dimensional vector spaces.

A basis for a vector space $V$ of dimension $m$ is any linearly independent set of $m$ vectors taken from $V$. The natural basis for $\mathbb{R}^M$ is the set $\{(1,0,\ldots,0), (0,1,0,\ldots,0), \ldots, (0,0,\ldots,1)\}$. As a matter of notation we write

$$e_1 = [1,0,0,\ldots,0]$$
$$e_2 = [0,1,0,\ldots,0]$$
$$\vdots$$
$$e_M = [0,0,\ldots,1]$$

(1.5)

to designate the natural basis of $\mathbb{R}^M$.

1.2.3 Linear Subspaces

Let $V$ be a vector space and let $U$ be a subset of vectors taken from $V$. Then $U$ is called a linear subspace of $V$ if it satisfies two requirements:

LS1. If $x$ is in $U$ and $y$ is in $U$, then $x + y$ is in $U$.
LS2. If $\alpha$ is in $U$ and $\alpha$ is any real number, then $\alpha x$ is in $U$.

Clearly $V$ satisfies both these requirements so that $V$ may be regarded as a linear subspace of itself. On the other hand, every linear subspace of a vector space is itself a vector space. That is, if $U$ is a linear subspace of $V$, then $U$ is a set endowed with operations of addition and multiplication by a real number "inherited" from the ambient vector space $V$, and these operations may be shown to have all the required properties described in V1-V8. In particular the zero vector of $U$ is the zero vector of $V$, for if $x$ is any vector of $U$, it follows from LS2 that $0 \times x = 0$ must also lie in $U$.

EXAMPLE: In $\mathbb{R}^3$, let $U$ be that subset of ordered triplets whose entries sum to zero. That is $[x_1, x_2, x_3]$ is in $U$ if and only if $x_1 + x_2 + x_3 = 0$. The reader may confirm that $U$ is a linear subspace of $\mathbb{R}^3$. (Note that the set of triplets whose entries sum to 1 is not a linear subspace of $\mathbb{R}^3$.)
EXAMPLE: Let \( V \) be a vector space, and let \( \{x_1, x_2, \ldots, x_k\} \) be a fixed set of vectors taken from \( V \). Let \( U \) be the set of all possible vectors which can be written in the form

\[
a_1x_1 + a_2x_2 + \ldots + a_kx_k
\]

where the \( a_i \) are real numbers. Then \( U \) is a linear subspace of \( V \) called the span of the set \( \{x_1, x_2, \ldots, x_k\} \). Hereafter, we denote the span of \( \{x_1, x_2, \ldots, x_k\} \) by the symbol \( L[\{x_1, x_2, \ldots, x_k\}] \). Clearly the set \( \{x_1, x_2, \ldots, x_k\} \) lies in its own span since

\[
x_1 = 1x_1 + 0x_2 + \ldots + 0x_k, \quad x_2 = 0x_1 + 1x_2 + \ldots + 0x_k, \ldots
\]

Since linear subspaces of vector spaces are vector spaces in their own right, it makes sense to speak of the dimension of a linear subspace. That is, a linear subspace has dimension \( m \) if one can find in that linear subspace a linearly independent set of \( m \) vectors but no linearly independent set of \( m + 1 \) vectors. In particular, we shall be concerned with the dimensions of linear subspaces defined as spans of vector sets. In this regard the following remark is helpful: \( L[\{x_1, x_2, \ldots, x_k\}] \) has dimension \( m \) if and only if the set \( \{x_1, x_2, \ldots, x_k\} \) contains a subset of \( m \) linearly independent vectors but no subset of \( m + 1 \) linearly independent vectors.*

EXAMPLE: Suppose that the vector space in question is \( \mathbb{R}^3 \). Let \( x_1 = [-1, 1, 0], x_2 = [0, -1, 1], \) and \( x_3 = [1, 0, -1] \). Then \( L[x_1, x_2, x_3] \) is the set of all vectors in \( \mathbb{R}^3 \) of the form

\[
a_1[-1, 1, 0] + a_2[0, -1, 1] + a_3[1, 0, -1]
\]

where \( a_1, a_2, \) and \( a_3 \) can be any real numbers. Equivalently, \( L[x_1, x_2, x_3] \) is the set of all vectors of the form \( [a_3 - a_1, a_1 - a_2, a_2 - a_3] \). By inspecting the set \( \{x_1, x_2, x_3\} \) the reader may establish that this set contains linearly independent subsets of two vectors (e.g., \( \{x_1, x_2\} \)) but no linearly independent set of three vectors. Hence, \( L[x_1, x_2, x_3] \) has dimension 2.

1.2.4 Parallels of a Linear Subspace

We have discussed linear subspaces of vector spaces because they are subsets of sufficiently important structure as to deserve special attention. There is yet another type of subset in vector spaces which is of considerable importance in reactor dynamics, and we shall study that type as well.

Let \( V \) be a vector space, and let \( U \) be a linear subspace of \( V \). Furthermore, let \( a \) be some fixed vector of \( V \) which is not

* The reader might try to prove this as an exercise. The "if" part is not entirely trivial. When \( k \) is small this remark usually permits determination of the dimension of \( L[\{x_1, x_2, \ldots, x_k\}] \) by inspection of the set \( \{x_1, x_2, \ldots, x_k\} \). However, when \( k \) is large more systematic methods are required to compute the dimension of \( L[\{x_1, x_2, \ldots, x_k\}] \). If \( \{x_1, x_2, \ldots, x_k\} \) are vectors of \( \mathbb{R}^M \), then one can form a \( k \times M \) matrix, the \( j \) th row of which is \( x_j \). The dimension of \( L[\{x_1, x_2, \ldots, x_k\}] \) is then the rank of that matrix, which may be computed using techniques discussed by Amundson (1966) and Hadley (1961).
necessarily in $U$. Now let us construct a new subset of $V$ in the following way: To every vector of $U$ we add the vector $a$. That is, a vector lies in our new set if and only if it can be written in the form $a + y$ for some $y$ in the linear subspace $U$. The set so constructed is denoted suggestively by the symbol $a + U$.

EXAMPLE: Let the vector space in question be $\mathbb{R}^2$, and let $U$ be the linear subspace of $\mathbb{R}^2$ consisting of all elements of the form $(a,-a)$, where $a$ is any real number. Then $[2,1] + U$ is the set of all elements in $\mathbb{R}^2$ of the form $[2,1] + [a,-a] = [2 + a, 1 - a]$.

Although this example is rather simple it can provide the basis for geometric insight into the ideas involved. In Figure 1.1 there is drawn a coordinate system comprised of an $x_1$ axis and an $x_2$ axis. Thus, any element $[x_1,x_2]$ in $\mathbb{R}^2$ can be represented in the usual manner as a point in the figure. The linear subspace $U$ of the example is shown, as is the set $[2,1] + U$. The figure suggests some terminology: If $U$ is a linear subspace of a vector space $V$, then any set of the form $a + U$ with $a$ in $V$ is called a parallel of $U$. It should be noted that even if $a \neq a'$ it may still be true that $a + U$ and $a' + U$ are identical parallels of $U$. (In our example $[2,1] + U$ and $[0,3] + U$ are identical sets.)

Here are some basic facts about parallels of linear subspaces [Nickerson et al. (1959)]: If $U$ is a linear subspace of a vector space $V$, then each vector of $V$ lies in one and only one parallel of $U$; two vectors of $V$ lie in the same parallel of $U$ if and only if their difference lies in $U$; and if $a'$ lies in $a + U$, then $a' + U$ is the same set as $a + U$.

![Figure 1.1. A Parallel of a Linear Subspace.](image)

1.2.5 The Scalar Product

Sometimes it is convenient to introduce into a vector space an additional operation beyond addition and multiplication by a real number. This third operation, called a scalar product, assigns to each pair of vectors, say $x$ and $y$, a real number denoted by $x \cdot y$. Just as the two basic operations in vector spaces are required to conform to certain
rules so is this additional operation. A scalar product in a vector space \( V \) is required to have these properties:

SP1. \( x \cdot x \geq 0 \) for all \( x \) in \( V \) with \( x \cdot x = 0 \) if and only if \( x = 0 \).

SP2. \( x \cdot y = y \cdot x \) for all \( x \) and \( y \) in \( V \).

SP3. \( x \cdot (y + z) = x \cdot y + x \cdot z \) for all \( x \), \( y \), and \( z \) in \( V \).

SP4. \( (\alpha x) \cdot y = \alpha (x \cdot y) \) for all \( x \) and \( y \) in \( V \) and every real number \( \alpha \).

EXAMPLE: The standard scalar product in \( \mathbb{R}^M \) is defined as follows: If \( x = [x_1, x_2, \ldots, x_M] \) and \( y = [y_1, y_2, \ldots, y_M] \), then

\[
 x \cdot y = x_1y_1 + x_2y_2 + \cdots + x_My_M \quad (1.6)
\]

It is easily verified that this definition satisfies the requirements for a scalar product. Henceforth, the vector space \( \mathbb{R}^M \) will be presumed to be endowed with the standard scalar product.

If \( V \) is a vector space with a scalar product, then two vectors in \( V \), say \( x \) and \( y \), are said to be orthogonal if \( x \cdot y = 0 \). If \( U \) is a linear subspace of \( V \), then the orthogonal complement of \( U \), denoted \( U^\perp \), is the set of all vectors in \( V \) which are orthogonal to every vector of \( U \). The reader might try to show that \( U^\perp \) is a linear subspace of \( V \).

EXAMPLE: In \( \mathbb{R}^2 \) let \( U \) be the linear subspace consisting of all vectors of the form \([\alpha, -\alpha] \), where \( \alpha \) is any real number. Then \( U^\perp \) is the set of all vectors of the form \([\beta, \beta] \), where \( \beta \) is any real number. Note that, for any \( \alpha \) and any \( \beta \), \([\alpha, -\alpha] \cdot [\beta, \beta] = \alpha \beta - \alpha \beta = 0 \). Note also that any vector not of the form \([\beta, \beta] \) fails to be orthogonal to all vectors of \( U \). For this example \( U \) and \( U^\perp \) are sketched in Figure 1.2.

![Figure 1.2. A Linear Subspace and Its Orthogonal Complement.](image)

Recall that if \( \{x_1, x_2, \ldots, x_k\} \) is a set in a vector space \( V \), then the span of the set, \( \mathbf{L}[x_1, x_2, \ldots, x_k] \), is the linear subspace of \( V \) consisting of all vectors representable in the form \( \alpha_1 x_1 + \alpha_2 x_2 + \cdots + \alpha_k x_k \). For the case in which \( V \) has a scalar
product we shall be interested in the nature of $L^1[x_1, x_2, \ldots, x_k]$, the orthogonal complement of $L[x_1, x_2, \ldots, x_k]$. A vector $\mathbf{y}$ in $V$ lies in $L^1[x_1, x_2, \ldots, x_k]$ if and only if $\mathbf{y} \cdot x_i = 0$, $i = 1, 2, \ldots, k$. The proof is left as an exercise for the reader.

1.2.6 Linear Transformations

A function consists of three ingredients: a set called the domain of the function, a (possibly different) set called the codomain of the function, and a rule, which assigns to each element of the domain a single element of the codomain. A mathematician might write $f: V + W$ to indicate a function which has as its domain a set $V$ and has as its codomain the set $W$; the arrow is intended to suggest that the function "maps" $V$ into $W$. Once the domain and codomain have been clearly indicated the function might thereafter be indicated simply as $f$ or $f(\cdot)$. As usual, if $v$ is an element of the domain, then $f(v)$ is that element of the codomain assigned to $v$ by the function.

We shall be particularly interested in functions for which domains and codomains are vector spaces (or parts thereof). A function $T: V + W$ is said to be a linear transformation if $V$ and $W$ are vector spaces and if both of the following requirements are satisfied:

**LT1.** $T(x + y) = T(x) + T(y)$ for all $x$ and $y$ in $V$.

**LT2.** $T(\alpha x) = \alpha T(x)$ for every $x$ in $V$ and every real number $\alpha$.

In dealing with linear transformations it is customary to drop parentheses when no confusion is likely to arise. That is, if $T$ is a linear transformation, we write $Tx$ in place of $T(x)$.

**EXAMPLE:** Consider the function $T: \mathbb{R}^2 \mapsto \mathbb{R}^3$ defined as follows:

$$T(x_1, x_2) = [x_1 + x_2, x_2, x_1 - x_2]$$

The reader may verify that $T$ is a linear transformation.

**EXAMPLE:** Let $V$ and $W$ be vector spaces, and let $0(V, W): V + W$ denote that function which maps every vector of $V$ into the zero vector of $W$. The function $0(V, W)$, called the zero transformation from $V$ into $W$, is easily shown to be a linear transformation.

Linear transformations are clearly a very special type of function from one vector space to another. Why is it, then, that this somewhat restricted class of functions is singled out for special attention? The fact of the matter is that linear transformations play an important role even in "nonlinear theories." This prominent place occupied by linear transformations is explained at least in part by their importance in the calculus of vector spaces, one aspect of which is considered in the next section.

1.2.7 Derivatives as Linear Transformations

We shall have need of a modest amount of vector calculus. Here we shall merely introduce an idea or two in a cavalier manner, drawing upon the reader's intuition and experience with elementary calculus. To do
otherwise would require more analysis* than can reasonably be presented here. A more thorough treatment can be found in Chapters 6, 7, and 8 of Advanced Calculus by Nickerson et al. (1959).

Our primary concern here is with the notion of derivative. Most of us were probably introduced to differentiation in consideration of functions with scalar domain and scalar codomain (e.g., temperature at a point in a body as a function of time). Perhaps somewhat later we were taught to extend our thinking to embrace differentiation of a vector-valued function of a scalar (e.g., position of a particle in space as a function of time). Both cases involved functions with scalar domain, and the essential ideas behind the derivative caused no undue conceptual difficulty. However, we shall also be interested in functions with domains which are not scalars, and it is this situation which compels us to think more deeply about what we mean by the derivative of a function.

Let us see what some of the problems are. Consider a function \( f: \mathbb{V} \rightarrow \mathbb{R} \) from a vector space \( \mathbb{V} \) into the real numbers, and let us suppose that this function is not necessarily linear but is reasonably "smooth." [For example, \( f(\cdot) \) may be thought of as giving temperature in some region of space as a function of position.] If \( \mathbf{x} \) is an element of \( \mathbb{V} \), let us see what difficulties we encounter in trying to develop a suitable notion of derivative of \( f(\cdot) \) at \( \mathbf{x} \). Loosely speaking, what we want is something which depends only on the vector \( \mathbf{x} \) and somehow reflects the rapidity of change in values that \( f(\cdot) \) takes as we move away from \( \mathbf{x} \). However, there will generally be many different "directions" along which we may move away from \( \mathbf{x} \); values that \( f(\cdot) \) takes may vary sharply as we move away from \( \mathbf{x} \) along one direction and not at all along another. This idea must somehow play a role in our considerations.

We can begin by investigating how values of \( f(\cdot) \) change as we move away from \( \mathbf{x} \) along some fixed direction. In order that this might be done in a cogent fashion we take notice of the following idea: If \( \mathbf{y} \) is any vector of \( \mathbb{V} \) and \( \theta \) is any real number, then \( \theta \mathbf{y} \) is a vector which "points" along \( \mathbf{y} \) (i.e., \( \theta \mathbf{y} \) is colinear with \( \mathbf{y} \)). Thus, the vector \( \mathbf{x} + \theta \mathbf{y} \) may be viewed as a new "position" in \( \mathbb{V} \) obtained by marching away from \( \mathbf{x} \) along a path parallel to \( \mathbf{y} \), the extent and direction of movement determined by the magnitude and sign of \( \theta \). When \( \theta \) is zero there is no departure from \( \mathbf{x} \) at all.

Since we are, for the moment, regarding \( \mathbf{x} \) and \( \mathbf{y} \) as fixed vectors, we can temporarily regard \( f(\mathbf{x} + \theta \mathbf{y}) \) as a function of \( \theta \) which tells us how values of \( f(\cdot) \) change as we move away from \( \mathbf{x} \) along a direction parallel to \( \mathbf{y} \). In the context of this view of things (with \( \mathbf{x} \) and \( \mathbf{y} \) held fixed) we might consider ourselves to be dealing with a function whose domain and codomain are each the set of real numbers: To

* In this intuitive discussion no attempt is made to discuss topologies on vector spaces under discussion. Readers interested in more precision might presume that all vector spaces in question are finite dimensional and are endowed with the norm topology; or, in more concrete terms, they might assume that all spaces are of the type \( \mathbb{R}^n \) endowed with the usual notion of distance between two points.
each real number \( \theta \) there is assigned a real number \( f(x + \theta y) \). Hence, there is no conceptual difficulty involved in taking the derivative of this function with respect to the variable \( \theta \). In particular, the number

\[
\frac{d}{d\theta} f(x + \theta y) \bigg|_{\theta=0}
\]

tells us how quickly values of \( f(\cdot) \) change near \( x \) as we move away from \( x \) along a direction parallel to \( y \). Clearly, the actual value obtained from this calculation will depend both on \( x \), the point of interest, and on \( y \), the vector which designates the direction along which we probe.

Now let us take a broader view of things. We shall continue to regard \( x \) as being held fixed, but now let us consider how \( \frac{d}{d\theta} f(x + \theta y) \bigg|_{\theta=0} \) varies as \( y \) changes. To each \( y \) in \( V \) there corresponds a value of \( \frac{d}{d\theta} f(x + \theta y) \bigg|_{\theta=0} \). In other words, there is a function \( F[x] : V \to \mathbb{R} \) which assigns to each \( y \) in \( V \) the corresponding value of \( \frac{d}{d\theta} f(x + \theta y) \bigg|_{\theta=0} \). It must be clearly understood that the symbol \( F[x] \) is intended to represent a function, not a number. The \( x \) in the bracket is intended to remind us that the function in question depends on the \( x \) at which we do our calculations. In summary, then, \( F[x] : V \to \mathbb{R} \) is a function defined by the requirement that, for every \( y \) in \( V \),

\[
F[x](y) = \frac{d}{d\theta} f(x + \theta y) \bigg|_{\theta=0} \tag{1.7}
\]

At this point the stage is set for a surprise which is both pleasant and important. In our deliberations we have allowed the function \( f : V \to \mathbb{R} \) to be nonlinear. Consequently, we might expect the function \( F[x] : V \to \mathbb{R} \) to be nonlinear. Yet, this is not the case. A fundamental fact of vector calculus is this: So long as \( f : V \to \mathbb{R} \) satisfies certain weak smoothness requirements the function \( F[x] : V \to \mathbb{R} \) is a linear transformation. Perhaps an example will lend credence to this statement and help make concrete the ideas under discussion.

**EXAMPLE:** Let \( V \) be a vector space endowed with a scalar product. Furthermore, let \( f : V \to \mathbb{R} \) be defined by

\[
f(x) = e^{a \cdot x} \tag{1.8}
\]

where \( a \) is some fixed vector of \( V \). Clearly, \( f(\cdot) \) is not linear. Now let us see what the function \( F[x] : V \to \mathbb{R} \) is by determining how \( F[x] \) acts upon an arbitrary vector \( y \) in \( V \). We find that
\[ f(\lambda)(\gamma) = \frac{d}{d\lambda} f(\lambda + \theta \gamma) \bigg|_{\theta=0} \]
\[ = \frac{d}{d\theta} e^{a \cdot (\lambda + \theta \gamma)} \bigg|_{\theta=0} \]
\[ = \frac{d}{d\theta} e^{a \cdot \lambda + \theta (a \cdot \gamma)} \bigg|_{\theta=0} \]
\[ = e^{a \cdot \lambda} \frac{d}{d\theta} e^{\theta (a \cdot \gamma)} \bigg|_{\theta=0} \]
\[ = e^{a \cdot \lambda} (a \cdot \gamma) e^{\theta (a \cdot \gamma)} \bigg|_{\theta=0} \]
\[ = e^{a \cdot \lambda} \]

As promised by the theory the function \( F(\lambda)(\cdot) \) is indeed a linear transformation; this may be readily confirmed. The nature of the linear transformation depends on \( \lambda \) through the exponential multiplier, and that dependence is not linear. The linearity is, of course, in the variable \( \gamma \).

Up to this point attention has been restricted to the differential calculus of functions which map a vector space into the real numbers. This choice of focus was made primarily to enable us to get through some difficult ideas without being burdened by the excess baggage of a more general codomain. Nevertheless, the essentials of our discussion carry over to functions of the type \( f: V \to W \), where \( W \) is a vector space.

In fact, let \( F(\lambda): V \to W \) be defined by

\[ F(\lambda)(\gamma) = \frac{d}{d\lambda} f(\lambda + \theta \gamma) \bigg|_{\theta=0} \]  \hspace{1cm} (1.9)

The right-hand side is now the derivative with respect to \( \theta \) of a vector-valued function of \( \theta \) (with \( \lambda \) and \( \gamma \) regarded fixed), but otherwise there is no essential difference between this and the case we have been considering all along. The same "pleasant surprise" carries over: If \( f: V \to W \) satisfies certain weak smoothness requirements then \( F(\lambda): V \to W \) is a linear transformation. Since the set of real numbers is merely an example of a vector space, this last statement is a generalization of our earlier one, and, conversely, our discussion of functions with numerical codomain can now be viewed as a special case of something broader.

The linear transformation \( F(\lambda): V \to W \) is called the derivative at \( \lambda \) of the function \( f: V \to W \). In a certain sense knowledge of the derivative \( F(\lambda) \) is equivalent to knowledge of rapidity of change in
values of \( f(\cdot) \) near \( \gamma \): If we wish to know how quickly values of \( f(\cdot) \) change as we move away from \( \gamma \) in some arbitrary direction, say parallel to a vector \( \gamma \), we need merely compute \( \dot{f}^{[\gamma]}y \) to obtain
\[
\frac{d}{d\theta} f(x + \theta y) \bigg|_{\theta=0}.
\]

ANOTHER EXAMPLE: In Section 1.4.3 we shall compute the derivative of a function which maps a vector space \( V \) into itself. (Of course, such a mapping is merely a special example of a function from one vector space to another.) In order that computation might be facilitated, let us lay some groundwork here. The notation is chosen to be suggestive of that used in Section 1.4.3. Let \( V \) be a vector space endowed with a scalar product, let \( q_r \) and \( q_p \) be fixed vectors of \( V \), and let \( \dot{f} : V + V \) be defined by
\[
\dot{f}(u) \equiv (e^{q_r \cdot u} - e^{q_p \cdot u})(q_p - q_r)
\]
(The independent variable is denoted \( u \) rather than \( \gamma \) to reflect the situation we shall encounter in Section 1.4.3.) Let us determine the derivative \( \dot{f}^{[\gamma]} : V + V \). We are trying to determine a function, which is to say that we wish to determine the action of \( \dot{f}^{[\gamma]} \) on vectors of \( V \). If \( \gamma \) is an element of \( V \), then by definition
\[
\dot{f}^{[\gamma]} \gamma = \frac{d}{d\theta} \dot{f}(u + \theta \gamma) \bigg|_{\theta=0}
\]
\[
= \frac{d}{d\theta} [(e^{q_r \cdot (u+\theta \gamma)} - e^{q_p \cdot (u+\theta \gamma)})(q_p - q_r)] \bigg|_{\theta=0}
\]
After executing the computation in a manner similar to that in the preceding example we may deduce that
\[
\dot{f}^{[\gamma]} \gamma = [e^{q_r \cdot \gamma} - e^{q_p \cdot \gamma}](q_p - q_r)
\]
(1.11)

In particular, let us examine \( \dot{f}^{[0]} \), the derivative of \( \dot{f}(\cdot) \) at \( u = 0 \). By simple substitution in Eq. (1.11) we find that, for all \( \gamma \) in \( V \),
\[
\dot{f}^{[0]} \gamma = (q_r \gamma - q_p \gamma)(q_p - q_r)
\]
\[
= -(q_p - q_r \gamma)(q_p - q_r)
\]
If we let \( g = q_p - q_r \gamma \), then we may write
\[
\dot{f}^{[0]} \gamma = -(g \cdot \gamma)g
\]
(1.12)
That is, \( \dot{f}^{[0]} : V + V \) is that linear transformation which maps each \( \gamma \) in \( V \) into the vector \(- (q \cdot \gamma)g\).
1.2.8 Vector Spaces of Linear Transformations

Having defined what we mean by a linear transformation and having explored the importance of linear transformations in vector calculus, we now turn to consideration of sets of linear transformations and the structure with which those sets are endowed. If $V$ and $W$ are vector spaces, there will, in general, be a wealth of linear transformations which map $V$ into $W$. What we wish to do is make explicit and exploit the internal "organization" possessed by the set of all such linear transformations.

In fact, our objective will be to show that the set of all possible linear transformations from $V$ into $W$, when taken with certain natural rules for addition and multiplication by a real number, constitutes a vector space. Clearly this involves a little "abstraction," but the effort is worth making. Once the set of all linear transformations from $V$ into $W$ is endowed with vector space structure, all theorems which flow from the definition of a vector space become available for our use.

Recall that a vector space consists of essentially three ingredients: a set, an addition rule, and a rule for multiplication by a real number; the two rules are required to conform to certain axioms. The set of interest here is the set of all possible linear transformations from a vector space $V$ into a vector space $W$.

Now let us see how linear transformations might be added to produce another linear transformation. Suppose that $T_1: V \rightarrow W$ and $T_2: V \rightarrow W$ are linear transformations. To define a linear transformation $(T_1 + T_2): V \rightarrow W$ it suffices to specify what $T_1 + T_2$ does to each element of $V$. With this in mind we shall define $T_1 + T_2$ as follows:

For each $x$ in $V$

$$(T_1 + T_2)x = T_1x + T_2x \quad (1.13)$$

Having defined how linear transformations are added, we turn to consideration of how linear transformations might be multiplied by real numbers. If $T: V \rightarrow W$ is a linear transformation and $\alpha$ is a real number, we define the linear transformation $(\alpha T): V \rightarrow W$ by indicating what $\alpha T$ does to each element of $V$:

For each $x$ in $V$

$$(\alpha T)x = \alpha (Tx) \quad (1.14)$$

We have bestowed upon the set of linear transformations from $V$ into $W$ an addition rule and a rule for multiplication by a real number. Have we a vector space? It must be confirmed that our operations satisfy the vector space axioms $V 1 - V 8$. In fact they do. In particular the zero "vector" is the zero transformation $0_{(V,W)}$, which, it will be recalled, maps every vector of $V$ into the zero vector of $W$. The vector space of linear transformations from $V$ into $W$ endowed with these natural operation rules is denoted $L(V,W)$.

Once we get used to the idea of viewing linear transformations from $V$ to $W$ as elements (or "vectors") of the vector space $L(V,W)$ we can, when it becomes desirable to do so, begin to think about linear transformations in the same way that we think about vectors. In particular it becomes meaningful to speak of the linear dependence or independence of sets of linear transformations from $V$ to $W$. All we need to do is recall our general definitions of these ideas and
particularize them to the vector space \( L(V,W) \).

Recognizing that the zero vector of \( L(V,W) \) is the zero transformation \( 0_{[V,W]} \), we say that a set of linear transformations from \( V \) to \( W \), say \( \{T_1,T_2,\ldots,T_k\} \), is linearly dependent if there exists a set of real numbers \( \{a_1,a_2,\ldots,a_k\} \), not all zero, such that

\[
a_1T_1 + a_2T_2 + \ldots + a_kT_k = 0_{[V,W]} \tag{1.15}
\]

Otherwise, we say that the set \( \{T_1,T_2,\ldots,T_k\} \) is linearly independent. But what does Eq. (1.15) mean? If the left-hand side is to equal the zero transformation, it is necessary and sufficient that the left-hand side, viewed as a linear transformation, map every vector of \( V \) into the zero vector of \( W \). Thus, we can say that \( \{T_1,T_2,\ldots,T_k\} \) is linearly dependent if and only if there exists a set of numbers, \( \{a_1,a_2,\ldots,a_k\} \), not all zero, such that for every \( x \) in \( V \)

\[
[a_1T_1 + a_2T_2 + \ldots + a_kT_k]x = 0_w
\]

or, equivalently,

\[
a_1(T_1x) + a_2(T_2x) + \ldots + a_k(T_kx) = 0_w \tag{1.16}
\]

where \( 0_w \) denotes the zero vector of \( W \).

**EXAMPLE:** Let us consider three linear transformations \( T_1, T_2, \) and \( T_3 \) from \( IR^2 \) into itself. That is, \( T_1, T_2, \) and \( T_3 \) are elements of \( L(IR^2,IR^2) \). (In our discussion we have considered the general case of linear transformations from a vector space \( V \) into a possibly different vector space \( W \). If, as in this example, \( V \) and \( W \) are identical, we are merely dealing with a special case of the more general situation.) \( T_1, T_2, \) and \( T_3 \) are defined by indicating what each does to an arbitrary element \( [x_1,x_2] \) of \( IR^2 \):

\[
T_1[x_1,x_2] = [2x_1,2x_2] \\
T_2[x_1,x_2] = [x_2,x_1] \\
T_3[x_1,x_2] = [x_1 + x_2,x_1 + x_2]
\]

\( \{T_1, T_2, T_3\} \) is a linearly dependent set in \( L(IR^2,IR^2) \) since

\[
(4)(T_1[x_1,x_2]) + (1)(T_2[x_1,x_2]) + (-1)(T_3[x_1,x_2]) = 4[2x_1,2x_2] + (1)[x_2,x_1] + (-1)[x_1 + x_2,x_1 + x_2] = [0,0]
\]

Having discussed linear independence of sets in \( L(V,W) \), we are in a position to consider a question which will have some importance to us. Suppose that a linear transformation \( T \) in \( L(V,W) \) is representable as a linear combination of a set of linear transformations \( \{T_1,T_2,\ldots,T_k\} \) in \( L(V,W) \). That is, suppose that there exists a sequence of numbers \( \{a_1,a_2,\ldots,a_k\} \) such that

\[
T = a_1T_1 + a_2T_2 + \ldots + a_kT_k \tag{1.17}
\]

Can there exist a different sequence \( \{a'_1,a'_2,\ldots,a'_k\} \) such that
\[ T = a_1T_1 + a_2T_2 + \ldots + a_kT_k \]  

or is the first sequence unique? The answer resides in Theorem 1.2.a, a theorem which applies just as well to \( L(V,W) \) as it does to any vector space. Thus, the "solution" \( \{a_1, a_2, \ldots, a_k\} \) to Eq. (1.17) is unique if and only if the set \( \{T_1, T_2, \ldots, T_k\} \) is linearly independent. This application of Theorem 1.2.a will play a significant role in Section 1.4 when we discuss mathematical techniques for the determination of kinetic rate constants in the context of intricate chemistry.

It is sometimes useful to think about linear subspaces of the vector space \( L(V,W) \). Once again we need merely particularize our general definition of linear subspace to \( L(V,W) \). Let us see how this works in an example:

**EXAMPLE:** Let \( V \) and \( W \) be vector spaces. Moreover, let \( U \) be a linear subspace of \( V \). It may happen that a linear transformation \( T: V \rightarrow W \) maps every vector of \( U \) into the zero vector of \( W, 0_w \). Let us denote by the symbol \( \Gamma_U \) the set of all elements of \( L(V,W) \) which have this property. How do we test to see if \( \Gamma_U \) is a linear subspace of \( L(V,W) \)? Recalling the definition of linear subspace, we must see if both properties \( LSI \) and \( LS2 \) are possessed by \( \Gamma_U \). Let us begin with \( LSI \). If \( T_1 \) and \( T_2 \) are elements of \( \Gamma_U \), we must see if \( T_1 + T_2 \) is in \( \Gamma_U \). Suppose that \( x \) is in \( U \). Then

\[ (T_1 + T_2)x = T_1x + T_2x = 0_w + 0_w = 0_w. \]

Hence, \( T_1 + T_2 \) is a member of \( \Gamma_U \) so that the property \( LSI \) is possessed by \( \Gamma_U \). Now suppose that \( T \) is in \( \Gamma_U \), and let \( \alpha \) be a real number. To see if \( \Gamma_U \) possesses the property \( LS2 \) we must see if \( \alpha T \) is in \( \Gamma_U \). If \( x \) is in \( U \), then

\[ (\alpha T)x = \alpha (Tx) = \alpha 0_w = 0_w. \]

Hence, \( \Gamma_U \) possesses the property \( LS2 \). Therefore, \( \Gamma_U \) is a linear subspace of \( L(V,W) \).

We have discussed the vector space \( L(V,W) \) and have shown how we might speak of linear dependence or independence of sets of linear transformations and how we might consider sets of linear transformations as linear subspaces of \( L(V,W) \). Having become accustomed to these ideas, we should have little difficulty with the idea of the dimension of \( L(V,W) \) or of the dimension of a linear subspace in \( L(V,W) \). Once again, we need merely apply our usual definition in the context of the particular vector space \( L(V,W) \). Thus, a linear subspace of \( L(V,W) \) has dimension \( p \) if we can find in that subspace a linearly independent set of \( p \) linear transformations from \( V \) into \( W \) but no such set containing \( p + 1 \) elements. It may be shown that if \( V \) and \( W \) have dimensions \( n \) and \( m \), respectively, then the dimension of \( L(V,W) \) is \( mn \).

1.2.9 Dyads of Vectors

We have discussed linear transformations in general. Here we shall focus attention upon linear transformations of a very special type, those which are "constructed" from vectors in a particular way. Throughout this section we shall presume that \( V \) is a vector space endowed with a scalar product. Now let \( q \) be a fixed vector of \( V \). By \( D(q): V \rightarrow V \) we mean a linear transformation constructed from \( q \), and we define \( D(q) \) by indicating how it operates on each \( x \) in \( V \).
For each \( x \) in \( V \)

\[
D(g)x = (g \cdot x)g
\]

(1.19)

We call \( D(g) \) the dyad* of \( g \). Note that \( D(g) \) maps each \( x \) in \( V \)
into a scalar multiple of the vector \( g \). Clearly, \( D(g) \) is an element of \( L(V,V) \).

EXAMPLE: In the vector space \( IR^2 \), \( D([2,1]): IR^2 \rightarrow IR^2 \) is the
linear transformation which maps \([x_1,x_2]\) into \((2x_1 + x_2)[2,1]\), since

\[
D([2,1])[x_1,x_2] = ([2,1] \cdot [x_1,x_2])[2,1]
\]

\[
= (2x_1 + x_2)[2,1]
\]

The expression on the right-hand side of Eq. (1.19) may seem
familiar. This is because we encountered an identical expression (apart
from sign) in the computation of \( \tilde{F}[g] \) in the second example of Section
1.2.7. Hence, we can now write \( \tilde{F}[\tilde{D}] = -D(g) \). Computations of a
similar nature will assume some importance for us in Section 1.4.3, and it
is for this reason that we are devoting special attention to dyads of
vectors.

There are some questions which we shall need to consider. Suppose
that \( \{g_1,g_2,...,g_k\} \) is a set of vectors in \( V \). For each of these
vectors we can construct the corresponding dyad to form a set
\( \{D(g_1),D(g_2),...,D(g_k)\} \) in the vector space \( L(V,V) \). Let us consider
two related questions. If \( \{g_1,g_2,...,g_k\} \) is a linearly independent
set, does this imply that \( \{D(g_1),D(g_2),...,D(g_k)\} \) is also a linearly
independent set? If \( \{g_1,g_2,...,g_k\} \) is linearly dependent, does this
imply that \( \{D(g_1),D(g_2),...,D(g_k)\} \) is also linearly dependent?

Although these questions are not excessively difficult, they are not
trivial either, and a decent treatment of each would take us beyond the
scope of this introductory chapter.** Nevertheless the answers will be
important to us. If \( \{g_1,g_2,...,g_k\} \) is a linearly independent set in
\( V \), then \( \{D(g_1),D(g_2),...,D(g_k)\} \) must be a linearly independent set in
\( L(V,V) \). On the other hand, even if \( \{g_1,g_2,...,g_k\} \) is a linearly
dependent set in \( V \), then \( \{D(g_1),D(g_2),...,D(g_k)\} \) may be a linearly
dependent set in \( L(V,V) \).

In fact, it happens very often that \( \{g_1,g_2,...,g_k\} \) is a linearly
dependent set while \( \{D(g_1),D(g_2),...,D(g_k)\} \) is a linearly independent
set.

---

* \( D(g) \) is usually denoted \( g \otimes g \), where \( \otimes \) is a symbol used to
denote a tensor product. We have chosen to use the symbol \( D(g) \) to
represent the dyad of \( g \) in order that its character as a linear trans
formation might be kept apparent; introduction of the tensor product
would be superfluous to this chapter.

** For a study of the relationship between the algebraic structures
of sets \( \{g_1,g_2,...,g_k\} \) and \( \{D(g_1),D(g_2),...,D(g_k)\} \) the reader might
wish to see Feinberg (1972, "On Chemical Kinetics...," Section 4) and
Feinberg, (1977, "Combinatorial Aspects..."),
This observation will play a crucial role in our discussion of how contributions of several coupled chemical reactions to overall chemical dynamics might be disentangled to deduce kinetics of individual reactions. In terms more suggestive than precise we might try to make the underscored statement plausible by considering the nature of the different spaces in which the sets \{g_1, g_2, ..., g_k\} and \{D(g_1), D(g_2), ..., D(g_k)\} reside.

Of course, \{g_1, g_2, ..., g_k\} is a set in the vector space \(V\). However, we can make a stronger statement: That set clearly resides in its own span, \(L[g_1, g_2, ..., g_k]\), which is a linear subspace of \(V\). (Recall Section 1.2.3) Now suppose that the dimension of \(L[g_1, g_2, ..., g_k]\) is \(s\). Then if \(k > s\), the set \{g_1, g_2, ..., g_k\} must certainly be linearly dependent, since, by definition of dimension, a linear subspace of dimension \(s\) cannot accommodate linearly independent sets with more than \(s\) elements.

On the other hand, the set \{D(g_1), D(g_2), ..., D(g_k)\} resides in the vector space \(L(V, V)\). Although proof is beyond the scope of this discussion, it can be shown that, in fact, this set lies in a linear subspace* of \(L(V, V)\) with dimension \(4s(s + 1)\), where \(s\) is the dimension of \(L[g_1, g_2, ..., g_k]\). Thus, even if \(k\) exceeds \(s\) (whereupon the set \{g_1, g_2, ..., g_k\} is linearly dependent), it may still be the case that \(k\) does not exceed \(4s(s + 1)\). In such a case linear independence of the \(k\) element set \{D(g_1), D(g_2), ..., D(g_k)\} is not precluded merely on grounds of "smallness" of the linear subspace in which it resides. Indeed one can construct linearly independent sets of this type for which \(k = 4s(s + 1)\).

In short, the set \{D(g_1), D(g_2), ..., D(g_k)\} resides in a more "spacious" environment than does the set \{g_1, g_2, ..., g_k\} - a spaciousness which admits linear independence of sets more readily.

In a private communication (1972), Noll has suggested an attractive computational criterion for determining whether or not a set \{D(g_1), D(g_2), ..., D(g_k)\} is linearly independent. Let \([(g_i \cdot g_j)^2]\) denote the \(k \times k\) matrix for which the entry in the \(i^{th}\) row and \(j^{th}\) column is the number \((g_i \cdot g_j)^2\). If \(\det \[(g_i \cdot g_j)^2]\) denotes the determinant of that matrix, then, according to Noll,**

\[
\det \[(g_i \cdot g_j)^2\] \geq 0
\]

(1.20)

with equality holding if and only if \{D(g_1), D(g_2), ..., D(g_k)\} is a linearly dependent set of elements in \(L(V, V)\).

---

* The linear subspace in question is the set of all linear transformations \(T: V \rightarrow V\) which have the following two properties: (1) \(Tx = 0\) for all \(x\) in \(L^2(g_1, g_2, ..., g_k)\), and (2) \(x \cdot Ty = y \cdot Tx\) for all \(x\) and \(y\) in \(V\). Linear transformations \(T: V \rightarrow V\) which possess property (2) are said to be symmetric with respect to the scalar product in \(V\).

** Noll's observation follows from application of the Gram determinant theorem [Greub (1967, p. 192)] after introduction of an appropriate scalar product in the vector space \(L(V, V)\).
EXAMPLE: Consider the vector space \( \mathbb{R}^2 \) endowed with the usual scalar product, and let \( \mathbf{g}_1 = [1, 0] \), \( \mathbf{g}_2 = [0, 1] \), and \( \mathbf{g}_3 = [1, 1] \). Then

\[
\det [(\mathbf{g}_1 \cdot \mathbf{g}_3)^2] = \det \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \\ 1 & 1 & 4 \end{bmatrix}
= 2
\]

Hence, \( \{D(\mathbf{g}_1), D(\mathbf{g}_2), D(\mathbf{g}_3)\} \) is a linearly independent set in \( L(\mathbb{R}^2, \mathbb{R}^2) \). Note that \( \{\mathbf{g}_1, \mathbf{g}_2, \mathbf{g}_3\} \) is a linearly dependent set in \( \mathbb{R}^2 \).

1.3 MECHANISMS, KINETICS, AND EQUILIBRIA

Every physical theory rests upon certain ideas which are primitive to that theory in the sense that they are taken as understood at the outset. Chemical reactor theory, at least in its present state, generally takes among its primitive ideas for a problem at hand these basic notions: a set of molecular species and their molar concentrations, a set of one or more chemical reactions among those species, and a set of scalar-valued rate functions, one for each reaction, which relate rates of reactions to conditions under which those reactions occur. We call the set of chemical reactions among the species of a mixture the mechanism for that mixture, and we call the set of rate functions the kinetics for that mechanism. Kinetics and mechanism taken together serve for construction of a species formation rate function or overall rate function, which, in closed homogeneous reactors, relates instantaneous rates of change of molar concentrations to the mixture state. In this way the overall rate function gives rise to dynamic equations which govern the chemical evolution of the mixture at hand.

In this section we shall begin with a discussion of mechanisms with an eye toward those aspects of mechanism structure and classification which will play important roles in subsequent sections. We shall then turn to a somewhat general discussion of kinetics for mechanisms in the context of isothermal, constant volume, homogeneous mixtures, and we shall describe in vectorial terms how the overall rate function and dynamical equations are constructed. In this general setting we shall introduce the important idea of detailed balancing at equilibria. Subsequently, we shall introduce the idea of complex balancing, a useful tool first exploited by Horn and Jackson (1972), and we shall give an example of how that tool might be used, in the context of arbitrary kinetics, to provide a striking characterization of equilibria. Finally, we shall turn to the critical case of mass action kinetics to set the stage for the balance of this chapter.

1.3.1 Aspects of Mechanism Structure

Our efforts in subsequent sections will focus upon questions such as these: What is the relationship between mechanism structure and the extent to which kinetic rate constants can be inferred from certain classes of dynamic experiments? What is the relationship between reactor stability and the structure of the underlying mechanism? In order that these questions might be addressed in a reasonably precise
fashion we must first focus upon certain important aspects of mechanism structure and develop a vocabulary with which these might be discussed.

Let us begin by considering a mixture of the species \( \{A_1, A_2, \ldots, A_7\} \) endowed with the following mechanism:

\[
\begin{align*}
2A_1 & \iff A_2 + A_3 \\
A_2 & \iff A_4 \\
A_1 + A_3 & \iff A_5 + A_6 \\
A_2 + A_3 & \iff A_7 \\
A_7 & \iff 2A_1(1.21a)
\end{align*}
\]

We shall call the entities which appear before and after the arrows of a mechanism the complexes for that mechanism. [Here we follow terminology of Horn and Jackson (1972).] Thus, in mechanism (1.21a) the complexes are \( 2A_1, A_2 + A_3, A_2, A_4, A_1 + A_3, A_5 + A_6, \) and \( A_7. \) Furthermore, we shall reserve the symbol \( n \) for the number of complexes in a mechanism under discussion. Thus, mechanism (1.21a) has seven complexes. (That the mechanism has seven complexes and involves seven species is, of course, coincidental.) We shall reserve the symbol \( M \) for the number of species.

Let us consider another example. Mechanism (1.22a) also involves seven species \( (M = 7) \), but there are only six complexes \( (n = 6) \). These are \( 2A_2, A_1, A_3, A_3 + A_4, A_5, \) and \( A_6 + A_7. \)

\[
\begin{align*}
2A_2 & \iff A_1 \\
2A_2 & \iff A_3 \\
A_3 + A_4 & \iff A_5 \\
A_3 + A_4 & \iff A_6 + A_7 \\
A_6 + A_7 & \iff A_5(1.22a)
\end{align*}
\]

It will prove useful in consideration of mechanism structure to focus upon certain "coarse-grained" features of the manner in which complexes are "linked" to each other by reaction arrows. Let us study mechanisms

* Mechanism (1.21a) is reversible in the sense that the occurrence of each reaction is accompanied by the occurrence of its "antireaction." For example, both \( 2A_1 + A_2 + A_3 \) and \( A_2 + A_3 \iff 2A_1 \) are reactions of the mechanism. For some purposes it is convenient to ignore reactions which proceed to such a small extent that their occurrences are inconsequential to the analysis at hand. Thus, in some applications, we might choose to "approximate" the mechanism governing a reactor by another mechanism obtained from the first by deleting one or more arrows. The deletion of arrows in this manner might yield an approximate mechanism which is not reversible despite the reversibility of the "true" mechanism. In Section 1.4 we shall be concerned exclusively with reversible mechanisms; in Section 1.5 we shall not. Here, then, for the sake of overview we shall discuss mechanisms which might or might not be reversible.
(1.21a) and (1.22b) with an eye toward investigation of linkage relations among complexes. In order that these might be seen with greater clarity we rewrite mechanisms (1.21a) and (1.22a) in such a way that each complex appears only once:

\[
\begin{align*}
A_2 & \xrightarrow[]{} A_4 \\
A_1 + A_3 & \xrightarrow[]{} A_5 + A_6 \\
2A_1 & \rightarrow A_2 + A_3 \\
& \xrightarrow[]{} A_7
\end{align*}
\]

\[
\begin{align*}
A_1 & \xleftarrow[]{} 2A_2 \rightarrow A_3 \\
A_3 + A_4 & \rightarrow A_5 \\
& \xrightarrow[]{} A_6 + A_7
\end{align*}
\]

(1.21b) (1.22b)

A glance at reaction diagram (1.22b) suggests that the six complexes of the mechanism may be partitioned into two linkage classes: \{A_2, A_4\} and \{A_3 + A_4, A_5, A_6 + A_7\}. Arrow directions aside, every complex in each linkage class is "linked," albeit indirectly, to every other member of that class, but no member of the class is "linked," however indirectly, to any complex outside that class. Similarly, the complexes shown in mechanism (1.21a) may be partitioned into three linkage classes: \{A_2, A_4\}, \{A_1 + A_3, A_5 + A_6\}, and \{2A_1, A_7, A_2 + A_3\}. Partition of the set of complexes of a mechanism into linkage classes is accomplished easily after a glance at a reaction diagram constructed such that each complex appears only once. We shall denote by the symbol \(\ell\) the number of linkage classes in a mechanism. Thus, for mechanism (1.21b) \(\ell = 3\), while for mechanism (1.22b) \(\ell = 2\).

We shall next turn to consideration of certain algebraic aspects of mechanism structure. In order that this might be done in a precise manner we shall introduce an appropriate mathematical setting for discussion of an \(M\) species mixture endowed with a prescribed mechanism. We shall find that the vector space \(\mathbb{R}^M\) provides a reasonably comfortable medium within which to work; henceforth, we shall designate \(\mathbb{R}^M\) by the symbol \(V\), and we shall call it species space. We remind the reader of the natural basis for \(V\): \(e_1 = [1,0,\ldots,0]\), \(e_2 = [0,1,0,\ldots,0]\), \ldots, \(e_M = [0,0,\ldots,0,1]\).

It will prove useful to identify the complexes of a mechanism with vectors of \(V\). This is best explained by example. If the mechanism in question is that shown in mechanism (1.21b), we take species space, \(V\), to be \(\mathbb{R}^7\) (since \(M = 7\)); the natural basis is \([e_1,e_2,\ldots,e_7]\). We choose to represent the complex \(2A_1\) by the vector \(2e_1\), \(A_2 + A_3\) by \(e_2 + e_3\), \(A_2\) by \(e_2\), \(A_4\) by \(e_4\), \(A_1 + A_3\) by \(e_1 + e_3\), etc. In this way the \(n\) complexes of a mechanism can be identified naturally with
members of a set of vectors \(\{y_1, y_2, \ldots, y_n\}\) in \(V\).*

We shall also want to represent reactions in a mechanism by vectors of \(V\). If, in the mechanism at hand, the \(i\)th complex reacts directly to the \(j\)th complex, then we represent that reaction by the vector \(y_j - y_i\).

Hence, for mechanism (1.21b), the reaction \(2A_1 + A_2 + A_3\) is represented in \(V\) by \(e_2 + e_3 - 2e_1\), \(A_2 + A_3 + 2A_1\) by \(2e_1 - (e_2 + e_3)\), \(A_2 + A_3\) by \(e_4 - e_2\), etc. If, in a mechanism, the \(i\)th complex reacts directly to the \(j\)th complex, we write for the purpose of notation \(i \pm j\).

Now that we have described how reactions in a mechanism are to be represented as vectors in \(V\) we are in a position to discuss the algebraic structure of the set of vectors so formed. In particular, we can ask the following question: For a mechanism under study, what is the maximum number of elements that can reside in a linearly independent set comprised of reaction vectors for the mechanism? We denote this maximum number by the symbol \(s\).

Perhaps an example will help make this clear. For mechanism (1.23) we take \(V = IR^3\), since there are three species.

\[
\begin{align*}
2A_1 & \rightarrow A_2 \\
\text{3} & \rightarrow A_3
\end{align*}
\] (1.23)

The reaction vectors are \(\{e_2 - 2e_1, e_2 - e_3, e_3 - e_2, 2e_1 - e_3\}\). It is easily verified that the two-element set \(\{e_2 - 2e_1, e_2 - e_3\}\) is linearly independent, but any set comprised of three or four reaction vectors is linearly dependent. Hence, for mechanism (1.23), \(s = 2\).

For mechanisms (1.21b) and (1.22b), \(s = 4\). In dealing with complicated mechanisms like these, determination of \(s\) is not always easy. However, readers interested in formal procedure might take note of the following idea. Reaction vectors are elements of \(IR^M\); that is, they are "M-tuples," where \(M\) is the number of species. Thus, the reaction vectors might be written as rows of a matrix with \(M\) columns; the number of rows is the number of reactions in the mechanism. The number \(s\) is then the rank of that matrix, which is computable using formal procedures discussed in books by Amundson (1966) and Hadley (1961).

At the risk of getting ahead of ourselves somewhat we can discuss the significance of the number \(s\) once we have introduced the stoichiometric subspace for a mechanism. We have shown how the reactions in a mechanism can be represented as a set of vectors in \(V\), the species space appropriate to the mixture under study. By the stoichiometric subspace for a mechanism we mean the span of the set of reaction vectors for that mechanism. (Recall Section 1.2.3.) The stoichiometric subspace is, of course, a linear subspace of \(V\), and we denote it by the symbol \(S\).

Hence, for a particular mechanism, \(S\) is the set of all vectors in \(V\) representable in the form

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* It should be understood that the numbering of complexes is purely arbitrary; one merely associates a number with each complex for the purpose of designation. The same is true of species in the designation of the species set \(\{A_1, A_2, \ldots, A_n\}\).
\[
\sum_{i,j=1}^{n} a_{ij} (y_j - y_i)
\]

where \(y_1, y_2, \ldots, y_n\) are vectors representing the complexes of the mechanism, where the \(a_{ij}\) are arbitrary real numbers, and where the summation is taken over all \(i,j\) permutations such that \(i + j\). In more symbolic terms we might write

\[
s = \sum_{i+j} [y_j - y_i]
\]

(1.24)

The right-hand side of Eq. (1.24) is intended to suggest that, for the mechanism at hand, we first construct the set of all reaction vectors (i.e., the set of all vectors of the form \(y_j - y_i\), where \(i + j\)) and then take the span of the resulting set.

It follows from the discussion in Section 1.2.3 and the manner in which the number \(s\) has been defined for a mechanism that \(s\) is the dimension of the stoichiometric subspace for that mechanism. Henceforth, we shall interpret the number \(s\) in this way.

At this point the reader might have difficulty imagining why the notion of stoichiometric subspace is singled out for special attention. In the next section the importance of the stoichiometric subspace will come into sharper focus when we show, among other things, that for a closed homogeneous reactor driven by some chemical mechanism composition trajectories represented in species space \(V\) are constrained to reside in parallels of the stoichiometric subspace for that mechanism.

In the meantime readers inclined toward a geometric view of things might wish to glance ahead at Figures 1.3 and 1.4 of Section 1.3.2. In Figure 1.3 the stoichiometric subspace for the simple mechanism \(2A_1 + A_2\) is shown as it appears in species space \(\mathbb{R}^2\). \(S\) contains the two reaction vectors, \(e_2 - 2e_1\) and \(2e_1 - e_2\). Since \(s = 1\), the stoichiometric subspace is of dimension 1 and assumes the shape of a line through the origin. In Figure 1.4 the stoichiometric subspace for mechanism (1.23) appears as a plane \((s = 2)\) through the origin in species space \(\mathbb{R}^3\) and contains the four reaction vectors \(e_3 - e_2\), \(e_2 - e_3\), \(e_2 - 2e_1\), and \(2e_1 - e_3\).

Thus far we have characterized a mechanism by the number of its complexes \(n\), by the number of its linkage classes \(l\), and by the dimension of its stoichiometric subspace \(s\). Now we shall define the deficiency of a mechanism, \(\delta\), by

\[
\delta = n - l - s
\]

(1.25)

Clearly, \(\delta\) is an integer; what is less clear is that for all mechanisms \(\delta\) is nonnegative [Feinberg, (1972, "Complex Balancing...")].

Mechanism (1.21b) is of deficiency zero since \(n = 7, l = 3,\) and \(s = 4\).
Mechanism (1.22b) is of deficiency zero since \(n = 6, l = 2,\) and \(s = 4\).
Mechanism (1.23) is of deficiency zero since \(n = 3, l = 1,\) and \(s = 2\).
The extensively studied mechanism (1.26) is also of deficiency zero since \(n = 3, l = 1,\) and \(s = 2\).
In fact, mechanisms with deficiencies exceeding zero are remarkably uncommon as has been demonstrated by F. Horn in a study of the "density" of zero deficiency mechanisms within the totality of all mechanisms of a large and common class.* The reader might wish to verify that mechanisms are quite often of deficiency zero by computing deficiencies of several mechanisms shown in chemistry books. That mechanisms of positive deficiency are not precluded on mathematical grounds is demonstrated by the examples shown below:

\[
2A_1 \rightarrow 2A_2
\]

\[
A_3 \rightarrow A_2 \rightarrow A_1 + A_2
\]

\[
2A_1 \rightarrow A_2 \rightarrow 2A_3
\]

Each of these mechanisms is of deficiency 1. For mechanism (1.27), \( n = 3, \ t = 1, \) and \( s = 1. \) For mechanism (1.28), \( n = 5, \ t = 2, \) and \( s = 2. \)

Mechanism deficiency will play an important role in three sections of this chapter which bear upon very different subjects: one having to do with determination of mass action rate constants in the context of complex chemistry, one having to do with the nature of equilibria for arbitrary kinetics, and one having to do with stability of open isothermal reactors endowed with intricate mechanisms. As a foretaste of those sections we provide, in terms more suggestive than precise, a sketch of the manner in which mechanism deficiency has worked its way through recent literature.

The first suggestion that mechanism deficiency might have some importance seems to have come in Krambeck's study (1970) of rate constant determination for mechanisms with a single linkage class and with every complex reacting directly to every other complex; in that context the condition \( n - 1 - s = 0 \) was shown to have a critical bearing upon whether the complete set of rate constants could be determined uniquely from isothermal experiments. In an entirely unrelated study based upon his work with Jackson (1972), Horn (1972) derived a sufficient condition on "pseudomechanisms" for open isothermal reactors with complex chemistry to ensure unique stable steady states, and Feinberg (1972, "Complex Balancing...") showed that Horn's stability condition could be recast** in a simpler form \( n - t - s = 0 \) which

---

* It should be mentioned that Horn's study, as yet unpublished, embraces "pseudomechanisms" of the type discussed in Section 1.5.1.

** For a brief informal description of the relationship between Horn's original condition and its reformulation, the reader might wish to see the discussion by Horn (1971).
reduces to Krambeck's condition in the case of a single linkage class. This is most surprising in view of the fact that studies on rate constant determination and on stability would seem to have little to do with one another. Subsequently, separate theorems of Horn (1972) and of Feinberg (1972, "Complex Balancing...") led to a theorem regarding the nature of equilibria with arbitrary kinetics for mechanisms of deficiency zero. Further delineating the role of mechanism deficiency in the problem of rate constant determination, Feinberg (1977, "Mechanism Deficiency...") showed that the large class of zero deficiency mechanisms resides within the still larger class of mechanisms for which complete sets of rate constants could be determined from composition trajectories in the vicinity of a single equilibrium. All these matters will be taken up in greater detail. Not discussed here are Horn's two articles (1973) which draw a connection between a mechanism's deficiency and graphical representations of its complexes.

Before closing our discussion of mechanism structure and classification, we shall need to introduce the idea of weak reversibility. We shall consider mechanisms (1.29) and (1.30), written such that each complex appears no more than once:

\[
\begin{align*}
A_1 & \quad A_3 \quad A_2 \\
A_2 \quad A_3 & \quad \Rightarrow \\
2A_1 & \quad \Rightarrow \\
A_2 \quad A_3 & \quad \Rightarrow \\
A_4 & \\
A_5 & \\
\end{align*}
\]

As mentioned earlier, a reversible mechanism is one in which each reaction is accompanied by its "antireaction." Neither of these mechanisms is reversible in that sense; although the reaction \( A_1 + A_2 \) is an element of mechanism (1.29), the reaction \( A_2 + A_1 \) is not. Yet both mechanisms are endowed with a reversibility of another kind: A mechanism will be deemed weakly reversible if whenever there is a directed arrow path from one complex to another, there is also a directed arrow path from the second complex back to the first. For example, in mechanism (1.30) there is a directed arrow path leading from the complex \( A_5 \) to the complex \( A_2 + A_3 \), and there is also a directed arrow path leading from complex \( A_2 + A_3 \) back to \( A_5 \) (via complex \( A_4 \)). The reader can check all other directed arrow paths in mechanism (1.30) to confirm its weak reversibility. Mechanism (1.22b) is not weakly reversible. Although there is a directed path from \( 2A_2 \) to \( A_3 \), there is no directed path from \( A_3 \) to \( 2A_2 \); although there are two directed paths from \( A_3 + A_4 \) to \( A_5 \), there is none from \( A_5 \) to \( A_3 + A_4 \). Clearly, reversibility is a special case of weak reversibility.

The ideas presented in this section are also discussed in an informal manner in Feinberg and Horn (1974) and more formally in Horn (1972) and Feinberg (1972, "Complex Balancing...").
1.3.2 Kinetics for Mechanisms, Stoichiometric Compatibility

Unless stated otherwise it will be understood that in this and subsequent sections attention is focused upon a closed spatially homogeneous ("well mixed") reactor, the contents of which are presumed to be maintained for all time at fixed volume and fixed temperature. We presume that the mixture contained within the reactor is composed of \( M \) molecular species and that those species undergo chemical reaction in accordance with the mechanism pertinent to the mixture. Hence, the molar concentrations of the species are permitted temporal variations by virtue of chemical changes.

We can draw upon species space, \( V \), of the last subsection to represent vectorially the chemical state of the mixture. If \( c_L(t) \) is the molar concentration of the \( L^{th} \) species at time \( t \), then the vector \( \mathbf{c}(t) \) in \( V \), defined by

\[
\mathbf{c}(t) = c_1(t)e_1 + c_2(t)e_2 + \ldots + c_M(t)e_M
\]

encodes the chemical state of the mixture at time \( t \). Because molar concentrations are deemed nonnegative, it is clear that at each instant \( \mathbf{c}(t) \) is a vector of \( V \) whose components (relative to the basis \( \{e_1, \ldots, e_M\} \) are nonnegative. We denote by \( V^- \) the set of all vectors of \( V \) which have no negative components. Similarly, we denote by \( V^+ \) the set of all vectors of \( V \) which have exclusively positive components.

If \( \dot{c}_L(t) \) is the time derivative at time \( t \) of the molar concentration of the \( L^{th} \) species, then the vector \( \dot{\mathbf{c}}(t) \) of \( V \), defined by

\[
\dot{\mathbf{c}}(t) = \dot{c}_1(t)e_1 + \dot{c}_2(t)e_2 + \ldots + \dot{c}_M(t)e_M
\]

encodes vectorially the instantaneous rate at which the mixture composition changes. Clearly, the vector \( \dot{\mathbf{c}}(t) \) is not constrained to lie in \( V^- \) since the molar concentrations of certain species might instantaneously decrease with time.

Of course, chemical change in a mixture comes about only by virtue of the occurrence of reactions contained in the mechanism pertinent to that mixture. Stated in terms more suggestive than precise, a fundamental assumption of reactor theory is that the rate of occurrence of each chemical reaction is dependent on the state of the mixture. If, for the reactor under discussion here, we suppress dependence of reaction rates upon parameters which are presumed time-invariant (e.g., temperature), then it is generally taken to be the case that individual reaction rates depend only on mixture composition.

With this in mind, we view a mechanism as a skeleton upon which a kinetics is built. By a kinetics we mean an assignment to each reaction in the mechanism of a scalar-valued rate function with domain \( V^- \); the rate functions are required to take nonnegative values on \( V^- \) and positive.*

* For example, consider the simple two-reaction mechanism for a mixture of species \( A_1, A_2, \) and \( A_3 \):

\[
A_1 + A_2 \rightarrow A_3
\]

For a mixture of species \( A_1, A_2, \) and \( A_3 \) such that \( c_1, c_2, \) and \( c_3 \) are all positive we require that both the reactions \( A_1 + A_2 \rightarrow A_3 \) and \( A_3 + A_1 + A_2 \) have positive rates.
values on $V^+$. A rate function for a particular reaction in a mechanism assigns to each $c$ in $V^+$ (that is, to each mixture composition) a nonnegative number called the rate* of that reaction.

For the homogeneous isothermal closed reactor upon which we have focused attention it is generally presumed that $\dot{c}$ at any instant is determined completely by $c$. That is, it is generally supposed that there exists a function $f(\cdot)$ such that

$$\dot{c} = f(c)$$

(1.31)

and that this differential equation suffices to determine chemical dynamics once an initial condition is specified.

The function $f(\cdot)$, called here the overall rate function, is not arbitrary; rather, it is constructed from knowledge of mechanism and its kinetics in accordance with a formalism which is perhaps best explained by example. Consider the following mechanism with rate functions assigned as shown.

$$\begin{array}{c}
\alpha(\cdot) \\
\beta(\cdot) \\
\gamma(\cdot) \\
\delta(\cdot)
\end{array}
\begin{array}{c}
2A_1 \\
A_3 + A_4 \\
A_2
\end{array}$$

(1.32)

Then the overall rate function $f(\cdot)$ is taken as

$$f(c) = \alpha(c)[2c_1 - (c_3 + c_4)] + \beta(c)[c_2 - 2c_1] + \gamma(c)[c_2 - (c_3 + c_4)] + \delta(c)[c_3 + c_4 - c_2]$$

(1.33)

We form the overall rate function by taking a linear combination of all the reaction vectors for the mechanism, the scalar multipliers being the corresponding individual rate functions. In component form the dynamic equations (1.31) and (1.33) reduce to

$$\begin{align*}
\dot{c}_1 &= 2\alpha(c) - 2\beta(c) \\
\dot{c}_2 &= \beta(c) + \gamma(c) - \delta(c) \\
\dot{c}_3 &= \dot{c}_4 = \delta(c) - \alpha(c) - \gamma(c)
\end{align*}$$

(1.34)

The formalism for construction of $f(\cdot)$ embodies the idea that chemical changes come about by virtue of the occurrence of chemical reactions and that the contributions of the several reactions which contribute to the change in concentration of a species are additive.

More generally, if $\{y_1, y_2, \ldots, y_n\}$ is the set of vectors representing the complexes in a mechanism and $f_{ij}(\cdot): V^+ \to R^+$ is the rate function* for the reaction whereby the $j$th complex reacts to the $i$th complex, then the overall rate function $f(\cdot): V^+ \to V$ is given by**

---

* More precisely, the rate per unit volume of reactor.
** $R^+$ represents the set of nonnegative real numbers.
*** As suggested by the notation the sum is taken over all $i, j$ permutations for which the $j$th complex reacts to the $i$th complex.
\[ f(c) \equiv \sum_{i,j=1}^{n} f_{ij}(c)(y_i - y_j) \quad (1.35) \]

At this point we can begin to comprehend the importance of the stoichiometric subspace for a mechanism, introduced in the preceding section. Recall that, for a mechanism, \( S \) is the set of all vectors in \( \mathbf{V} \) which can be represented as a linear combination of the reaction vectors for that mechanism. Now it follows from Eq. (1.35) that, for each \( c \) in \( \mathbf{V}^+ \), the vector \( f(c) \) certainly has this property; the scalar multipliers are the numbers \( f_{ij}(c) \). Consequently, values that the function \( f(\cdot) \) takes cannot be arbitrary vectors of \( \mathbf{V} \); they must lie in \( S \).

Let us go further. It follows from Eqs. (1.31) and (1.35) that for each instant of time, \( \tau \), the following differential equation must be satisfied:

\[ \dot{c}(\tau) = \sum_{i,j=1}^{n} f_{ij}(c(\tau))(y_i - y_j) \quad (1.36) \]

Equation (1.36) governs the composition state of the reactor under study. Once an initial composition \( c(0) \) is specified a solution to Eq. (1.36) subject to that initial condition tells us what \( c(t) \) will be for \( t \geq 0 \). We call the path in \( \mathbf{V} \) that the concentration vector follows as time progresses a composition trajectory. It follows from Eq. (1.36) that the nature of composition trajectories corresponding to different initial compositions bears a close relationship to the nature of \( S \), the stoichiometric subspace for the underlying mechanism.

Let us see why this is so. Suppose that \( c(t) \) and \( c(t') \) are concentration vectors along a composition trajectory and that these correspond to two instants \( t \) and \( t' \). Integration of Eq. (1.36) yields

\[ c(t) - c(t') = \sum_{i,j=1}^{n} \left[ \int_{t'}^{t} f_{ij}(c(\tau)) \; d\tau \right] [y_i - y_j] \quad (1.37) \]

If we take \( t' = 0 \) and let \( c(0) \) represent the initial composition of our reactor, then it follows easily from Eq. (1.37) that, for all \( t \geq 0 \),

\[ c(t) = c(0) + \sum_{i,j=1}^{n} \left[ \int_{0}^{t} f_{ij}(c(\tau)) \; d\tau \right] [y_i - y_j] \quad (1.38) \]
Now let us take note of the fact that the right-hand side of Eq. (1.37) and the second term on the right-hand side of Eq. (1.38) are both elements of $S$, the stoichiometric subspace for the mechanism, since both are linear combinations of the reaction vectors. Thus, Eq. (1.38) tells us that, for each $t \geq 0$, $\zeta(t)$ is the sum of $\zeta(0)$ with a time-dependent vector of $S$. That is, for all $t \geq 0$, $\zeta(t)$ is an element of the parallel $\zeta(0) + S$. (Recall Section 1.2.4.) Hence, composition trajectories cannot wander promiscuously through $V$; they are constrained to reside in parallels of the stoichiometric subspace. Moreover, Eq. (1.37) tells us that two concentration vectors can reside on the same trajectory only if their difference is an element of $S$ or, equivalently, only if they lie in the same parallel of $S$. (That these conditions are equivalent follows from remarks at the end of Section 1.2.4.) What we are saying, in effect, is that one composition state in our reactor may evolve from another only if the two states are compatible with respect to the stoichiometry imposed by the underlying mechanism.

With this in mind we say that, for a mechanism with stoichiometric subspace $S$, two concentration vectors $\zeta$ and $\zeta'$ are stoichiometrically compatible if and only if $\zeta - \zeta'$ is a vector $S$ or, equivalently, if an only if $\zeta$ and $\zeta'$ lie in the same parallel of $S$. Accordingly, we may partition the set of all possible concentration vectors for our reactor (i.e., vectors of $V^+$) into the stoichiometric compatibility classes of $V^+$. Two vectors of $V^+$, $\zeta$ and $\zeta'$, lie in the same stoichiometric compatibility class of $V^+$ if and only if $\zeta$ and $\zeta'$ are stoichiometrically compatible. Each stoichiometric compatibility class of $V^+$ is the intersection of a parallel of $S$ with $V^+$.

We shall have occasion to restrict attention to concentration vectors with strictly positive components. Consequently, we likewise partition the set of all such concentration vectors (i.e., vectors of $V^+$) into the stoichiometric compatibility classes of $V^+$. These are the same as the stoichiometric compatibility classes of $V^+_+$ except that we exclude vectors for which one or more components are zero. Each stoichiometric compatibility class of $V^+$ is the intersection of a parallel of $S$ with $V^+$.

The stoichiometric compatibility classes of $V^+_+$ and $V^+$ are sometimes called the nonnegative and positive reaction simplices, respectively.

Figures 1.3 and 1.4 may help bring these ideas into focus. In Figure 1.3 the stoichiometric subspace for the simple mechanism $2A_1 \rightarrow A_2$ is shown as a line in species space ($V = \{R^2 \}$; $S$ contains the two reaction vectors $\xi_2 - 2\xi_1$ and $2\xi_1 - \xi_2$. If our reactor has initial composition $\zeta(0)$, then the ensuing composition trajectory is constrained to reside in the parallel $\zeta(0) + S$, which is also shown. The stoichiometric compatibility class of $V^+$ which contains $\zeta(0)$ is that part of $\zeta(0) + S$ which lies in $V^+$; it does not contain the two points on the coordinate axes. The corresponding stoichiometric compatibility class of $V^+_+$ does contain these points.
Figure 1.3. Stoichiometric Subspace and a Stoichiometric Compatibility Class for the Mechanism $2A_1 \leftrightarrow A_2$.

In Figure 1.4 there is shown for mechanism (1.23) the stoichiometric subspace, which contains the reaction vectors $e_3 - e_1$, $e_2 - e_3$, $2e_1 - e_3$, and $2e_2 - e_3$. Here species space is $\mathbb{R}^3$. If our reactor has initial composition $\zeta(0)$, the ensuing trajectory is constrained to reside in $\zeta(0) + S$, the plane (not shown) parallel to $S$ which contains $\zeta(0)$. The shaded triangle together with its three sides is the stoichiometric compatibility class of $V^+$ which contains $\zeta(0)$; it is the intersection of $\zeta(0) + S$ with $V^+$. The interior of the triangle is the corresponding stoichiometric compatibility class of $V^+$. 
1.3.3 Kinetics for Reversible Mechanisms: An Alternative View

Reversible mechanisms are sufficiently important in applications and have sufficiently "special" structure that it will prove worthwhile to introduce for them some additional ideas and terminology. Essentially, what we wish to do is exploit and make explicit the fact that reversible mechanisms are composed of reaction pairs which proceed in opposite "directions."

Consider the following simple reversible mechanism for a four-species mixture, and suppose that the rate functions are given as shown:

\[
2A_1 \xrightarrow{\alpha(\cdot)} A_2 \xleftarrow{\beta(\cdot)} A_3 \xrightarrow{\gamma(\cdot)} A_4 \xleftarrow{\delta(\cdot)} A_2 + A_3
\]

(1.39)
Then the overall rate function, constructed in accordance with the formalism of the preceding section, is

\[ f(c) = a(c)[e_2 - 2e_1] + \beta(c)[2e_1 - e_2] + \gamma(c)[e_3 + e_4 - e_2] + \delta(c)[e_2 - (e_3 + e_4)] \]  

(1.40)

In view of the fact that the vector representing each reaction is just the negative of the vector representing its "antireaction" we can, if we wish, combine terms pairwise in Eq. (1.39):

\[ f(c) = [a(-c) - \beta(c)][e_2 - 2e_1] + [\gamma(c) - \delta(c)][e_3 + e_4 - e_2] \]  

(1.41)

If we choose to regard \(2A_1 + A_2\) as the "forward" reaction of the pair \(2A_1 \leftrightarrow A_2\) and \(A_2 \rightarrow 2A_1\) as the "backward" reaction, then we can regard \(a(c) - \beta(c)\) as the net rate for the pair \(2A_1 \leftrightarrow A_2\) in the forward direction. Similarly, we can regard \(\gamma(c) - \delta(c)\) as the net rate of the pair \(A_2 \leftrightarrow A_3 + A_4\) in the forward direction \(A_2 + A_3 + A_4\). Of course, our choice for the forward direction in each reaction pair is arbitrary; were a different choice made the net rate would merely change sign.

For reversible mechanisms it is often convenient to regard a pair of reactions as a single entity represented vectorially by the reaction vector for one reaction of the pair (the arbitrarily chosen forward reaction) and to associate with that pair a net rate function which assigns to each \(c\) in \(V^+\) the net rate of reaction in the assigned forward direction. Thus, with each reversible mechanism we can associate a set of vectors \(\{q_1, q_2, \ldots, q_k\}\) in \(V\); each represents a pair of reactions with an assigned forward direction. From the kinetics we can construct a set of net rate functions \(\{r_1(\cdot), r_2(\cdot), \ldots, r_k(\cdot)\}\), where \(r_\alpha(\cdot) : V^+ \to \mathbb{R}\) gives the net rate\(^*\) in the assigned forward direction of the pair of reactions represented by \(q_\alpha\).

Thus, in mechanism (1.39) the vector \(q_1 = e_2 - 2e_1\) represents the pair \(2A_1 \leftrightarrow A_2\) with \(2A_1 + A_2\) the chosen forward direction, and \(q_2 = e_3 + e_4 - e_2\) represents the pair \(A_2 \leftrightarrow A_3 + A_4\) with \(A_2 + A_3 + A_4\) the chosen forward direction. Then \(r_1(c) = a(c) - \beta(c)\), and \(r_2(c) = \gamma(c) - \delta(c)\). Hence, Eq. (1.41) can be rewritten:

\[ f(c) = r_1(c)q_1 + r_2(c)q_2 \]

More generally, if a reversible mechanism has \(k\) reaction pairs (with assigned directions) represented by vectors \(\{q_1, q_2, \ldots, q_k\}\) and if the corresponding net rate functions are \(\{r_1(\cdot), r_2(\cdot), \ldots, r_k(\cdot)\}\), then

\[ f(c) = \sum_{\alpha=1}^{k} r_\alpha(c)q_\alpha \]  

(1.42)

With each pair of reactions with assigned direction we can associate a reactant complex and a product complex. We designate by \(q_{ar}\) and \(q_{ap}\) the vectorial representations of the reactant and product complexes

\(^*\) Clearly, a net rate function need not take values in the nonnegative real numbers. \(\mathbb{R}\) represents the set of all real numbers.
in the \(n\)th reaction pair. Thus, for the reaction pair \(2A_1 \rightleftharpoons A_2\) with forward direction \(2A_1 \rightarrow A_2\) we regard \(A_1\) to be the reactant complex and \(A_2\) to be the product complex; the reactant and product complexes are represented vectorially by \(\mathbf{g}_1\) and \(\mathbf{g}_2\), respectively.

Clearly, for every reaction pair with assigned direction,

\[
\mathbf{g}_a = \mathbf{g}_{ap} - \mathbf{g}_{ar}
\]

(1.43)

Thus, for the example we have been studying, \(\mathbf{g}_{1p} = \mathbf{e}_2\), \(\mathbf{g}_{1r} = 2\mathbf{e}_1\), and

\[
\mathbf{g}_1 = \mathbf{e}_2 - 2\mathbf{e}_1; \quad \mathbf{g}_{2p} = \mathbf{e}_3 + \mathbf{e}_4, \quad \mathbf{g}_{2r} = \mathbf{e}_2, \quad \text{and} \quad \mathbf{g}_2 = \mathbf{e}_3 + \mathbf{e}_4 - \mathbf{e}_2.
\]

The reader may easily verify the following: If a reversible mechanism has \(k\) reaction pairs with assigned direction represented by vectors \(\{\mathbf{g}_1, \mathbf{g}_2, \ldots, \mathbf{g}_k\}\), then the stoichiometric subspace, \(S\), for that mechanism (as defined by Eq. (1.24)) is also given by

\[
S = L (\mathbf{g}_1, \mathbf{g}_2, \ldots, \mathbf{g}_k)
\]

(1.44)

In this section we have introduced for reversible mechanisms the idea of reaction pairs with arbitrarily assigned "direction," and we suggested that these might be represented by vectors \(\{\mathbf{g}_1, \mathbf{g}_2, \ldots, \mathbf{g}_k\}\). We should properly call each \(\mathbf{g}_a\) a "reaction pair with assigned direction vector"; however, when no confusion is likely to rise we shall simply call \(\mathbf{g}_a\) a reaction vector. As a rule we shall reserve the symbols \(\mathbf{g}_1, \mathbf{g}_2, \ldots\), for vectors representing reaction pairs with assigned direction. As in Sections 1.3.2 and 1.3.3 we shall use \(\gamma_i - \gamma_j\) to represent the single reaction whereby the \(j\)th complex in a mechanism reacts to the \(i\)th complex.

It must be emphasized most emphatically that for a reversible mechanism the reactions \(\{\mathbf{g}_1, \mathbf{g}_2, \ldots, \mathbf{g}_k\}\) need not be linearly independent. For example, the very simple mechanism (1.26) has reaction vectors \(\mathbf{g}_1 = \mathbf{e}_2 - \mathbf{e}_1, \quad \mathbf{g}_2 = \mathbf{e}_3 - \mathbf{e}_2, \quad \mathbf{g}_3 = \mathbf{e}_1 - \mathbf{e}_3\); note that

\[
\mathbf{g}_1 + \mathbf{g}_2 + \mathbf{g}_3 = \mathbf{0}.
\]

1.3.4 Equilibrium and Detailed Balancing

Consider a mixture endowed with a certain mechanism, and suppose that a kinetics for that mechanism gives rise to an overall rate function \(f(\cdot)\). Then the chemical dynamics for the reactor under study is governed by the differential equation

\[
\dot{c} = f(c)
\]

(1.45)

If \(c^*\) in \(\overline{c}\) is such that \(f(c^*) = 0\), then at the mixture composition represented by \(c^*\) no chemical change occurs, and \(c^*\) is called an equilibrium for the kinetics.

Suppose now that the underlying mechanism is reversible with reaction vectors \(\{\mathbf{g}_1, \mathbf{g}_2, \ldots, \mathbf{g}_k\}\), and suppose that the kinetics is such that the corresponding net rate functions are \(\{r_1(\cdot), r_2(\cdot), \ldots, r_k(\cdot)\}\). Then

\[
f(c) = r_1(c)\mathbf{g}_1 + r_2(c)\mathbf{g}_2 + \ldots + r_k(c)\mathbf{g}_k
\]

(1.46)

It follows easily from Eq. (1.46) that if \(c^*\) is such that \(r_\alpha(c^*) = 0, \quad \alpha = 1, 2, \ldots, k\), then \(f(c^*) = 0\) so that \(c^*\) is an equilibrium.

We shall consider whether the converse statement is always true.

Suppose that \(c^*\) is such that \(f(c^*) = 0\). Does it follow from this and from Eq. (1.46) alone that \(r_\alpha(c^*) = 0, \quad \alpha = 1, 2, \ldots, k\)? That is, does
Eq. (1.46) by itself ensure that at an equilibrium the net rate of each reaction is zero? Theorem 1.2a can help us resolve this question.

Suppose that \( \{g_1, g_2, \ldots, g_k\} \) is a linearly independent set. If the left-hand side of Eq. (1.46) is the zero vector [i.e., \( f(c^*) = 0 \)], then \( r_\alpha(c^*) = 0, \ \alpha = 1, 2, \ldots, k \), is certainly a "solution" to Eq. (1.46); moreover, the theorem ensures that this is the only "solution" to Eq. (1.46). Hence, if \( \{g_1, g_2, \ldots, g_k\} \) is a linearly independent set, then \( f(c^*) = 0 \) implies that \( r_\alpha(c^*) = 0 \) for each \( \alpha = 1, 2, \ldots, k \).

Suppose, on the other hand, that \( \{g_1, g_2, \ldots, g_k\} \) is a linearly dependent set. Although it is true that \( r_\alpha(c^*) = 0, \ \alpha = 1, 2, \ldots, k \), is a "solution" to Eq. (1.46), the theorem tells us that there exist other "solutions." Hence, if \( \{g_1, g_2, \ldots, g_k\} \) is linearly dependent, then \( f(c^*) = 0 \) and Eq. (1.46) do not of themselves ensure that at \( c^* \) the net rates of the individual reactions all take the value zero.*

Accordingly, we wish to distinguish between equilibria for which the net rates of all reactions are zero and those for which this is not the case. We shall say that detailed balance obtains at an equilibrium if, at that equilibrium, the net rate function for each reaction takes the value zero.

It follows from this discussion that for reversible mechanisms for which the reactions \( \{g_1, g_2, \ldots, g_k\} \) constitute a linearly independent set any kinetics has the property that detailed balancing obtains at all equilibria. If \( \{g_1, g_2, \ldots, g_k\} \) is linearly dependent, one can construct hypothetical kinetics for which detailed balancing obtains at some equilibria but not at others; there can also exist kinetics for which detailed balancing obtains at all equilibria despite the linear dependence of the set of reactions. In the latter case it just happens that the net rate functions are "orchestrated" to preclude equilibria at which net rates of individual reactions are nonzero.

We shall want to focus upon those kinetics which are such that detailed balancing obtains at every equilibrium in \( V^+ \). Consider a kinetics for a reversible mechanism; let the net rate functions be \( \{r_1(\cdot), r_2(\cdot), \ldots, r_k(\cdot)\} \), and let \( f(\cdot) \) be the overall rate function. Then the kinetics is said to be detailed balanced if

**DB1.** There exists at least one equilibrium in \( V^+ \). That is, there exists \( c^* \) in \( V^+ \) such that \( f(c^*) = 0 \).

and

**DB2.** At every equilibrium in \( V^+ \) detailed balancing obtains. That is,

\[
f(c) = 0, \quad c \text{ lies in } V^+ \implies r_\alpha(c) = 0, \quad \alpha = 1, 2, \ldots, k
\]

Classical thermodynamics supplies no reason to suppose that true mechanisms should be reversible and that detailed balance should obtain at equilibria in closed homogeneous systems of the type we have been

---

* Of course this whole argument might be based directly upon the definition of linear independence rather than upon Theorem 1.2a.
considering. Nevertheless, chemists hold to the belief that this should be the case*; the rationale for this supposition is usually rooted in molecular arguments. [See, for example, Onsager (1931).] Here, we take the position that, whether or not one finds those arguments compelling in every aspect, the belief that kinetics should be detailed balanced is so widely held that special study of detailed balanced kinetics is natural.

1.3.5 Equilibrium and Complex Balancing

Having discussed detailed balancing, we turn our attention toward complex balancing, an idea first considered by Horn and Jackson (1972). Unlike detailed balancing, which chemists hold to be a fact of nature, complex balancing should, at present, be viewed merely as a surprisingly useful conceptual tool. In Section 1.3.6 we shall provide an example of the manner in which this tool enters into proofs of theorems which, at first glance, seem to have nothing whatsoever to do with complex balancing. A deeper example will be offered in Section 1.5.4.

We revert to the general framework of Section 1.3.2, abandoning for the moment the special framework tailored for reversible mechanisms. If \( \{Y_1, Y_2, \ldots, Y_n\} \) are the complex vectors for a mechanism under consideration and \( f_{ij}(\cdot) \) is the rate function for the reaction whereby the \( j \)th complex reacts to the \( i \)th complex, then the expression for the overall rate function given in Eq. (1.35) may be rewritten as

\[
f(\mathbf{c}) \equiv \sum_{i=1}^{n} \left( \sum_{j=1}^{n} f_{ij}(\mathbf{c}) - \sum_{j=1}^{n} f_{ji}(\mathbf{c}) \right) Y_i \quad (1.47)
\]

We may view the quantity in the brackets to be the net rate at which the \( i \)th complex is formed from all other complexes. Accordingly, we call the function \( g_i(\cdot): \mathbb{R}^+ \rightarrow \mathbb{R} \) defined by

\[
g_i(\mathbf{c}) \equiv \sum_{j=1}^{n} f_{ij}(\mathbf{c}) - \sum_{j=1}^{n} f_{ji}(\mathbf{c}) \quad (1.48)
\]

the \( i \)th complex formation rate function. Then Eq. (1.47) becomes

\[
f(\mathbf{c}) \equiv \sum_{i=1}^{n} g_i(\mathbf{c}) Y_i \quad (1.49)
\]

Now suppose that \( \mathbf{c}^* \) is such that \( g_i(\mathbf{c}^*) = 0, \quad i = 1, 2, \ldots, n \). That is, suppose that \( \mathbf{c}^* \) is such that at that composition the net rate of formation of each complex is zero. In such a case we say that

* However, recall the footnote at the beginning of Section 1.3.1.
complex balancing obtains at the equilibrium \( \xi^* \). That \( \xi^* \) is indeed an equilibrium follows easily from Eq. (1.49). One can construct examples of mechanisms with assigned kinetics (in fact, mass action kinetics) such that equilibria exist at which complex balancing fails to obtain [Horn and Jackson (1972) and Horn (1972)].

In the context of reversible mechanisms, detailed balancing obtains at an equilibrium \( \xi^* \) if for each reaction pair the net rate at \( \xi^* \) is zero, i.e., if \( f_{ij}(\xi^*) - f_{ji}(\xi^*) = 0 \) for all \( i \) and \( j \) such that \( i \neq j \). It follows from Eq. (1.48) that detailed balancing implies complex balancing; the converse is not generally true.

Drawing an analogy with detailed balanced kinetics, we say that a kinetics is complex balanced if

**CB1.** There exists at least one equilibrium in \( V^+ \). That is, there exists \( \xi^* \) in \( V^+ \) such that \( \xi(\xi^*) = 0 \)

and

**CB2.** At every equilibrium in \( V^+ \) complex balancing obtains. That is, if \( n \) is the number of complexes in the underlying mechanism, then

\[ \xi(\xi) = 0, \quad \xi \text{ lies in } V^+ \longrightarrow g_i(\xi) = 0, \quad i = 1, 2, \ldots, n \]

In the context of arbitrary kinetics* two theorems regarding complex balancing are of importance. The first is due to Horn (1972); it provides a necessary condition on mechanism structure in order that there might exist equilibria in \( V^+ \) at which complex balancing obtains.

**THEOREM 1.3.a:** No kinetics for a mechanism can give rise to an equilibrium in \( V^+ \) at which complex balancing obtains unless that mechanism is weakly reversible.

The second theorem is due to Feinberg (1972, "Complex Balancing...")**:

**THEOREM 1.3.b:** Any kinetics for a mechanism of deficiency zero has the property that complex balancing obtains at all its equilibria.

1.3.6 Complex Balancing as a Tool: An "Extinction" Theorem

Let us pose a question. Consider the following mechanism:

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* The reader is reminded that a kinetics is constrained only by the requirement that rate functions take nonnegative values on \( V^+ \) and positive values on \( V^+ \).

** In the language of Feinberg's paper \( V^+ \) is a uniform subdomain of deficiency zero under the hypothesis of Theorem 1.3.b, and it is readily shown that uniform subdomains in the boundary of \( V^+ \) are also of deficiency zero.
Can a kinetics for this mechanism give rise to an equilibrium at which all species concentrations are positive (i.e., in $V^+$)? Or are all equilibria characterized by the absence of one or more species?

At first glance one is struck with the thought that the reaction $A_1 + A_2$ will consume whatever $A_1$ is present, driving its concentration to zero in any equilibrium state. On the other hand, that reaction produces $A_2$ and, as long as $A_5$ is present, the reaction $A_2 + A_5 + A_1 + A_3$ regenerates $A_1$. Then again, if $A_3$ is present, the reaction $A_1 + A_3 + A_4$ serves to deplete $A_1$. But $A_4$ serves to produce $A_2$ and $A_5$, which in turn causes regeneration of $A_1$ and $A_3$. The question is not a simple one, particularly since it is posed for arbitrary kinetics, subject only to the requirement that rate functions take positive values on $V^+$ and nonnegative values on $\overline{V^+}$.

Let us see how Theorems 1.3.a and 1.3.b help. Suppose that we have a mechanism of deficiency zero endowed with some kinetics which gives rise to an equilibrium in $V^+$. Theorem 1.3.b ensures that complex balancing obtains at that equilibrium. Yet, Theorem 1.3.a tells us that this can be the situation only if the mechanism is weakly reversible. Hence, the two theorems taken together give us

**Theorem 1.3.c**: For a mechanism of deficiency zero which is not weakly reversible no kinetics can give rise to an equilibrium in $V^+$.

This theorem provides an answer to the question posed earlier. Mechanism (1.50), like most mechanisms we are likely to encounter in practice, is of deficiency zero; it is not weakly reversible. Hence no kinetics for it will give rise to an equilibrium at which all species are present; any equilibrium is characterized by the absence of one or more species.

Thus, systems driven by zero deficiency mechanisms which are not weakly reversible have the property that mixtures initially characterized by the presence of all species can come to rest only if one or more species become "extinct." Remarks are made in Feinberg and Horn, (1974) regarding possible applications of Theorem 1.3.c (and its generalizations) to ecology.

There exist mechanisms of deficiency in excess of zero which are not weakly reversible but for which kinetics can give rise to equilibria in $V^+$. A modified version of the system, first studied by Wegscheider (1902), serves as an example:

* The juxtaposition of Theorems 1.3.a and 1.3.b to produce Theorem 1.3.c was first noticed by Horn (1972). A more general version is reported in Feinberg (1972, "Complex Balancing ..."). From the broader version one can come to conclusions regarding regions of the boundary of $\overline{V^+}$ in which equilibria cannot reside.
\[ A_1 \rightarrow A_2 \]
\[ 2A_2 \rightarrow 2A_1 \]  
(1.51)

This simple mechanism is of deficiency 1, and kinetics (in fact, mass action kinetics) can be constructed which give rise to equilibria in $V^+$. The Lotka mechanism of Section 1.5 serves as another example.

It is interesting to note that Theorem 1.3.1 makes no mention of complex balancing. Yet the idea of complex balancing served as a working tool in its proof. In Section 1.5.4 we shall discuss the connection drawn by Horn and Jackson (1972) between complex balancing and stability of open reactors, and we shall show how this connection leads to important stability theorems in which complex balancing plays no explicit role.

### 1.3.7 Mass Action Kinetics

Having discussed kinetics in general, we turn now to consideration of mass action kinetics, an important subclass with which the reader no doubt has some acquaintance. We begin by introducing mass action kinetics within the general framework of Section 1.3.2; subsequently, we shall discuss the subject within the alternative framework (Section 1.3.3) particularly suited to reversible mechanisms.

It will prove useful to begin with an example. Consider mechanism (1.32) with rate functions designated as shown. Then, with mass action kinetics, those rate functions would take the form

\[
\begin{align*}
\alpha(c) &\equiv k_\alpha c_3 c_4 \\
\beta(c) &\equiv k_\beta c_1^2 \\
\gamma(c) &\equiv k_\gamma c_3 c_4 \\
\delta(c) &\equiv k_\delta c_2
\end{align*}
\]  
(1.52)

Here $k_\alpha$, $k_\beta$, $k_\gamma$, and $k_\delta$ are positive rate constants for the individual reactions. The essential idea is that, according to the mass action prescription, the rate of each reaction is proportional to the product of all the molar species concentrations, each raised to a power taken to be the stoichiometric coefficient of that species in the reactant complex for the reaction in question.

Thus, with mass action kinetics, the rate functions bear an intimate relation to the underlying mechanism. Substituting Eq. (1.52) into Eq. (1.34), the reader will see that mass action kinetics gives rise to a set of differential equations which are at once coupled and nonlinear.

In a more general vein, consider (as in Section 1.3.2) a mechanism with complex vectors \( \{y_1, y_2, \ldots, y_n\} \) and let \( f_{ij}(\cdot) : V^+ \rightarrow \mathbb{R}^+ \) be the rate function for the reaction whereby the \( j \)th complex reacts to the \( i \)th complex. Then we say that a kinetics for the mechanism is mass action if, for each reaction of the mechanism, there exists a positive rate constant \( k_{ij} \) such that

\[ f_{ij}(c) \equiv k_{ij} c_j^m \]  
(1.53)

where

\[ c_j^m = \prod_{L=1}^{M} (c_L)^{y_{jL}} \]  
(1.54)
Here \( c_L \) is the Lth component of the concentration vector \( c \), and \( y_j \) is the Lth component of the jth complex vector \( y_j \). The compact notation given by Eq. (1.54) was introduced by Horn and Jackson (1972).

With mass action kinetics Eqs. (1.31) and (1.35) become

\[
\dot{c} = f(c) = \sum_{i,j=1}^{n} k_{ij} c^y_j (y_i - y_j)
\]

(1.55)

On one hand, it is plain that mass action kinetics confronts one with complex differential equations which are sufficiently "rich" as to describe a robust spectrum of intricate chemical dynamics. On the other hand, the intimate relationship between the differential equations and the underlying mechanism affords hope that mechanism structure of itself might provide a clue to the quality of the dynamics one might expect.

It is this interplay of mechanism and dynamics (for both closed and open systems) which is at the heart of recent research on mathematical aspects of mass action kinetics.

For the special case of mass action kinetics, the ith complex formation function takes the form

\[
g_i(c) = \sum_{j=1}^{n} k_{ij} c^y_j - \sum_{j=1}^{n} k_{ji} c^y_i
\]

(1.56)

Horn and Jackson (1972) proved the following theorem regarding complex balancing in the context of mass action kinetics:

**THEOREM 1.3.d:** Consider a mechanism endowed with mass action kinetics. If, for that kinetics, there exists an equilibrium in \( V^+ \) at which complex balancing obtains, then the kinetics is complex balanced. That is, complex balancing obtains at all equilibria in \( V^+ \).

A similar theorem holds true for detailed balancing.

For some mechanisms we may readily construct examples of kinetics for which there exist equilibria in \( V^+ \) at which complex balancing obtains and other equilibria in \( V^+ \) at which complex balancing does not obtain. (It follows from Theorems 1.3.a and 1.3.b that such mechanisms must be weakly reversible and of deficiency 1 or more.) Theorem 1.3.d ensures, however, that with mass action kinetics complex balancing obtains at no equilibrium in \( V^+ \) or at all equilibria in \( V^+ \). Hence, with mass action kinetics, we need only establish that complex balancing obtains at a single equilibrium in \( V^+ \) to be certain that the kinetics is complex balanced.

In studying dynamics of open chemical systems Section (1.5), we shall want to know circumstances under which a mass action kinetics for a mechanism gives rise to an equilibrium in \( V^+ \) at which complex balancing obtains. It follows from Horn's Theorem 1.3.a that there is no point in asking the question for mechanisms which are not weakly
reversible, for no such equilibria exist. Feinberg's Theorem 1.3.b tells us that, for mechanisms of deficiency zero, complex balancing will obtain for whatever equilibria exist; but the theorem says nothing about the existence of equilibria in $V^+$, nor does it provide any information regarding mechanisms of deficiency in excess of zero. Hence, we are compelled to wonder what interplay of rate constants and mechanism structure is required in order that a mass action kinetics be complex balanced.

The matter was settled definitively by Horn (1972). The next theorem* follows from his work and work by Feinberg (1972, "Complex Balancing...").

**THEOREM 1.3.e:** For any weakly reversible mechanism of deficiency zero every mass action kinetics is complex balanced; that is, for any choice of rate constants there exist equilibria in $V^+$, and at all equilibria complex balancing obtains.

Horn also established conditions on sets of rate constants to ensure complex balancing of mass action kinetics for weakly reversible mechanisms of deficiency in excess of zero. He showed that for such mechanisms one can always find sets of rate constants such that equilibria exist in $V^+$ at which complex balancing does not obtain.

We would like to introduce mass action kinetics into the special framework for reversible mechanisms constructed in Section 1.3.3. Suppose that, within the context of that framework, the reaction pairs are represented by $\{g_1, g_2, \ldots, g_k\}$, and let $g_{ap}$ and $g_{ar}$ represent the designated product and reactant complexes of the $a$th reaction pair. Then, with mass action kinetics, the net rate function $r_a(\cdot): V^+ \to \mathbb{R}$ for the $a$th reaction pair takes the form

$$r_a(\cdot) = k_{ar}g_{ar} - k_{ap}g_{ap} \quad \text{(1.57)}$$

where $k_{ar}$ is the rate constant for the designated forward reaction of the pair and $k_{ap}$ is the rate constant for the backward reaction. In accordance with Eq. (1.47), the overall rate function takes the form

$$f(\cdot) = \sum_{a=1}^{k} [k_{ar}g_{ar} - k_{ap}g_{ap}] g_a \quad \text{(1.58)}$$

---

* Work by Horn leading to Theorem 1.3.e preceded Feinberg's proof of Theorem 1.3.b. In a study focused exclusively on mass action kinetics Horn showed that, for weakly reversible mechanisms such that two linear subspaces (induced by the mechanism) of a certain vector space "sum" to that vector space, every set of rate constants gives rise to a complex balanced kinetics. In a private communication, Feinberg showed that Horn's condition on mechanism structure was equivalent to $\delta = n - \ell - s = 0$. [See Horn (1971) for a short sketch of Horn's work and the relation between the two conditions.] Subsequently, Feinberg proved that for arbitrary kinetics $\delta = 0$ ensures that complex balancing obtains at all equilibria.
If \( \zeta^* \) is an equilibrium at which detailed balance obtains, then the net rate functions must all take the value zero at \( \zeta^* \). Hence, if detailed balance obtains at \( \zeta^* \), then from Eq. (1.57)

\[
k_{ar}(\zeta^*) g_{ar} = k_{ap}(\zeta^*) g_{ap}, \quad a = 1, 2, \ldots, k
\]

(1.59)

1.3.8 A Useful Change of Variable

Just as in some fluid mechanics problems it is useful to work in cylindrical rather than rectangular coordinates, so it is that, with problems involving mass action kinetics, it is sometimes useful to work in variables other than molar concentrations. We shall be concerned primarily with mixtures for which equilibria exist in \( V^* \). Let \( \zeta^* \) be such an equilibrium. Then we define the function \( \psi(\cdot) : V^* \rightarrow V \) by

\[
\psi(\zeta) \equiv \sum_{L=1}^{M} \ln \left( \frac{c_{L}}{c_{L}^*} \right) e_{L}
\]

(1.60)

where \( c_{L} \) is the molar concentration of the \( L \)th species, i.e., the \( L \)th component of the vector \( \zeta \). Similarly, \( c_{L}^* \) is the concentration of the \( L \)th species in the equilibrium represented by the vector \( \zeta^* \). To each \( \zeta \) in \( V^* \) Eq. (1.60) assigns a vector \( \psi \) in \( V \), and to each \( \psi \) in \( V \) there corresponds a concentration \( \zeta \) in \( V^* \). We regard (1.60) as giving a change of variable.\(^*\) Note that

\[
\psi(\zeta^*) = 0
\]

(1.61)

We record for future use mass action rate functions written in terms of the new variable. With only modest effort we can show that Eq. (1.53) for rates of individual reactions becomes\(^**\)

\[
f_{ij}(\psi) \equiv k_{ij}(\zeta^*)^{-1} e_{i} e_{j}
\]

(1.62)

and that the overall rate function given in Eq. (1.55) becomes

\[
f(\psi) \equiv \sum_{i,j=1}^{n} k_{ij}(\zeta^*)^{-1} e_{i} e_{j} (y_{i} - y_{j})
\]

(1.63)

Similarly, we can reformulate Eq. (1.57) for net rates appropriate to reversible mechanisms:

\(^*\) The overall rate function for a mixture generally gives rise to a wealth of equilibria. Naturally, the choice of \( \zeta^* \) plays a role in the construction of \( \psi(\cdot) \). Nevertheless, once the choice is made it is retained.

\(^**\) We use the caret to distinguish between functions written in terms of concentrations and those written in terms of the new variable.
\[ r_\alpha (\zeta) \equiv \kappa_\alpha (\zeta^*) \frac{q_{ar}}{e^{-} - e^{+}} - k_{ap} (\zeta^*) \frac{q_{ap}}{e^{-}} \]  
\[ (1.64) \]
and the corresponding formula for the overall rate function can be rewritten as well.

Now suppose that detailed balance obtains at the equilibrium \( \zeta^* \). Then Eq. (1.59) holds, and we may cast Eq. (1.64) in a simple form:

\[ r_\alpha (\zeta) \equiv \kappa_\alpha \left[ e^{q_{ar} - q_{ap}} - e^{-q_{ap}} \right] \]  
\[ (1.65) \]
where

\[ \kappa_\alpha \equiv k_{ar} (\zeta^*) = k_{ap} (\zeta^*) \]  
\[ (1.66) \]

Note that \( \kappa_\alpha > 0, \alpha = 1, 2, \ldots, k \). The overall rate function takes the form

\[ \dot{\zeta} (\zeta) \equiv \sum_{\alpha = 1}^{k} \kappa_\alpha \left[ e^{q_{ar} - q_{ap}} - e^{-q_{ap}} \right] \left[ q_{ap} - q_{ar} \right] \]  
\[ (1.67) \]

1.4 THE DETERMINATION OF RATE CONSTANTS FOR INTRICATE MECHANISMS: THEORETICAL ASPECTS

In this section we shall inquire how, at least in principle, one might extract from dynamic experiments rate constants for reactions comprising an intricate mechanism. We shall focus upon the case for which the kinetics is mass action and detailed balanced. The experiments we shall think about are highly idealized: We presume that in an isothermal closed homogeneous reactor the investigator can choose any initial composition he wishes and can subsequently record accurately the concentrations of all species as functions of time; we presume also that the experiment can be repeated as often as one wishes with varying initial compositions. If this does not suggest the best of all possible worlds, it at least suggests a world more congenial than our own.

Nevertheless, these are prototypes of experiments we ponder in chemical kinetics, and, as in the classic case of the three-species butene isomerization "triangle" studied experimentally by Haag and Pines (1960), the ideal can sometimes be approached closely, if not achieved. But even for that relatively simple mechanism there remained the problem of analysis, of attributing to each reaction its proper contribution to the overall chemical dynamics observed. The Wei and Prater (1962) analysis, now studied in our classrooms, exploited the pseudomonomolecular character of the system at hand to bring algebraic tools to the solution of the problem.

Here we shall discuss analytic aspects of the problem for mechanisms of arbitrary complexity. The emphasis is not upon computational aspects for specific mechanisms, important as these may be. Rather, we focus upon questions of a coarser grain. Consider, as an example, the following mechanism:
\[ \begin{align*}
2A_1 & \rightleftharpoons A_2 + A_3 \\
A_2 & \rightleftharpoons A_4 \\
A_1 + A_3 & \rightleftharpoons A_5 + A_6 \\
A_2 + A_3 & \rightleftharpoons A_7 \\
A_7 & \rightleftharpoons 2A_1
\end{align*} \] (1.68)

Species \( A_1 \) is produced and consumed in the first, third, and fifth reaction pairs. Species \( A_2 \) is produced and consumed in the first, second, and fourth. Other species are also produced and consumed in several reaction pairs. Even if we are granted the idealized experiments discussed at the outset and even if we are given that the kinetics is mass action and detailed balanced, how are we to disentangle the contributions of the several reaction to overall dynamics in order to attribute rate constants to each? Can this in fact be done? If so, how much information do we need from our idealized experiments?

The first thorough study of questions such as these seems to have come in a paper by Krambeck (1970). It is his work and subsequent work by Feinberg (1972, "On Chemical Kinetics..."; 1977, "Mechanism Deficiency...") that we shall consider here. Throughout this section we shall presume that the mechanism, as in the Wei-Prater analysis, is known.

**1.4.1 Some General Considerations**

We shall focus upon reversible mechanisms endowed with detailed balance mass action kinetics, but, before we do, it will prove useful to see how far we can go without placing any restrictions whatever on the kinetics. In this way we can gain some general overview and see what obstacles must be overcome. We shall work within the framework tailored for reversible mechanisms (Section 1.3.3).

Suppose that the system under study is driven by a known mechanism with reactions \( \{g_1, g_2, ..., g_k\} \) and that the corresponding net rate functions \( \{r_1(\cdot), r_2(\cdot), ..., r_k(\cdot)\} \) are unknown. The overall rate function is given by

\[ f(c) = r_1(c)g_1 + r_2(c)g_2 + ... + r_k(c)g_k \] (1.69)

and, for the idealized experiments under consideration, the governing differential equation is

\[ \dot{c} = f(c) \] (1.70)

We ask whether from those experiments we can, in principle, determine \( r_1(\cdot), r_2(\cdot), \) etc. Determination of the function \( r_\alpha(\cdot) : \mathbb{V}^+ \rightarrow \mathbb{R} \) requires not that we be able to construct an "analytic" expression for \( r_\alpha(\cdot) \) but rather that we be able to determine the number \( r_\alpha(c) \) for any and all \( c \) in \( \mathbb{V}^+ \).

Now suppose that we wish to find the values that the net rate functions take at some particular composition, say \( \bar{c} \). In principle we could, in our idealized experiment, form a mixture of composition \( \bar{c} \), allow it to react, and measure the initial \( \bar{c} \). In this way we would know \( f(\bar{c}) \) from Eq. (1.70). We then ask whether Eq. (1.69), of itself, suffices to determine \( r_1(\bar{c}), r_2(\bar{c}), \) etc.
Suppose that the reactions \( \{ q_1, q_2, \ldots, q_k \} \) constitute a linearly independent set. Then Theorem 1.2.a tells us that \( f(\zeta) \) and Eq. (1.69) determine \( r_1(\zeta), r_2(\zeta), \) etc., completely. In this way, the idealized experiments enable us to obtain values taken by the net rate functions at whatever compositions we wish. Hence, the function \( f(\cdot) \), obtainable in principle from the idealized experiments*, suffices for determination of all the net rate functions completely and unambiguously. Moreover, the discussion of Section 1.3.4 ensures that the kinetics must be such that detailed balance obtains at all equilibria.

Suppose, on the other hand, that \( \{ q_1, q_2, \ldots, q_k \} \) is a linearly dependent set. Then Theorem 1.2.a tells us that \( f(\zeta) \) and Eq. (1.69) do not of themselves suffice for determination of the complete set \( \{ r_1(\zeta), \ldots, r_k(\zeta) \} \). Even if the overall rate function \( f(\cdot) \) were known completely, we could find a variety of sets of net rate functions which would be compatible with Eq. (1.69); some of these would exhibit detailed balance at all equilibria, while others would not.

Now determination of the complete overall rate function in the pointwise manner suggested is impractical, to say the least. Nevertheless, the discussion suggests that, at least in principle, systems for which the reaction set \( \{ q_1, q_2, \ldots, q_k \} \) is linearly independent do not inherently give rise to uniqueness problems. On the other hand, even if we grant ourselves the fiction of complete determination of \( f(\cdot) \) from the idealized experiments, then systems with linearly dependent reaction sets give rise to uniqueness problems which can be circumvented only if additional constraints are imposed upon the kinetics.

It is easily shown that if the stoichiometric subspace \( S \) of a mechanism with reactions \( \{ q_1, q_2, \ldots, q_k \} \) [see Eq. (1.44)] has dimension \( s \), then those reactions will constitute a linearly dependent set if and only if

\[
\begin{align*}
k &> s 
\end{align*}
\]

Hence, it is for situations in which Eq. (1.71) holds that we expect difficulties.

The mechanism (1.68) has reactions (with "forward" direction taken from left to right)

\[
\begin{align*}
g_1 &= e_2 + e_3 - 2e_1 \\
g_2 &= e_4 - e_2 \\
g_3 &= e_5 + e_6 - (e_1 + e_3) \\
g_4 &= e_7 - (e_2 + e_3) \\
g_5 &= e_7 - 2e_1
\end{align*}
\]

For this mechanism \( s = 4 \) and \( k = 5 \), so that the reactions are linearly dependent. (In particular, \( g_1 + g_5 + g_4 = 0 \).) Hence Eq. (1.68) falls into the "troublesome" class.

* That is, \( f(\zeta) \) is determinable for any \( \zeta \) in \( \mathbb{V}^+ \) from our experiments in the manner described.
1.4.2 Some General Remarks on Detailed Balanced Mass Action Kinetics

In the preceding discussion we examined the problem of determination of kinetics from the overall rate function when nothing about the kinetics is presumed in advance, and we found that, in such a case, linear dependence of the set of reactions gives rise to uniqueness problems. However, more often than not we suppose in advance that the kinetics is of a certain form and that we need only determine values of parameters appropriate to that form. Given form specification as additional information we may reconsider the questions raised in the preceding section. In particular, we presume that the kinetics under study is mass action and detailed balanced and that we wish to study the extent to which the complete set of rate constants might be determined from experiments of the type we have been considering.

In this context an observation is in order. It has already been pointed out that mechanism (1.26) has a linearly dependent set of reactions. (See the end of Section 1.3.3.) Yet we know that rate constants for that mechanism are uniquely determinable from our idealized experiments, for Wei and Prater have shown us how they might be obtained. This example raises the hope that, at least for studies involving mass action detailed balanced kinetics, this specification of form will invariably circumvent the uniqueness problem.

Krambeck has shown us that, unfortunately, this is not the case. We consider a simplified version of a mechanism studied by him (1970). It is shown below with two alternative sets of rate constants (in the context of mass action kinetics):

\[
\begin{align*}
A_1 + A_2 & \rightarrow 2A_2 \\
2A_1 & \rightarrow 1/2 \rightarrow 2A_2
\end{align*}
\]

Both kinetics are detailed balanced, and both give rise to the same overall rate function. The reader may easily show that both kinetics give rise to identical dynamic equations, which, in component form, are

\[
\begin{align*}
c_1 &= -3c_1^2 + 3c_2^2 \\
c_2 &= 3c_1^2 - 3c_2^2
\end{align*}
\]

Consequently, experiments of the type we have been considering cannot serve to distinguish between the two kinetics since both kinetics give rise to identical dynamics.

Of course mechanism (1.73) is not one intended to represent "real" chemistry. Rather, it serves to tell us that even if we consider only mass action kinetics with detailed balance the uniqueness problem persists, at least for some mechanisms. If a simple, albeit unrealistic, mechanism such as (1.73) gives rise to uniqueness problems, then who is to say that more intricate real mechanisms cannot do likewise?

Apparently, then, even in the context of detailed balanced mass action kinetics some mechanisms give rise to uniqueness problems, while others do not. We would like to be able to draw a connection between mechanism structure and the extent to which rate constants for the mechanism can be determined completely.
Krambeck offered the first concrete results along these lines. He showed that for those special mechanisms of a single linkage class with each of the \( n \) complexes reacting directly to every* other complex, as in mechanism (1.73), the condition

\[
\delta = n - 1 - s = 0
\]  

(1.75)

is necessary and sufficient for the overall rate function \( f(\cdot) \) to determine uniquely all rate constants. The reader will observe that for mechanism (1.75) \( n = 3 \) and \( s = 1 \) so that \( \delta = 1 \). We remark in passing that the mechanism

\[
2A_1 \rightleftharpoons A_1 + A_2 \rightleftharpoons 2A_2
\]  

(1.76)

is one for which, in the context of detailed balanced mass action kinetics, rate constants can be determined uniquely from \( f(\cdot) \) despite the fact that \( n - 1 - s = 1 \). The complex \( 2A_1 \) does not react directly to \( 2A_2 \) so that mechanism (1.76) falls outside the class considered by Krambeck.

We would like to move beyond results of the type described in two ways:

First, we would like to delineate a broader class of mechanisms for which uniqueness is to be expected.

Second, we would like to come to some understanding of how much or how little information need be obtained from our experiments in order that complete sets of rate constants might be determined when, in fact, that complete set can be determined at all. Up to this point we have been asking whether rate constants could, in principle, be obtained if we could "measure" \( f(\cdot) \) completely. Not only is it impossible to measure \( \xi \) at every \( \xi \) in \( \nabla \xi \) in order to know \( f(\cdot) \); if we knew \( f(\cdot) \) we probably would not care very much about the rate constants if all we wanted to do is design reactors. For that purpose knowledge of \( f(\cdot) \) alone suffices. The real questions we want to consider are these: For what mechanisms can we determine the complete set of rate constants uniquely from a limited amount of experimental information in order that \( f(\cdot) \) can be constructed? How much information do we need?

1.4.3 The Determination of Rate Constants from Experiments Near a Single Equilibrium

In this section we shall discuss results of Feinberg (1972, "On Chemical Kinetics..."; 1977, "Mechanism Deficiency...") which tell us that for a remarkably broad class of intricate mechanisms (in fact, most that we are likely to encounter in practice) the complete set of rate constants is uniquely determinable from a surprisingly small amount of

* Krambeck's view is different from the one taken here. Where we take the mechanism to be known a priori, Krambeck in effect takes the complexes and the stoichiometric subspace \( S \) as known and admits the possibility of reaction between any pair of complexes \( Y_i \) and \( Y_j \) so long as \( Y_i - Y_j \) lies in \( S \). Thus, where we might examine uniqueness for the mechanism (1.76), Krambeck would examine the uniqueness question for mechanism (1.76) augmented by the reactions \( 2A_1 \rightleftharpoons 2A_2 \).
information. It will be understood that we are working within the context of detailed balanced mass action kinetics for arbitrary reversible mechanisms and that the experiments we consider are those described at the outset.

Since the kinetics under study is detailed balanced it follows from DB1 in Section 1.3.4 that there exists at least one equilibrium, say \( \mathbf{c}^* \), in \( \mathbf{v}^* \). Accordingly, we may construct the function \( \varphi(\cdot) \) in Eq. (1.60) to induce a change of variable. Since from our experiments we can in principle find \( \varphi(\mathbf{c}) \) for any \( \mathbf{c} \), it follows that we can know \( \varphi(\mathbf{y}) \) for any \( \mathbf{y} \). In fact, \( \varphi(\mathbf{y} \circ \mathbf{c}) \) is just equal to \( \varphi(\mathbf{c}) \). In particular, we recall that \( \varphi(\mathbf{c}^*) = 0 \) so that \( \mathbf{y} = 0 \) "corresponds" to the equilibrium \( \mathbf{c}^* \); since \( \varphi(\mathbf{c}^*) = 0 \), it follows that \( \varphi(0) = 0 \).

We must make an important point. If we could know \( \varphi(\cdot) \) completely from our experiments, then we could, in principle, compute the derivative \( \varphi'(0) : \mathbf{v} + \mathbf{v} \) of \( \varphi'(\cdot) \) at \( \mathbf{y} = 0 \). (See Section 1.2.7) In fact, we observe that computation of \( \varphi'(0) \) requires considerably less than knowledge of values that \( \varphi'(\cdot) \) takes on its entire domain. A glance at the definition of the derivative suggests that we need only know values that \( \varphi'(\cdot) \) takes in an arbitrarily small neighborhood of \( \mathbf{y} = 0 \). Loosely speaking, then, knowledge of chemical dynamics "near" the equilibrium \( \mathbf{c}^* \) suffices for computation of \( \varphi'(0) \).

We know that the function \( \varphi'(\cdot) \) takes the form of Eq. (1.67). What we do not know are the values of the parameters \( \{\kappa_1, \kappa_2, \ldots, \kappa_k\} \); everything else on the right-hand side of Eq. (1.67) pertains to the mechanism, which is presumed known. If we could find the set \( \{\kappa_1, \kappa_2, \ldots, \kappa_k\} \), then we would know all rate constants through Eq. (1.66).

Our objective, then, is to find that set.

We can find how \( \varphi'(0) : \mathbf{v} + \mathbf{v} \) relates to \( \{\kappa_1, \kappa_2, \ldots, \kappa_k\} \) by computing* that derivative from Eq. (1.67). After using Eq. (1.43) we find that for every \( \mathbf{y} \) in \( \mathbf{v} \)

\[
\varphi'(0)\mathbf{y} = \kappa_1(g_1 \cdot \mathbf{y})g_1 + \kappa_2(g_2 \cdot \mathbf{y})g_2 + \cdots + \kappa_k(g_k \cdot \mathbf{y})g_k
\]

(1.77)

Invoking our definition of dyads of vectors (Section 1.2.9) we obtain for all \( \mathbf{y} \) in \( \mathbf{v} \)

\[
\varphi'(0)\mathbf{y} = [\kappa_1\mathbf{D}(g_1) + \kappa_2\mathbf{D}(g_2) + \cdots + \kappa_k\mathbf{D}(g_k)]\mathbf{y}
\]

(1.78)

Since (1.78) holds for all \( \mathbf{y} \) in \( \mathbf{v} \), we conclude that the linear transformation \( \varphi'(0) \) is the same as the linear transformation in the brackets. That is,

\[
\varphi'(0)\mathbf{y} = \kappa_1\mathbf{D}(g_1) + \kappa_2\mathbf{D}(g_2) + \cdots + \kappa_k\mathbf{D}(g_k)
\]

(1.79)

Let us examine Eq. (1.79). It is an equation which states that one vector (i.e., \( \varphi'(0) \)) of \( L(\mathbf{v}, \mathbf{v}) \) which we can deduce, in principle, from experiments near a single equilibrium is a linear combination of other vectors of \( L(\mathbf{v}, \mathbf{v}) \) (i.e., \( \mathbf{D}(g_1), \mathbf{D}(g_2), \) etc.) which can be reconstructed from reaction vectors \( \{g_1, g_2, \ldots, g_k\} \) presumed known a priori. We seek

---

* Recall the computation executed in the second example of Section 1.2.7. We note in passing that Eq. (1.77) implies that \( \varphi'(0) \) is symmetric. That is, \( \mathbf{x} \cdot \varphi'(0)\mathbf{y} = \mathbf{y} \cdot \varphi'(0)\mathbf{x} \) for all \( \mathbf{x} \) and \( \mathbf{y} \) in \( \mathbf{v} \).
values for the scalar multipliers \( \{ \kappa_1, \kappa_2, \ldots, \kappa_k \} \).

Theorem 1.2.a tells us that this set of numbers may be determined completely if and only if

\[
\{ D(g_1), D(g_2), \ldots, D(g_k) \}
\]

(1.80)

constitutes a linearly independent set of vectors of \( L(V, V) \). If, in fact, this condition is satisfied, then determination of \( \{ \kappa_1, \kappa_2, \ldots, \kappa_k \} \) (and hence the complete set of rate constants) amounts to little more than solving Eq. (1.79).\(^*\)

We shall state a theorem:

**THEOREM 1.4.a**: The rate constants of a detailed balanced mass action kinetics for a mechanism with reactions \( \{ g_1, g_2, \ldots, g_k \} \) are completely and uniquely determined by \( \bar{F}[0] \) if and only if

\[
\{ D(g_1), D(g_2), \ldots, D(g_k) \}
\]

is a linearly independent set in \( L(V, V) \). That is, if this condition is satisfied, then the entire set of rate constants can be determined uniquely from knowledge of the chemical dynamics in an arbitrarily small neighborhood of a single equilibrium in \( V^+ \).

We can draw upon Noll’s computational criterion for independence of dyads (Section 1.2.9) to state a corollary:

**COROLLARY 1.4.b**: The rate constants of a detailed balanced mass action kinetics for a mechanism with reactions \( \{ g_1, g_2, \ldots, g_k \} \) are completely and uniquely determined by \( \bar{F}[0] \) if and only if

\[
\det \left[ (g_a \cdot g_b)^2 \right]_{a, \beta = 1, 2, \ldots, k} > 0
\]

(1.81)

**REMARK 1.4.c**: The argument leading to Theorem 1.4.a was made in terms of the variable \( \psi \) rather than \( \zeta \) merely because a discussion in terms of the concentration vector would have been somewhat awkward. Nevertheless, it may be shown that knowledge of \( \bar{F}[0] \), the derivative of \( \bar{F}(\cdot) \) at \( \psi = 0 \), is equivalent to knowledge of \( \bar{F}[\zeta^*] \), the derivative of \( \bar{f}(\cdot) \) at the equilibrium \( \zeta^* \). We need only invoke the "chain rule" for derivatives to get one from the other; however, a discussion would be beyond the scope of this article.

In fact, it may be shown that we need not know what the linear transformation \( \bar{F}[\zeta^*] \): \( V \rightarrow V \) does to every vector of \( V \) to know \( \bar{F}[0] \); it suffices to know how \( \bar{F}[\zeta^*] \) acts upon \( S \), the stoichiometric subspace, which is, of course, a linear subspace of \( V \). (The reader should not be troubled if this is not immediately apparent; the proof is not entirely easy.) That is, we need only know \( \bar{F}|_S[\zeta^*] \): \( S \rightarrow S \), what mathematicians would call the restriction

\(^*\) We have not discussed how one actually goes about solving Eq. (1.79) for \( \kappa_1, \kappa_2, \ldots, \kappa_k \). Nevertheless, we remark in passing that the solution amounts to little more than solving a system of linear scalar equations.
of $F[c^*]$ to $S$. $F_S[c^*]$: $S + S$ is that linear transformation such that, for each $y$ in $S$,

$$F_S[c^*]y = \frac{d}{dz} f(c^* + \theta y) \bigg|_{\theta = 0}$$

That the codomain of $F_S[c^*]$ can be taken to be $S$ follows from the fact that $f(\cdot)$ takes values in $S$.

In summary, then, Theorem 1.4.a and its corollary are both valid with $F_S[c^*]$ inserted in place of $F[S]$, since each is determinable from the other.

Theorem 1.4.a tells us that if the condition on the dyads of the reactions is satisfied, then not only are the rate constants completely and uniquely determinable but also they are determinable from a surprisingly small amount of information. The question, then, becomes this: Are mechanisms which satisfy the requirements of the theorem rare or common?

The fact of the matter is that mechanisms which do not satisfy the condition of the theorem are rare.

In very "qualitative" terms we can see why this might be so: If the dimension of the stoichiometric subspace is $s$, then it follows from the discussion in Section 1.2.9 that the dyads of the reactions reside in a subspace of $L(V,V)$ of dimension $(s(s + 1))$. Thus if, as for mechanism (1.68), $s = 4$, the dyads lie in a subspace of dimension 10. While the stoichiometric subspace is too small to accommodate a linearly independent set of five reactions [as in mechanism (1.68)], the five dyads of those reactions lie in a considerably larger space. Of course, this is not an argument which ensures independence of the dyads; it is merely an argument for the plausibility of their independence.

In an attempt to delineate the relationship between the algebraic structure of the reaction set and the extent to which the dyads of the reactions might be independent, Feinberg (1972, "On Chemical Kinetics...") proved theorems which do, in fact, strongly support the claim that, for most mechanisms we are likely to encounter, dependence of the dyads of the reactions is an unlikely prospect. In fact, the following theorem subsequently [Feinberg (1977, "Mechanism Deficiency..."')] emerged from that work:

**THEOREM 1.4.d:** Consider a reversible mechanism with reactions $\{g_1, g_2, \ldots, g_k\}$. If the mechanism is of deficiency zero (i.e., $\delta = n - k - s = 0$), then the set

$$\{D(g_1), D(g_2), \ldots, D(g_k)\}$$

is linearly independent. Moreover, there also exist mechanisms of deficiency in excess of zero for which that set is linearly independent.

We have asserted earlier that most mechanisms one is likely to encounter are of deficiency zero. Thus, Theorem 1.4.d assures us that, for that very large class of mechanisms, the condition of Theorem 1.4.a is satisfied. Moreover, Theorem 1.4.d tells us that even outside that class there are mechanisms such that the condition is met. For example,
the following mechanism,

\[ 2A_1 \rightleftharpoons A_2 \rightleftharpoons 2A_3 \]
\[ A_1 \rightleftharpoons A_3 \]  \hspace{1cm} (1.82)

is of deficiency 1; yet, Noll's criterion Section (1.2.9) tells us that
the dyads of the three reaction vectors constitute a linearly
independent set. Thus, the large class of zero deficiency mechanisms
resides within the still larger class of mechanisms for which rate
constants can be determined completely and uniquely from knowledge of
chemical dynamics within an arbitrarily small neighborhood of a single
equilibrium.

In light of these results we reconsider the mechanism (1.68) discussed
at the outset. In the beginning we considered the problem of determining
kinetics for that mechanism from experiments of a reasonable, if some-
what idealized, class, and we concluded that the problem was one of
discerning the contributions of individual reactions to the observed
overall dynamics. In the context of unspecified kinetics we deduced
that, because of the linear dependence of the reactions comprising the
mechanism, no experiments of the class considered would suffice to
determine the complete set of individual rate functions. Now we observe
that mechanism (1.68) is of deficiency zero since \( n = 7 \), \( s = 4 \), and
\( \ell = 3 \). (That \( \ell = 3 \) may be seen easily if the mechanism is rewritten
such that each complex appears only once.). Consequently, if the
kinetics is detailed balanced and mass action, then not only is the
complete set of 10 rate constants uniquely determinable from experiments
of the class under consideration, we need only observe chemical dynamics
in an arbitrarily small neighborhood of a single equilibrium. Equation
(1.79) serves to "disentangle" the contributions of the individual
reactions, and determination of the rate constants, from an analytic
viewpoint, amounts to little more than solution of that linear equation.

In summary, then, Theorems 1.4.a and 1.4.d take us somewhat beyond
Krambeck's result for a single "fully linked" linkage class. These
theorems tell us that for a very large class of reversible mechanisms,
including all reversible mechanisms of deficiency zero, rate constants
for detailed balanced mass action kinetics are a completely and uniquely
determinable from a surprisingly small amount of information: \( \mathbb{F}_S[\cdot] \)
evaluated at a single equilibrium, for example, suffices. Moreover,
that class of mechanisms encompasses almost all we are likely to
encounter in practice.

Nevertheless, we offer a few brief remarks regarding rate constant
determination for mechanisms which reside outside this class, unrealistic
as those might be. (It will be understood that, as before, we consider
detailed balanced mass action kinetics.) As Krambeck has shown, there
exist mechanisms [e.g., mechanism (1.73)] for which no experiments of
the type we have been considering will suffice to determine rate
constants completely and uniquely. However, there do exist mechanisms
for which rate constants are completely and uniquely determinable, but
not from knowledge of, say, \( \mathbb{F}_S[\cdot] \), evaluated at a single equilibrium
in \( V^\dagger \). Thus, the following mechanism

\[ 2A_1 \rightleftharpoons 2A_2 \]
\[ A_1 \rightleftharpoons A_2 \]  \hspace{1cm} (1.83)
does not satisfy the condition of Theorem 1.4.a or its corollary; yet the four rate constants may be determined from knowledge of the values that $F_S[\cdot]$ takes at two* equilibria in $V^+$. (Recent unpublished results obtained by Feinberg on the determinability of rate constants from knowledge of $F_S[\cdot]$ at several equilibria are not included here because, for most mechanisms, Theorem 1.4.a gives all we need.) Nevertheless, there do exist mechanisms [e.g., mechanism (1.76)] for which rate constants are completely and uniquely determinable from experiments of the type we have been considering but for which near-equilibrium information alone will not suffice: That is, even if we knew the values that $F_S[\cdot]$ takes at all equilibria in $V^+$, we would not, from that information alone, be able to deduce uniquely and completely all rate constants.

In a private communication, Krambeck (1974) has reported a generalization of his early results to mechanisms with several linkage classes, in each of which every complex is directly linked to every other complex. Moreover, the mechanisms he considers are required to have the property that if $\gamma_i$ and $\gamma_j$ are complexes which reside in different linkage classes, then $\gamma_i - \gamma_j$ does not lie in $S$.** For such mechanisms, he deduces conditions under which rate constants are completely and uniquely determinable form any experiments of the type we have been considering. Krambeck reports that, for those mechanisms he considers, rate constants are completely and uniquely determinable if and only if each linkage class, viewed as a mechanism unto itself, has deficiency zero.

Mechanism (1.83) falls into the class studied by Krambeck. Although that mechanism has deficiency 1, each of its linkage classes, viewed as a mechanism unto itself, has deficiency zero. Thus, according to Krambeck's theory, the four rate constants are uniquely determinable. Of course, this is compatible with our earlier observation that the rate constants are determinable from experiments near two equilibria.

1.4.4 Some Remarks Concerning Uses of the Theory

We have observed that, for most mechanisms we are likely to encounter, rate constants for detailed balanced mass action kinetics may be uniquely determined from the value that $F_S[\cdot]$ takes at a single equilibrium in $V^+$, say $c^*$. (See Remark 1.4.c.) We are then compelled to wonder how that linear transformation $F_S[c^*]: S \rightarrow S$ might effectively be obtained from the experiments we have been considering. One procedure is suggested by the idea that, in the vicinity of an equilibrium $c^*$, the approach to that equilibrium is governed by the "linearized" differential equation

$$\dot{c}(t) = F_S[c^*]c(t)$$  \hspace{1cm} (1.84)

[Note: We shall show in Section 1.5 that detailed balanced mass action kinetics generally admit a wealth of equilibria in $V^+$, in fact exactly one in each stoichiometric compatibility class of $V^+$.

** Recall that Krambeck takes the stoichiometric subspace and the complexes $\{\gamma_1, ..., \gamma_n\}$ to be given, not the mechanism itself. He then allows for all reactions between complexes which are stoichiometrically compatible in the sense that their differences lie in the stoichiometric subspace.]
where $\xi(t)$ is a vector of the stoichiometric subspace defined by

$$\xi(t) = \xi(t) - \xi^*$$  \hspace{1cm} (1.85)

That $\xi(t) - \xi^*$ is a vector of $S$ results from the fact that $\xi(t)$ and $\xi^*$ can lie on the same composition trajectory only if $\xi(t)$ and $\xi^*$ are stoichiometrically compatible. (Recall Section 1.3.2.)

It may be shown without excessive difficulty that, with detailed balanced mass action kinetics, there exists for the stoichiometric subspace $S$ a basis composed entirely of eigenvectors* of $F_S[c^*]$; moreover, it may be shown that the eigenvalues to which these correspond are all negative real numbers. Suppose that $\{b_1, b_2, ..., b_s\}$ is such an eigenvector basis for $S$ and that $\{\lambda_1, \lambda_2, ..., \lambda_s\}$ are the corresponding eigenvalues. Then the solution to Eq. (1.84) is

$$\xi(t) = \sum_{\theta = 1}^{s} \xi(0)e^{\lambda_\theta t} b_\theta$$  \hspace{1cm} (1.86)

where $\xi(0)$ is the $\theta$th component of $\xi(0)$ relative to the basis $\{b_1, ..., b_s\}$.

Since the eigenvalues $\{\lambda_1, ..., \lambda_s\}$ of $F_S[c^*]$ and its eigenvectors $\{b_1, b_2, ..., b_s\}$ appear explicitly in Eq. (1.86), that equation offers the hope that careful study of composition trajectories approaching the equilibrium $c^*$ might yield $\{\lambda_1, \lambda_2, ..., \lambda_s\}$ and $\{b_1, b_2, ..., b_s\}$. With these in hand, we may readily reconstruct the linear transformation $F_S[c^*]: S \to S$ as follows: If

$$y = \sum_{\theta = 1}^{s} Y_\theta b_\theta$$  \hspace{1cm} (1.87)

is any vector of $S$, then

$$F_S[c^*]y = \sum_{\theta = 1}^{s} \lambda_\theta Y_\theta b_\theta$$  \hspace{1cm} (1.88)

Having $F_S[c^*]$ we may construct $F[0]$ (see Remark 1.4.c), and if the underlying mechanism is a member of the very large class for which the condition of Theorem 1.4.a is satisfied, we may readily compute the complete set of rate constants using Eqs. (1.79) and (1.66).

Equation (1.86) does indeed enable us to obtain $\{\lambda_1, ..., \lambda_s\}$ and $\{b_1, ..., b_s\}$ from composition trajectories. In fact, we may obtain those eigenvalues and eigenvectors of $F_S[c^*]$ in a procedure highly

---

* The reader unfamiliar with differential equations of the type (1.84) or with the theory of eigenvectors might consult Nickerson et al. (1959). Alternatively, this section can be skipped over without loss in continuity.
suggestive of the Wei-Prater approach; a reasonable discussion would be beyond the scope of this chapter.

Nevertheless, we shall report results of an unpublished computer "experiment" performed at the University of Rochester. W. D. Smith simulated digitally a three-species chemical system driven by mechanism (1.82)* taken with mass action detailed balanced kinetics. The six rate constants built into the simulation were kept suitably hidden from users of the program, which enabled one to choose initial concentrations of the three species and subsequently obtain the resulting composition trajectory in its approach to equilibrium. Using the method sketched above to obtain $F_5[c^*]$ at a single equilibrium, A. Shapiro calculated the six "hidden" rate constants. Of his six calculated constants, the worst was within 4⅓% of the "true" value, while the best was within 1¾% of the true value. Of course the gulf between what we might extract from computer "experiments" and from real experiments is of ample proportions.

There should be no misunderstanding regarding the intent underlying our entire discussion of rate constant determination for intricate mechanisms. It has not been our primary purpose to suggest new experiments or to make strong arguments in support of diagnostic tools rooted in the theory. In the final analysis, these matters can be settled only by the experimentalists. Rather, it has been our intention to explore in a careful manner that which is possible in principle and to call attention to that which is not.

Readers interested in the possibility of determining mechanisms from near equilibrium experiments of the type we have considered might wish to see Feinberg, (1972, "On Chemical Kinetics..."). Readers might also wish to consult the review by Hammes and Schimmel (1970) containing a description of Manfred Eigen's brilliantly conceived near-equilibrium experiments and a survey of techniques currently in use for extracting rate constants from them. The theoretical material in that review is complementary to material presented here.

1.5 THE STABILITY OF OPEN ISOTHERMAL REACTORS WITH COMPLEX CHEMISTRY

Up to this point we have focused exclusively upon closed isothermal reactors. In this section we shall discuss the statics and dynamics of open isothermal reactors driven by intricate mechanisms, and we shall be particularly interested in the extent to which these systems can display bistability, sustained chemical oscillations, and other dynamic "exotica."

Chemical engineers have known for some time that nonisothermal reactors driven by simple mechanisms, perhaps consisting of but a single

* That mechanism is of deficiency 1 but satisfies the condition of Theorem 1.4.a. It was chosen for the study not because it reflects real chemistry, but rather because it has a mix of second- and first-order complexes and because each species is produced or consumed in four reactions as in the Wei-Prater study. At the same time it contains only three species, thereby permitting reasonable analysis of trajectories with a hand calculator.
reaction, can give rise to a multiplicity of steady states, some of which are stable, and others of which are not. Recently biologists have called to our attention the fact that even isothermal systems endowed with sufficiently complex physicochemical makeup can display similar phenomena. [The reader might wish to consult the review article by Higgins (1967).] The essential idea is that for even moderately complex isothermal systems the governing differential equations are sufficiently rich as to give rise to the possibility of unusual statics and dynamics. Here we shall discuss recent results which serve to distinguish between those systems which might exhibit pathology and those which cannot. These derive from a study initiated by Horn and Jackson (1972) and from subsequent findings obtained by Horn (1972) and Feinberg (1972, "Complex Balancing..."; 1977, "A Sufficient Condition..."; 1977 "Chemical Oscillators...").

1.5.1 Pseudoreactions and Pseudokinetics for a Class of Open Reactors

In order that results in subsequent sections be clearly understood it is essential that the reader grasps fully the ideas of "mechanism" and "kinetics" for an open reactor. It is the purpose of this section to introduce these ideas and to provide motivation for their use.

In our study of closed systems we took as a starting point the idea of mechanism, a schematic encoding of the chemistry underlying the dynamics. With the mechanism there was associated a kinetics, usually mass action, and the mechanism taken together with its kinetics served for construction, according to a prescribed formalism, of the governing differential equations. We discovered that (as in Theorem 1.3.c) mechanism structure plays an explicit and prominent role in results pertaining to the statics and dynamics to which those differential equations give rise.

Accordingly, we would like somehow to encode the physicochemical makeup of open systems in sets of reactions and pseudoreactions in the hope that we might draw connections between the statics and dynamics of an open system and the structure of its "mechanism." In this section we shall suggest a prescription for writing "mechanisms" for a class of open systems. We shall then show, by way of examples, how these mechanisms might be endowed with mass action kinetics; the "rate constants" are chosen such that mechanism and kinetics, taken with the formalism of Eq. (1.55) for construction of differential equations, give rise to precisely those equations one would write for open systems from first principles. In this way, closed and open systems are drawn into a common mathematical framework within which we might articulate relationships between statics and dynamics on one hand and "mechanism" and "kinetics" on the other.

Consider a homogeneous reactor maintained at time-invariant volume and temperature; the reactor is permitted to exchange matter with its environment in any or all of the following ways:

(A) One or more chemical species might be supplied to the reactor at constant rate.

(B) One or more chemical species might be removed from the reactor,

* Some of the discussion immediately following is taken almost verbatim from Feinberg and Horn, (1974).
each at a rate proportional to that species’ molar concentration within the reactor.

(C) One or more chemical species might be supplied to or removed from the reactor in such a manner as to keep the molar concentration of that species within the reactor constant in time.

Situations (A) and (B) are encountered in the usual operation of continuous stirred-tank reactors familiar to chemical engineers; feed of fixed composition is supplied at a constant volumetric flow rate, the concentration of each species in the efflux being identical to its concentration in the reactor. In this case, all species present in the reactor are in the efflux; this is not essential to the theory, which we intend to be broad enough to embrace situations for which the exchange of matter between the reactor and its environment is accomplished by transport through membranes rather than by convection. (In this case some species may be denied passage outward.) Situation (C) plays less of an explicit role in chemical engineering problems than it seems to play in biochemical studies. [See, for example, Walter (1966).] Nevertheless, even in chemical engineering studies condition (C) is often implicitly involved in a de facto sense. For instance, this is the case in some analyses of circumstances in which a reactant is present in such large supply that its concentration in the reactor can, for practical purposes, be regarded as time-invariant.

Open reactors of the class described above are encoded in a set of pseudoreactions in the following manner: One begins by writing down the set of chemical reactions occurring within the reactor. Then,

(A') If a species, say $A_4$, is supplied to the reactor at a constant rate, a reaction $0 + A_1$ (read “zero reacts to $A_1$”) is added to the set of chemical reactions.

(B') If a species, say $A_4$, is removed from the reactor at a rate proportional to its concentration within the reactor, one adds the reaction $A_j + 0$ (read “$A_j$ reacts to zero”).

(C') If a species, say $B_4$, is supplied or removed from the reactor in such a manner as to maintain the concentration of $B_4$ in the reactor time-invariant, then $B_4$ is "stripped" from any reactions in which $B_4$ appears. (For example, the reaction $A_1 + B_1 + 2A_2$ would be replaced by $A_1 + 2A_2$, and the reaction $A_3 + 2B_4$ would be replaced by $A_3 + 0$.)

We regard the resulting set of "reactions" as a schematic encoding of the system under study. (For closed systems that encoding is just the set of true chemical reactions.) In any case we call the resulting set of "reactions" the mechanism for the system at hand, there being no terminological distinction made between sets of "reactions" for closed and open systems.

We shall consider some examples of open systems. In each case we shall construct the appropriate mechanism and show how a mass action kinetics can be associated with the mechanism such that the formalism of Eq. (1.55) for construction of differential equations gives rise to equations we would normally write from first principles.

EXAMPLE 1: Consider a continuous stirred-tank reactor whose contents, a mixture of $A_1$ and $A_2$, are maintained homogeneous, isothermal, and of fixed volume $V$. Feed is supplied to the reactor
at volumetric flow rate $g$ with molar concentrations of $A_1$ and $A_2$ equal to $c_1^f$ and $c_2^f$, respectively; $g$, $c_1^f$, and $c_2^f$ are time-invariant. The contents of the reactor are removed at a volumetric flowrate $g$. In the reactor only the chemical reactions

$$2A_1 \xrightarrow{k} A_2 \quad \text{(1.89)}$$

occur. These reactions proceed at rates governed by mass action kinetics with rate constants as shown. The governing differential equations constructed from first principles are

\begin{align*}
\cdot \quad c_1 &= \frac{g c_1^f}{V} - \frac{g}{V} c_1 + 2 k' c_2 - 2 k c_1^2 \\
\cdot \quad c_2 &= \frac{g}{V} c_2^f - \frac{g}{V} c_2 + k c_1^2 - k' c_2 \\
\text{(1.90)}
\end{align*}

In accordance with rules (A') and (B') for constructing mechanisms for open systems, the mechanism for the reactor under consideration is

$$2A_1 \xrightarrow{k} A_2 \xrightarrow{g/V} 0 \xrightarrow{g c_1^f/V} A_1 \xrightarrow{g/V} A_2 \xrightarrow{g c_2^f/V} 0 \quad \text{(1.91)}$$

If we assign mass action kinetics to the mechanism with rate constants as shown in mechanism (1.91), then the formalism for construction of differential equations from mechanism and kinetics gives rise* to precisely Eqs. (1.90).

**EXAMPLE 2 (The Lotka System):** Consider a reactor whose contents, a mixture of $A_1$, $A_2$, $B$, and $D$, are maintained homogeneous, isothermal, and at constant volume. In the reactor there occur the reactions

$$\begin{align*}
A_1 + B &\xrightarrow{k} 2A_1 \\
A_1 + A_2 &\xrightarrow{k'} 2A_2 \\
A_2 &\xrightarrow{k''} D \\
\text{(1.92)}
\end{align*}$$

The reactions are governed by mass action kinetics with rate constants as shown in mechanism (1.92). Pure $B$ is fed to the

---

* Note that the "zero complex" is represented vectorially by the zero vector in $V$. Note also that Eq. (1.54) applied to the "zero complex" gives

$$c_0^0 = 1$$

Thus, with mass action kinetics, the rate of a reaction like $0 + A$ with rate constant $\gamma$ is just $\gamma c_0^0 = \gamma$.  

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reactor in such a manner as to maintain its concentration at a fixed level \( c_B^* \). D is removed from the reactor in such a manner as to maintain its concentration at a fixed level \( c_D^* \). The governing differential equations are

\[
\begin{align*}
\dot{c}_1 &= k_c^* c_1 - k' c_1 c_2 \\
\dot{c}_2 &= k' c_1 c_2 - k'' c_2
\end{align*}
\]  

(1.93)

where \( c_1 \) and \( c_2 \) are molar concentrations of \( A_1 \) and \( A_2 \), respectively. In accordance with rule \( (C') \) for construction of mechanisms for open systems, the mechanism for the system at hand becomes

\[
\begin{align*}
\kappa c_B^* & \quad A_1 \longrightarrow 2A_1 \\
A_1 + A_2 & \quad \kappa' \quad 2A_2 \\
A_2 & \quad \kappa'' \quad 0
\end{align*}
\]  

(1.94)

If we assign mass action kinetics to the mechanism with rate constants as shown in mechanism (1.94), then the formalism (1.55) for construction of differential equations from mechanism and kinetics gives rise to precisely Eqs. (1.93). The mechanism (1.94) is sometimes called the Lotka mechanism and has a history rooted in ecological considerations [Lotka (1920)], \( A_1 \) and \( A_2 \) representing two animal species.

EXAMPLE 3 (The Edelstein System): A homogeneous reactor whose contents are maintained at constant volume and temperature contains a mixture of species \( A_1, A_2, A_3, B, \) and \( D \). The following reactions occur on the interior of the reactor:

\[
\begin{align*}
A_1 + B & \quad \kappa_a \quad 2A_1 \\
& \quad \kappa_b \\
A_1 + A_2 & \quad \kappa_c \quad A_3 \quad \kappa_e \quad A_2 + D \\
& \quad \kappa_d \\
& \quad \kappa_f
\end{align*}
\]  

(1.95)

Reaction rates are governed by mass action kinetics; the rate constants are those shown in mechanism (1.95). Species \( B \) and \( D \) are supplied and removed in such a manner as to maintain their molar concentrations in the reactor at \( c_B^* \) and \( c_D^* \), respectively. The governing differential equations are

\[
\begin{align*}
\dot{c}_1 &= k_a c_B^* c_1 - k_b c_1^2 - k_c c_1 c_2 + k_d c_3 \\
\dot{c}_2 &= (k_d + k_e) c_3 - k_c c_1 c_2 - k_f c_D^* c_2 \\
\dot{c}_3 &= k_c c_1 c_2 + k_f c_D^* c_2 - (k_d + k_e) c_3
\end{align*}
\]  

(1.96)

The appropriate open system mechanism, obtained by applying rule \( (C') \), is
\[
\begin{align*}
\frac{\text{k}_a\text{c}_B}{\text{A}_1} & \quad \frac{\text{k}_b}{2\text{A}_1} \\
\frac{\text{k}_c}{\text{A}_1 + \text{A}_2} & \quad \frac{\text{k}_d}{\text{A}_3} \\
& \quad \frac{\text{k}_e}{\text{A}_2} \\
& \quad \frac{\text{k}_f\text{c}_D}{\text{A}_3}
\end{align*}
\]

If we associate with that mechanism mass action kinetics with rate constants as shown in mechanism (1.97), then the formalism of Eq. (1.55) for construction of differential equations gives rise to precisely Eqs. (1.96). The system described here was studied by Edelstein (1970). He took the underlying chemistry [mechanism (1.95)] to represent autocatalytic production of \text{A}_1 followed by its enzymatic degradation, the species \text{A}_2 playing the role of enzymatic agent.

These examples suggest how open systems might be assigned mechanisms endowed with mass action kinetics and how the governing differential equations are related to mechanism and kinetics in a manner reminiscent of closed systems. In fact, once that association is made, open and closed systems can be discussed in common terms. With both there are associated mechanisms and kinetics. For both we can construct in species space* the stoichiometric subspace, \text{S}, induced by the mechanism at hand in accordance with Eq. (1.24). For both we can construct the overall rate function \( f(x) \) and study dynamics governed by the differential equation

\[
\text{d}c\text{t} = f(c)
\]  

(1.98)

For both we may study the nature of static states to which Eq. (1.98) gives rise; we shall say that \( c^* \) is an equilibrium if \( f(c^*) = 0 \), there being made no terminological distinction between closed system equilibria and open system steady states. Finally, we observe that remarks in Section 1.3.2 regarding the nature of composition trajectories for closed systems apply to open systems as well: Solutions to Eq. (1.98) cannot wander promiscuously through \( V^+ \); if \( c(t) \) and \( c(t') \) are two compositions along a solution, then \( c(t) = c(t') \) must reside in \( S \), the stoichiometric subspace for the open system mechanism in question. That is, each solution to Eq. (1.98) should reside entirely within a stoichiometric compatibility class of \( V^+ \). (See Section 1.3.2.)

In summary, then, we conclude that just as the statics and dynamics of closed systems can be discussed in relation to mechanism and rate constants, so can open system statics and dynamics be so discussed. Closed and open systems are drawn into a common framework within which it becomes meaningful to raise questions regarding the relationship

* For open systems in which certain species are maintained at constant concentration those species are ignored in choosing species space. Thus, for Example 2, in which \text{A}_1, \text{A}_2, \text{B}, \text{and D} \text{ are present, species space would be chosen to be } \text{IR}^2 \text{ to reflect the idea that } \text{A}_1 \text{ and } \text{A}_2 \text{ are the only species for which we would write differential equations. In a sense } \text{B} \text{ and } \text{D} \text{ might be regarded as inerts.
between mechanism and kinetics, on one hand, and, on the other hand, statics and dynamics to which these give rise. A theory which might serve to answer those questions should clearly be broad enough to embrace mechanisms with seemingly strange "reactions" (e.g., \(0 \rightarrow A_1\), \(A_2 \rightarrow 2A_2\)) and for which the assigned kinetics violate conditions perhaps appropriate only to closed systems (e.g., detailed balance).

### 1.5.2 Chemical Statics and Dynamics: Some Examples and Some Questions

We shall now turn to consideration of the variety of statics and dynamics to which mechanisms, taken with mass action kinetics, can give rise. In the spirit of the preceding section we shall use the term "mechanism" in its broad sense, and we shall allow ourselves the liberty of examining sets of reactions and rate constants which would be offensive to our sensibilities had we focused solely upon closed systems. In fact, we shall indulge ourselves to a point some might regard as sinful: We shall even consider a mechanism with trimolecular complexes, certainly not one which might be expected to arise naturally even in the realm of open system mechanisms.

Having so expressed our culpability, let us at least enter a plea of extenuating circumstances. We wish to examine open isothermal systems which exhibit interesting phenomena: multiple steady states, sustained chemical oscillations, and the like. Those real biochemical systems which do, in fact, display unusual statics and dynamics are either poorly understood in detail or are rather complex. Thus, we are faced with a choice: On one hand, we might begin with discussion of a realistic, but highly elaborate, mechanism which displays phenomena we wish to study; for this we pay a price in obsfuscation. On the other hand, we can begin by considering systems such as those of Lotka and Edelstein, which are, in a sense, contrived but which are at once both interesting and simple, involving two or three species at most. We opt for the latter course, keeping in mind that the results we shall ultimately present are proven theorems which hold true for systems both contrived and real, both simple and complex.

Our discussion will focus primarily (but not exclusively) upon three mechanisms, each involving only two species and each taken with mass action kinetics. They are intended to display in a simple manner features shared with more realistic but more complex open system mechanisms. There are presented three figures; in each there is shown the mechanism under consideration (with rate constants), the dynamic equations constructed in accord with the formalism of Eq. (1.55), and a sketch in which are shown some equilibria, the stoichiometric subspace, and some stoichiometric compatibility classes of \(V^+\).

In Figure 1.5 we consider a very simple reversible mechanism. The stoichiometric subspace is one-dimensional and contains the vector \(\xi_2 - 2\xi_1\). The stoichiometric compatibility classes of \(V^+\) are those parts of parallels of \(S\) which lie in \(V^+\). For all choices of the positive rate constants \(k\) and \(k^r\) there exists in each stoichiometric compatibility class of \(V^+\) exactly one equilibrium toward which all trajectories originating in that class proceed in the limit with increasing time. We associate this behavior with "mundane" statics and dynamics; initial compositions in \(V^+\) which are stoichiometrically compatible all ultimately evolve toward the same equilibrium.
Figure 1.5. Mechanism Exhibiting Normal Statics and Dynamics.

It is evident from Figure 1.6 that the Lotka mechanism gives rise to considerably more exotic dynamics. The stoichiometric subspace coincides with $V$, and composition trajectories are not constrained to lie in line segments. There is only one stoichiometric compatibility class of $V^+$, that being $V^+$ itself. There is a single equilibrium in $V^+$. Trajectories originating at other compositions in $V^+$ are cyclic with a finite period of oscillation.

Figure 1.6. Statics and Dynamics of the Lotka Mechanism.
Higgins (1967) has shown by means of analog computation that mechanism (1.99) also gives rise to apparently sustained chemical oscillations for some sets of rate constants:

\[
\begin{align*}
0 & \rightarrow A_1 \\
A_1 + A_2 & \rightarrow A_3 + A_4 \\
A_3 & \rightarrow A_2 \quad \leftrightarrow A_4 + A_5 \\
A_4 + A_6 & \rightarrow A_7 \rightarrow A_6
\end{align*}
\] (1.99)

Mechanism (1.99) represents schematically part of the glycolytic pathway whereby glucose is metabolized in biological cells. For more detail, the reader might consult Higgins' article, in which a review of pertinent experimental work is offered.

In Figure 1.7 there is shown a trimolecular mechanism studied extensively by Horn and Jackson (1972). For the sake of discussion the rate constants of two reactions are set to unity, while those for the two remaining reactions are set to \( \epsilon \). The mechanism induces a one-dimensional stoichiometric subspace, and the stoichiometric compatibility classes of \( V^+ \) are those parts of parallels of \( S \) which reside in \( V^+ \). For the case \( \epsilon \geq 1/6 \) there is exhibited the "mundane" behavior akin to that in Figure 1.5. In each stoichiometric...
compatibility class of $V^+$ there is exactly one equilibrium toward which all trajectories originating in that class tend with time. For the case $0 < \epsilon < 1/6$ the situation is markedly different. In each stoichiometric compatibility class of $V^+$ there exist three equilibria; the center one is unstable, and the others are locally stable. Thus, a reactor governed by the mechanism shown in Figure 1.7 with $0 < \epsilon < 1/6$ might respond in strikingly different ways to two slightly different initial composition settings, both residing in the same stoichiometric compatibility class of $V^+$.

The Edelstein (1970) system, the mechanism for which is repeated below, shares features with the system shown in Figure 1.7.

$$A_1 \xrightarrow{2} 2A_1$$
$$A_1 + A_2 \xrightarrow{} A_3 \xrightarrow{} A_2$$

For some sets of rate constants* there exists in each stoichiometric compatibility class of $V^+$ exactly one equilibrium. For other sets of rate constants three equilibria exist in each stoichiometric compatibility class of $V^+$, one of which is unstable.

Yet, mechanism (1.101), only slightly different from the Edelstein mechanism (1.100), has the property that for all choices of rate constants there exists in each stoichiometric compatibility class of $V^+$ exactly one equilibrium, and that equilibrium is asymptotically stable**; no cyclic trajectories reside within $V^+$.

$$A_1 \xrightarrow{} 2A_1$$
$$A_1 + A_2 \xrightarrow{} A_3 \xrightarrow{} 2A_2$$

Having exhibited a variety of statics and dynamics to which different mechanisms might give rise, we are in a position to raise some questions. Apparently, some mechanisms taken with mass action kinetics exhibit unusual statics and dynamics for at least some sets of rate constants. Other mechanisms exhibit "normal" statics and dynamics for all sets of rate constants: In each stoichiometric compatibility class of $V^+$ there is exactly one equilibrium, and that equilibrium is asymptotically stable relative to initial compositions in that class; no cyclic trajectories reside within $V^+$. The questions we pose are these: Can we delineate a large class of mechanisms which, when taken with mass action kinetics, give rise to normal statics and dynamics for all sets of rate constants? For mechanisms outside that class, can we delineate sets of rate constants for which normal statics and dynamics are to be expected?

1.5.3 Quasi-thermodynamic Mass Action Kinetics: A Useful Idea

In an attempt to answer some of these questions Horn and Jackson

* Note that for the Edelstein system, as discussed in Example 3, some of the rate constants can be readily altered by choosing different values for $c_0^*$ and $c_0^-$.

** In fact, mechanism (1.101) gives rise to only one stoichiometric compatibility class of $V^+$, $V^+$ itself. The difference in behavior exhibited by the two similar mechanisms (1.100) and (1.101) was brought to the attention of the author by F. Horn.
(1972) utilized the idea of quasi-thermodynamic mass action kinetics. To explain the workings of this tool we shall require a modest amount of preliminary discussion.

Suppose that we are considering a system (open or closed) describable in terms of a mechanism taken with mass action kinetics. It is understood that the "reactions" and "rate constants" might be those appropriate to an open system in the sense of Section 1.5.1. Let us assume that the system under consideration possesses at least one equilibrium, say \( \mathbf{c}^* \), in \( V^+ \). Then, based upon \( \mathbf{c}^* \), we may construct the function \( \mu(\cdot) \) as in Eq. (1.60) to induce a change of variable, and we may subsequently rewrite the overall rate function in terms of the new variable, as in Eq. (1.63), to construct the function \( \bar{f}(\cdot) : V + V \). Given that function we may calculate for any \( \mathbf{u} \) in \( V \) the number \( \mathbf{u} \cdot \bar{f}(\mathbf{u}) \). It sometimes happens that the kinetics is such that, for all \( \mathbf{u} \) in \( V \), \( \mathbf{u} \cdot \bar{f}(\mathbf{u}) \leq 0 \) with equality holding if and only if \( \mathbf{u} \) lies in \( -S^+ \), the orthogonal complement of the stoichiometric subspace for the mechanism in question. (See Section 1.2.5.) This idea serves as motivation for a definition.

Consider a mechanism with complexes \( \{ \mathbf{y}_1, \mathbf{y}_2, \ldots, \mathbf{y}_n \} \) and stoichiometric subspace \( S \), and suppose that the mechanism is endowed with mass action kinetics. The kinetics is said to be quasi-thermodynamic* if the rate constants are such that there exists an equilibrium \( \mathbf{c}^* \) in \( V^+ \) for which

\[
\sum_{i,j=1}^{n} k_{ij}(\mathbf{c}^*) y_{je} y_{ij} (y_{i1} \cdot \mathbf{u} - y_{ij} \cdot \mathbf{u}) \leq 0
\]

(1.102)

for all \( \mathbf{u} \) in \( V \) with equality holding only if \( \mathbf{u} \) lies in \( -S^+ \). The left-hand side of Eq. (1.102) is merely \( \mathbf{u} \cdot \bar{f}(\mathbf{u}) \), where \( \bar{f}(\mathbf{u}) \) is given by Eq. (1.63).

Horn and Jackson (1972) proved the following theorem:

**THEOREM 1.5.a:** Consider a mechanism endowed with a quasi-thermodynamic mass action kinetics. Then the induced differential equations give rise to statics and dynamics with the following qualities: In each stoichiometric compatibility class of \( V^+ \) there exists exactly one equilibrium; every equilibrium in \( V^+ \) is asymptotically stable relative to the stoichiometric compatibility class in which it resides; and there can exist no cyclic composition trajectories which reside in \( V^+ \) (except for the trivial \( \mathbf{c}(\cdot) = \) constant).

* The definition offered here may be shown to be formally equivalent to that offered by Horn and Jackson. The words "an equilibrium" in our definition are redundant in the following sense: It may be shown that if a vector \( \mathbf{c}^* \) satisfies the requirements of the definition it must be an equilibrium for the kinetics in question. It may also be shown that if those requirements are met by one equilibrium in \( V^+ \) they are met by every other equilibrium in \( V^+ \).
This theorem tells us that if we can show, for a mechanism taken with mass action kinetics, that the rate constants are such that the kinetics is quasi-thermodynamic, then we should not expect statics and dynamics of the type displayed either in Figure 1.6 or in Figure 1.7 for the case \( 0 < \varepsilon < 1/6 \). This, then, is a step forward in our search for answers to questions we have posed. However, while the theorem certainly provides us with a tool, it is not one which we can use easily; it is not a simple matter to have in hand a set of rate constants and to know that the kinetics is quasi-thermodynamic. What we require are theorems which provide help in deciding that a kinetics is indeed of that class, and it is toward this end that we shall work.

For the sake of brevity we shall, in the future, refer to statics and dynamics as normal if they possess the qualities described in Theorem 1.5.a.

1.5.4 Sufficient Conditions for Normal Statics and Dynamics

In this section we shall develop conditions on kinetics and mechanism structure which ensure normality of statics and dynamics; these all derive from ideas of the last section. The reader is forewarned that the details are somewhat laborious and, to some extent, dull. Nevertheless, our efforts build toward a surprising result: Any weakly reversible mechanism of deficiency zero endowed with mass action kinetics gives rise to normal statics and dynamics, regardless of rate constants. Readers who find themselves put off by the sequence of steps leading to this result can, without serious loss in continuity, accept its truth and skip to Section 1.5.5. Those who are too guilt-ridden to do this comfortably might try a compromise: pass directly to Theorem 1.5.b or Theorem 1.5.d and read from there. As for the rest, let us proceed.

In the same paper in which they proved Theorem 1.5.a Horn and Jackson introduced the idea of complex balancing and revealed its connection with quasi-thermodynamicity. With the considerable benefit of insight afforded by their work, Feinberg (1975, "A Sufficient Condition ...") was able to broaden their results somewhat to obtain a theorem which shows as a special case the quasi-thermodynamic character of complex balanced mass action kinetics. Since the broader results may be obtained in a fairly straightforward manner, we shall sketch their derivation here. Nevertheless, the original results of Horn and Jackson remain the key to part 3 of Theorem 1.5.h, perhaps the most intriguing of our theorems on reactor stability.

To obtain the broadened results we begin by considering a mechanism with complexes \( \{Y_1, Y_2, \ldots, Y_n\} \) and stoichiometric subspace \( S \). We presume the mechanism to be endowed with mass action kinetics. Suppose that the rate constants are such that there exists a vector \( \xi^* \) in \( V^* \) with the property

\[
\sum_{i,j=1}^{n} k_{ij}(\xi^*) Y_j (e^{Y_i - Y_j}) \leq 0 \quad \text{for all } \mu \text{ in } V \quad (1.103)
\]

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We wish to show that this ensures that the kinetics is quasi-thermodynamic. Once this is done we shall put Eq. (1.103) in a simpler form. We begin with the following observation regarding the exponential function: If \( \theta \) and \( \phi \) are real numbers, then

\[
e^{\phi} (\phi - \theta) \leq e^\phi - e^\theta
\]

with equality holding if and only if \( \phi = \theta \). By invoking this inequality termwise we may write that, for all \( \phi \) in \( \mathbb{V} \),

\[
\sum_{i,j=1}^{n} k_{ij}(\zeta^*) \phi_{ij} \phi_{ij} (\phi_{i} \cdot \phi_{j} - \phi_{j} \cdot \phi_{j}) \leq \sum_{i,j=1}^{n} k_{ij}(\zeta^*) \phi_{ij} (e^{\phi_{i} \cdot \phi_{j}} - e^{\phi_{j} \cdot \phi_{j}})
\]

(1.105)

Let us explore conditions under which equality can hold in Eq. (1.105). Since each term in the sum on the right exceeds or is equal to the corresponding term in the sum on the left, the equality can hold in Eq. (1.105) for some \( \phi \) if and only if equality holds termwise. But, because of the nature of Eq. (1.104), this can happen if and only if, for each term, \( \phi_{i} \cdot \phi_{j} = \phi_{j} \cdot \phi_{j} \), or, equivalently, if and only if \( \phi_{i} - \phi_{j} \cdot \phi_{i} = 0 \). Since terms in the sum are those for which \( j + i \), we can conclude that equality holds in Eq. (1.105) for some \( \phi \) in \( \mathbb{V} \) if and only if \( \phi \) is orthogonal to all vectors of the form \( \phi_{i} - \phi_{j} \), where \( j + i \) -that is, if and only if \( \phi \) is orthogonal to all reaction vectors of the mechanism at hand. In turn, this implies that equality holds in Eq. (1.105) if and only if \( \phi \) lies in \( \mathbb{S}^+ \), where, as usual, \( \mathbb{S} \) is the span of the reaction vectors. (Recall the discussion at the close of Section 1.2.5.)

Now suppose that Eq. (1.103) holds. Then Eq. (1.105) implies that there exists a vector \( \zeta^* \) in \( \mathbb{V}^+ \) such that, for all \( \phi \) in \( \mathbb{V} \),

\[
\sum_{i,j=1}^{n} k_{ij}(\zeta^*) \phi_{ij} \phi_{ij} (\phi_{i} \cdot \phi_{j} - \phi_{j} \cdot \phi_{j}) \leq 0
\]

(1.106)

To prove that the kinetics is quasi-thermodynamic it remains to be shown that equality holds in Eq. (1.106) only for those \( \phi \) which lie in \( \mathbb{S}^+ \). Suppose that for some \( \phi \) in \( \mathbb{V} \) the equality holds in Eq. (1.106). Then Eqs. (1.103) and (1.105) imply that equality must hold* in Eq. (1.105) for that \( \phi \). But we have established that equality holds in Eq. (1.105) only for those \( \phi \) which reside in \( \mathbb{S}^+ \).

Hence, we have established that the existence of \( \zeta^* \) in \( \mathbb{V}^+ \) at which Eq. (1.103) holds ensures that the kinetics is quasi-thermodynamic. Now we may regroup terms in Eq. (1.103) to restate that condition as follows:

* In fact, both sides of Eq. (1.105) must be zero.
\[
\sum_{i=1}^{n} g_i(c^*) e^{y_i} \leq 0 \text{ for all } y \text{ in } V \tag{1.107}
\]

where \( g_i(*) \) is the \( i \)th complex formation function defined by Eq. (1.56). In turn, this condition may be shown to be equivalent to

\[
\sum_{i=1}^{n} g_i(c^*) e^{y_i} \leq 0 \text{ for all } c \text{ in } V^+ \tag{1.108}
\]

Thus, the existence of a vector \( c^* \) in \( V^+ \) such that either Eq. (1.107) or (1.108) holds suffices for a mass action kinetics to be quasi-thermodynamic. This result constitutes a part of a theorem [Feinberg, (1977, "A Sufficient Condition ...")].

**THEOREM 1.5.b:** Consider an \( n \) complex mechanism endowed with mass action kinetics, and let \( g_i(*) : V^+ \rightarrow \mathbb{R} \) be the \( i \)th complex formation function constructed from the kinetics in accordance with Eq. (1.56). If there exists in \( V^+ \) a vector \( c^* \) such that

\[
\sum_{i=1}^{n} g_i(c^*) e^{y_i} \leq 0 \text{ for all } c \text{ in } V^+ \tag{1.109}
\]

then \( c^* \) is an equilibrium of the kinetics, and the kinetics is quasi-thermodynamic. Moreover, if there exists in \( V^+ \) a single equilibrium \( c^* \) such that the condition (1.109) is satisfied then that condition is satisfied for any other equilibrium in \( V^+ \).

We invoke Theorems 1.5.a and 1.5.b to state the following:

**THEOREM 1.5.c:** For a mechanism endowed with a mass action kinetics satisfying the condition of Theorem 1.5.b the induced differential equations give rise to normal statics and dynamics.

To use Theorem 1.5.c for a mechanism taken with mass action kinetics with specified rate constants we must ascertain the existence of an equilibrium \( c^* \) in \( V^+ \) for which Eq. (1.109) is satisfied. [If Eq. (1.109) is not satisfied for one equilibrium in \( V^+ \), it will not be satisfied for any other.] If the existence of such an equilibrium is affirmed, then we can be certain that the system at hand cannot exhibit "abnormal" statics and dynamics.

Thus, the condition for normality provided by Theorem 1.5.c requires the computation of an equilibrium \( c^* \) in \( V^+ \) (if one exists); with such an equilibrium in hand we may readily compute the numbers \( g_i(c^*) \), \( i = 1, 2, \ldots, n \). Subsequently, we must ascertain that the condition

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(1.109) is satisfied. This amounts to determining whether a polynomial (usually of order no higher than 2) in molar concentrations can take positive values with positive arguments. Without benefit of additional theory this need not be a simple matter, but it is considerably easier than affirming quasi-thermodynamicity directly. For reasonably simple mechanisms Eq. (1.109) can usually be tested in an ad hoc fashion without excessive difficulty. Additional help is afforded by theory presented in Feinberg (1977), "A Sufficient Condition ... "). Moreover, Horn has communicated to the author a test for Eq. (1.109) when complexes are no more than bimolar in nature; his test, applicable to very complex mechanisms, is readily effected with the help of a digital computer.

In light of perspective afforded by Theorems 1.5.b and 1.5.c, the striking prior results obtained by Horn and Jackson (1972) emerge as an important special case. Suppose that the kinetics in question is complex balanced. Then, by definition, there exists in \( V^+ \) an equilibrium \( c^* \) for which \( g_j(c^*) = 0, \ i = 1, 2, \ldots, n \), and the requirements of Theorem 1.5.b are easily met. Hence, we may state a theorem first proved by Horn and Jackson:

**THEOREM 1.5.d:** Consider a mechanism endowed with complex balanced mass action kinetics. The kinetics is quasi-thermodynamic, and the induced differential equations give rise to normal statics and dynamics.

As has been mentioned in our earlier discussion of complex balancing, Horn (1972) derived necessary and sufficient conditions on the interplay of rate constants and mechanism structure in order that a kinetics be complex balanced. Thus, Horn's conditions become sufficient conditions for normal statics and dynamics. However, it should be mentioned that, although the hypothesis of Theorem 1.5.b can be satisfied for mechanisms which are not weakly reversible, the hypothesis of Theorem 1.5.d cannot. This follows from Theorem 1.3.a. Nevertheless, by exploiting a certain technique suggested by Horn and Jackson (i.e., "macroequivalence") Theorem 1.5.d may still be of help in establishing normality for situations in which the underlying mechanism is not weakly reversible. This technique will be discussed briefly at the close of Section 1.5.6.

Theorem 1.5.d has an immediate corollary. Since every detailed balanced kinetics is complex balanced, we have

**COROLLARY 1.5.e:** Consider a reversible mechanism endowed with detailed balanced mass action kinetics. The kinetics is quasi-thermodynamic, and the induced differential equations give rise to normal statics and dynamics.

Underlying our introductory discussion pertaining to exotic statics and dynamics was the unstated belief that abnormal phenomena would be exhibited only by open systems. If we embrace the view held by some physical chemists that true kinetics for closed systems are detailed balanced, then Corollary 1.5.e provides support for our instinctual feeling that closed mass action systems can display only normal statics.
and dynamics. It is only for mass action kinetics not constrained by
detailed balance that we might find static and dynamic exotics; for
mass action pseudokinetics appropriate to open systems this constraint
has no clearly compelling justification.

Now let us explore the relationship between Theorem 1.5.d and
Theorem 1.3.e of Section 1.3.5. The first of these tells us that a
mechanism endowed with complex balanced mass action kinetics can give
rise only to normal statics and dynamics. On the other hand, Theorem
1.3.e tells us that for a weakly reversible mechanism of deficiency
zero every mass action kinetics, regardless of rate constants, is
complex balanced. Thus, the two theorems taken together provide a
remarkable consequence: Any weakly reversible mechanism of deficiency
zero endowed with mass action kinetics gives rise to normal statics and
dynamics, regardless of rate constants.

1.5.5 Composition Cycles and Equilibria: Some Further Thoughts

Very well. We have established that weakly reversible mechanisms of
deficiency zero endowed with mass action kinetics can give rise only to
normal statics and dynamics, regardless of values that the individual
rate constants take. But if we wish to know whether a mechanism of
deficiency zero which is not weakly reversible might, for example, give
rise to a cyclic composition trajectory, we have, as yet, no analogous
results which offer any help.

This situation is, in a sense, unsatisfying. There is currently
considerable interest in chemical oscillations, part of which is
reflected in attempts to construct mechanisms to model experimentally
observed oscillatory phenomena. Like the Lotka mechanism (1.94) and
Higgins' mechanism (1.99) for glycolysis, the mechanisms currently
under study are generally not weakly reversible. Of course what we
would like is a criterion for distinguishing, on one hand, between
mechanisms which might model systems giving rise to sustained
oscillations and, on the other hand, those which cannot. In view of the
nature of models currently in vogue, we would like whatever theorems we
might prove to be broad enough to embrace mechanisms which are not
weakly reversible.

Hence, we are compelled to wonder whether mechanisms of deficiency
zero which are not weakly reversible can, when taken with mass action
kinetics, give rise to cyclic composition trajectories. We already
know, by virtue of Theorem 1.3.c, that these mechanisms cannot admit
equilibria in $V^+$, and, to some extent, this is a source of our
difficulty: Let us remember that most results on stability to this
point flowed from Theorem 1.5.a on quasi-thermodynamic kinetics. But,
remember also that a kinetics can be quasi-thermodynamic only if there
exists for it an equilibrium in $V^+$. Thus, it is no surprise that a
theoretical line emanating from Theorem 1.5.a yields nothing decisive
regarding zero deficiency mechanisms which are not weakly reversible.

Pursuing a different line, Feinberg (1977, "Chemical Oscillations ...
"") was able to show that a certain class of mechanisms, when taken
with arbitrary kinetics, cannot give rise to composition cycles in $V^+$;

* See, for example, the mechanism put forth by Field and Noyes (1974)
to explain the apparently oscillatory Belousov-Zhabotinskii system.
This class includes all mechanisms of deficiency zero which are not weakly reversible. On the other hand, it includes no mechanisms which are weakly reversible. Thus, the theory of the last section and the theory we are about to explore are, in a sense, complementary.

Let us consider a mechanism with complexes \( \{y_1, y_2, \ldots, y_n\} \), and let us suppose that our mechanism is endowed with a kinetics, mass action or otherwise. That is, we presume (as in Section 1.3.2) that there is associated with every reaction of our mechanism a rate function; we denote by \( f_{ij}(\cdot): V^+ \to \mathbb{R}^+ \) the rate function associated with the reaction whereby the \( j \)th complex reacts to the \( i \)th complex. Remember that we require of rate functions that they take nonnegative values everywhere on \( \overline{V^+} \) and strictly positive values on \( V^+ \). That is, \( f_{ij}(c) \geq 0 \) for all \( c \) in \( \overline{V^+} \), and \( f_{ij}(c) > 0 \) for all \( c \) in \( V^+ \).

Let us also suppose that rate functions are required to be continuous. When we speak of arbitrary kinetics, we shall mean a kinetics subject only to these constraints.

In accordance with the formalism of Section 1.3.2 our system is governed by the differential equation (1.36), of which Eq. (1.37) is a consequence. Now suppose that Eq. (1.36) admits a continuous solution in \( \overline{V^+} \) which contains a cycle. That is, suppose that a solution (in \( V^+ \)) to Eq. (1.36) has the property that at two distinct instants, \( t \) and \( t' \), it is true that \( c(t) = c(t') \). Then it follows from Eq. (1.37) that

\[
0 = \sum_{i,j=1}^{n} \int_{t'}^{t} f_{ij}(c(\tau)) \, d\tau \, (y_i - y_j) \tag{1.110}
\]

Since the rate functions are required to take nonnegative values everywhere on \( V^+ \), it follows that the integrals in the sum cannot be negative. Indeed, if somewhere along our cycle \( c(\tau) \) (where \( t' \leq \tau \leq t \)) lies in \( \overline{V^+} \), then all the integrands take positive values, whereupon all the integrals are positive. Hence, for our mechanism to give rise to a composition cycle with a point in \( V^+ \) it is necessary, at the very least, that the equation

\[
0 = \sum_{i,j=1}^{n} a_{ij} (y_i - y_j) \tag{1.111}
\]

admit a strictly positive solution. That is, there must exist a set of positive numbers \( \{a_{ij}\} \), one for each reaction, such that Eq. (1.111) is satisfied.

In fact, this is also a necessary condition for a mechanism, taken with arbitrary kinetics, to give rise to an equilibrium in \( V^+ \). This follows from Eq. (1.35): Suppose that \( c^* \) in \( V^+ \) is such that \( f(c^*) = 0 \). Then Eq. (1.35) implies that

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\[
0 = \sum_{i,j=1}^{n} f_{ij}(\xi^*)(y_i - y_j)
\]  

(1.112)

Since \( \xi^* \) is in \( V^+ \), each rate function is required to take a positive value at \( \xi^* \), so that the numbers \( f_{ij}(\xi^*) \) in Eq. (1.112) are all positive. Hence, for \( \xi^* \) in \( V^+ \) to be an equilibrium it is necessary, at the very least, that Eq. (1.111) have a strictly positive solution.

These ideas lead to the following theorem:

**Theorem 1.5.f**: An arbitrary kinetics for a mechanism with complexes \( \{y_1, y_2, \ldots, y_n\} \) can give rise to an equilibrium in \( V^+ \) or to a composition cycle in \( V^+ \) with a point in \( V^+ \) only if the mechanism is such that the equation

\[
\sum_{i,j=1}^{n} a_{ij}(y_i - y_j) = 0
\]

admits a strictly positive solution \( \{a_{ij}\}_{i,j=1}^{n} \).

It is readily shown that any weakly reversible mechanism satisfies this condition, so that Theorem 1.5.f tells us almost nothing about mechanisms of this class. It is for mechanisms which are not weakly reversible that Theorem 1.5.f offers some utility.

In fact, let us see how this theorem enables us to draw conclusions about mechanisms of deficiency zero. We need the following lemma, proof* of which is not trivial: A mechanism of deficiency zero satisfies the condition of Theorem 1.5.f if and only if it is weakly reversible. Since mechanisms of deficiency zero which are not weakly reversible cannot satisfy this criterion, we are led to the following extension of Theorem 1.3.c:

**Theorem 1.5.g**: For a mechanism of deficiency zero which is not weakly reversible, no kinetics can give rise to an equilibrium in \( V^+ \) or to composition cycle in \( V^+ \) with a point in \( V^+ \).

We note in passing that the class of mechanisms which fail to satisfy the condition of Theorem 1.5.f is larger than the class of mechanisms embraced by Theorem 1.5.g. To cite a trivial example, let us consider the following mechanism:

---

* The proof draws upon ideas similar to those in papers by Horn (1972) and Feinberg (1972, "Complex Balancing ") and closely resembles the proof of Theorem 1.3.c.
This mechanism is of deficiency 1 \( (n = 6, \xi = 3, s = 2) \). The reaction vectors are \( \mathbf{e}_2 - \mathbf{e}_1, \mathbf{e}_4 - \mathbf{e}_3, \) and \( \mathbf{e}_2 + \mathbf{e}_4 - (\mathbf{e}_1 + \mathbf{e}_3) \), and it is clear that no strictly positive linear combination of these yields the zero vector. Hence, Theorem 1.5.f serves to preclude equilibria in \( V^+ \) and composition cycles (of the type described) for a larger class of mechanisms than does Theorem 1.5.g.

Let us cite an example of a mechanism which is not weakly reversible but which does satisfy the condition of Theorem 1.5.f. (By virtue of Theorem 1.5.g such a mechanism must have deficiency in excess of zero.) Indeed, the Lotka mechanism (1.94), which has deficiency 1, gives rise to an equilibrium in \( V^+ \) and to cycles in \( V^+ \), so that it must satisfy the condition of Theorem 1.5.f. The reaction vectors are:

\[ 2\mathbf{e}_2 - \mathbf{e}_1 = \mathbf{e}_1, \quad 2\mathbf{e}_2 - (\mathbf{e}_1 + \mathbf{e}_2) = \mathbf{e}_2 - \mathbf{e}_1, \quad \text{and} \quad 0 - \mathbf{e}_2 = -\mathbf{e}_2. \]

Since \((1)\mathbf{e}_1 + (1)(\mathbf{e}_2 - \mathbf{e}_1) + (1)(-\mathbf{e}_2) = 0\), the condition is satisfied.

Before we close this section, let us make an observation. We have taken the domain of the rate functions \( f_{ij}(\cdot) \) to be \( V^+ \), reflecting the idea that we presumed rates of reactions to depend only on mixture composition. In a more ambitious analysis, perhaps for nonisothermal systems, we would allow these to depend on other variables as well. In such an undertaking we might still presume that the rate functions take only nonnegative values and positive values whenever the concentration vector resides in \( V^+ \). Equation (1.36) would still govern our mixture composition, except that the rate functions would have augmented arguments, and Eq. (1.37) would hold as well, modified accordingly. Despite these modifications, the discussion contained within this section would carry over completely to the more general situation, and Theorems 1.5.f and 1.5.g would still obtain.

One further remark: The discussion in this section centered about an arbitrary kinetics. Had we focused upon mass action kinetics, stronger results could have been deduced. However, these are beyond the scope of this chapter.

1.5.6 The Zero Deficiency Theorem

Now let us gather together what we know about the essentially stable character of systems driven by mechanisms of deficiency zero*:

**THEOREM 1.5.h:** Consider a mechanism for which the number of complexes is \( n \), for which the number of linkage classes is \( \xi \), and for which the stoichiometric subspace has dimension \( s \). Suppose

---

* As stated, the theorem leaves unresolved some questions regarding the possibility of composition cycles which reside entirely within the boundary of \( V^+ \) or, in the case of weakly reversible mechanisms, the possibility of a composition cycle which reside partially in \( V^+ \). In fact, it may be shown that mechanisms of deficiency zero, weakly reversible or otherwise, cannot give rise to any nontrivial composition cycles when taken with mass action kinetics.
that \( n - l - s = 0 \); that is, suppose that the mechanism has deficiency zero. Then the following statements hold true:

1. If the mechanism is not weakly reversible, then for arbitrary kinetics (mass action or otherwise), the induced dynamic equations cannot give rise to an equilibrium in \( V^+ \).
2. If the mechanism is not weakly reversible, then for arbitrary kinetics (mass action or otherwise), the induced dynamic equations cannot give rise to a composition cycle in \( V^+ \) containing a point in \( V^+ \).
3. If the mechanism is weakly reversible, then for mass action kinetics with any choice of positive rate constants there exists in each stoichiometric compatibility class of \( V^+ \) exactly one equilibrium composition, every equilibrium composition in \( V^+ \) is asymptotically stable relative to the stoichiometric compatibility class in which it resides, and the dynamic equations cannot give rise to a composition cycle in \( V^+ \) [except the trivial \( \zeta(\cdot) = \text{constant} \)].

This theorem, in its various parts, is due to Horn, Jackson, and Feinberg. An earlier version was reported by Feinberg and Horn (1974) at a time when part 2 had yet to be proven, although it was conjectured that its content held true for mass action kinetics. It should be borne in mind that Theorem 1.5.h represents merely part of what we know. Thus, Theorem 1.5.f can be used to preclude the possibility of composition cycles generated by some mechanisms of positive deficiency. And for mechanisms of positive deficiency, Theorems 1.5.c and 1.5.d serve to delineate sets of rate constants (in the context of mass action kinetics) for which normal statics and dynamics are assured. Hence, the theory takes us a considerable way toward answers to questions like those posed at the close of Section 1.5.2.

Let us examine some mechanisms to see what light our theory sheds. Most of these we have encountered before.

We begin by considering two mechanisms, differing only in their "arrow" structure:

\[
\begin{align*}
A_1 & \longrightarrow A_2 \\
A_1 + A_3 & \longrightarrow A_4 \\
& \quad \downarrow
A_2 + A_5 \\
& \quad \downarrow
A_1 & \longrightarrow A_2 \\
A_1 + A_3 & \longrightarrow A_4 \\
& \quad \downarrow
A_2 + A_5
\end{align*}
\] (1.114) (1.115)
Both mechanisms are of deficiency zero (\( n = 5, \ell = 2, s = 3 \) for both), so that both are embraced by Theorem 1.5.h. Mechanism (1.114) is not weakly reversible; hence, no kinetics (mass action or otherwise) for it can give rise to an equilibrium in \( \mathbb{V}^+ \) or to a composition cycle in \( \overline{\mathbb{V}}^+ \) with a point in \( \mathbb{V}^+ \). On the other hand, mechanism (1.115) is weakly reversible. With mass action kinetics (for any choice or rate constants) not only is there an equilibrium in \( \mathbb{V}^+ \), but there is exactly one in each stoichiometric compatibility class of \( \mathbb{V}^+ \); only normal statics and dynamics are to be expected.

Now let us examine two mechanisms which differ only in one complex:

\[
\begin{align*}
A_1 & \rightleftharpoons 2A_1 \\
A_1 + A_2 & \rightleftharpoons A_3 \rightleftharpoons 2A_2
\end{align*}
\]  

(1.116)

\[
\begin{align*}
A_1 & \rightleftharpoons 2A_1 \\
A_1 + A_2 & \rightleftharpoons A_3 \rightleftharpoons A_2
\end{align*}
\]  

(1.117)

The first of these is reversible (and therefore weakly reversible) and is of deficiency zero (\( n = 5, \ell = 2, s = 3 \)). Part 3 of Theorem 1.5.h tells us that, with mass action kinetics, we can expect normal statics and dynamics for all sets of rate constants. On the other hand, the Edelstein mechanism (1.117) is weakly reversible but of deficiency 1 (\( n = 5, \ell = 2, s = 2 \)). It is not embraced by Theorem 1.5.h. Indeed, for some sets of rate constants (in the context of mass action kinetics) the Edelstein mechanism gives rise to three equilibria in each stoichiometric compatibility class of \( \mathbb{V}^+ \); two of these are asymptotically stable, while the third is unstable. (See Figure 1.7, \( 0 < \epsilon < 1/6 \), for a qualitatively similar situation.)

Let us turn to examples of mechanisms which give rise to composition cycles. Both the Lotka mechanism (shown in Figure 1.6) and Higgins' mechanism (1.99) for glycolysis give rise to sustained chemical oscillations. Since these mechanisms are of deficiency 1, composition cycles are not precluded by Theorem 1.5.h. Indeed, both mechanisms satisfy the necessary condition for oscillations articulated in Theorem 1.5.f. Moreover, Figure 1.6 tells us that mechanisms of positive deficiency can give rise to equilibria in \( \mathbb{V}^+ \) even if they are not weakly reversible.

Theorem 1.5.h is generous in the breadth of systems which it encompasses. Nevertheless, there are mechanisms lying outside the class it covers which, when taken with mass action kinetics, also give rise to normal statics and dynamics for all choices of rate constants. For example the simple, albeit unrealistic, mechanism

\[
\begin{align*}
2A_1 & \rightarrow A_1 + A_2 \leftarrow 2A_2
\end{align*}
\]  

(1.118)

is neither weakly reversible nor of deficiency zero. Yet, for all choices of rate constants normal statics and dynamics result. * That is,  

* In fact, it can be shown that the hypothesis of Theorem 1.5.b is satisfied for all choices of rate constants; hence, normal statics and dynamics are assured by Theorem 1.5.c.
the conclusion of Theorem 1.5.1, part 3, remains true, although its hypothesis is not satisfied. Hence, this example suggests the existence of theorems, as yet unreported, which ensure normal statics and dynamics under weaker conditions than those afforded by Theorem 1.5.1.

Finally, let us consider a mechanism which, in the context of mass action kinetics, displays normal statics and dynamics for some sets of rate constants but not for others, and let us see how Theorems 1.5.c and 1.5.d help us to delineate sets of rate constants for which normal statics and dynamics are assured. The mechanism shown in Figure 1.7 is weakly reversible but of deficiency 2 (n = 4, \( l = 1, s = 1 \)); hence, it falls outside the class embraced by part 3 of Theorem 1.5.1. Indeed, when \( 0 < \varepsilon < 1/6 \) three equilibria reside in each stoichiometric compatibility class of \( V^+ \), although normal statics and dynamics obtain for \( \varepsilon \geq 1/6 \).

It may be shown that the condition of Theorem 1.5.b is satisfied if and only if \( \varepsilon \geq 1 \). (Complex balancing obtains if and only if \( \varepsilon = 1 \).) Hence, for \( \varepsilon \geq 1 \), normality in statics and dynamics is ensured by Theorem 1.5.c. While this result "covers" a decent range, it is certainly clear that Theorems 1.5.b and 1.5.c do not serve to delineate completely the full range of rate constants for which statics and dynamics are normal. In particular, the range \( 1/6 \leq \varepsilon \leq 1 \) is left "uncovered."

However, Horn and Jackson (1972) have shown how some ideas in Section 1.4 might be exploited to broaden results obtainable from theorems such as 1.5.b and 1.5.d. In Section 1.4.2 we showed how it sometimes happens that, in the context of mass action kinetics, different sets of rate constants for the same mechanism give rise to identical dynamical equations and, consequently, to identical statics and dynamics. (In terminology used by Horn and Jackson, the two systems are macro-equivalent.) Thus, if a set of rate constants may be shown to give rise to the same differential equations as does a set for which the kinetics is complex balanced, then the original set can give rise only to normal statics and dynamics. Skillfully exploiting this idea, Horn and Jackson showed that even the special Theorem 1.5.d suffices, for the system shown in Figure 1.7, to ensure normality in the range \( \varepsilon \geq 1 \). The more general Theorem 1.5.c may be similarly broadened.

In summary, then, we have explored the variety of statics and dynamics which might be displayed by open chemical systems; we have seen that some of these might exhibit peculiar behavior; and we have presented theorems which serve to distinguish between those which might display pathology and those which cannot.

1.6 CONCLUDING REMARKS

In Sections 1.4 and 1.5 we examined two areas related to chemical reaction networks with intricate structure, and, at first glance, the two seemed disjoint. Yet, we have seen that the large class of zero deficiency mechanisms plays a surprisingly prominent role in both. In their use of "macroequivalence" to strengthen results on reactor stability, Horn and Jackson touched upon one facet of the manner in which the two areas intertwine. But somehow we are left with the
feeling that there is more to all this than easily meets the eye. Indeed, the emergence of common ideas in different lines of inquiry and the subtle interplay between those lines encourage belief that there is theory of greater depth yet to be uncovered. It remains to be seen what turn future developments will take.

ACKNOWLEDGMENT

The author wishes to express gratitude to F. J. M. Horn for countless hours of stimulating discussion, to John Friedly and Arnold Shapiro for valuable criticism in preparation of the manuscript, and to the Camille and Henry Dreyfus Foundation for support in the form of a Teacher-Scholar Grant.

REFERENCES


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NOMENCLATURE

$A_1, A_2, \ldots, A_M$ molecular species

$B_1, B_2, \text{etc.}$ molecular species

$C_L$ concentration of the $L$th species, moles/vol.

$D$ molecular species

$D(g)$ dyad of $g$; see Section 1.2.9

$\xi_1, \xi_2, \ldots, \xi_M$ natural basis for $\mathbb{R}^M$

$f_{ij}(-), \hat{f}_{ij}(-)$ rate function for the reaction $j + i$, moles/time-vol.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f(\cdot)$, $\hat{f}(\cdot)$</td>
<td>overall rate function, moles/time-vol.</td>
</tr>
<tr>
<td>$g$</td>
<td>volumetric flow rate, vol./time</td>
</tr>
<tr>
<td>$g_i(\cdot)$</td>
<td>complex formation rate function for the $i$th complex, moles/time-vol.</td>
</tr>
<tr>
<td>$g_\alpha$</td>
<td>vector representing the $\alpha$th reaction pair with assigned direction</td>
</tr>
<tr>
<td>$g_{ap}$, $g_{ar}$</td>
<td>product and reactant complexes of the $\alpha$th pair reaction</td>
</tr>
<tr>
<td>$k_1$, $k_2$, $k_3$, etc.</td>
<td>rate constants</td>
</tr>
<tr>
<td>$k_{ij}$, $k_a$, $k_b$, etc.</td>
<td>rate constants</td>
</tr>
<tr>
<td>$\ell$</td>
<td>number of linkage classes in a mechanism</td>
</tr>
<tr>
<td>$M$</td>
<td>number of species in a mixture</td>
</tr>
<tr>
<td>$n$</td>
<td>number of complexes in a mechanism</td>
</tr>
<tr>
<td>$0$</td>
<td>zero complex</td>
</tr>
<tr>
<td>$\mathbf{0}$</td>
<td>zero vector</td>
</tr>
<tr>
<td>$r_\alpha(\cdot)$</td>
<td>net rate function for the $\alpha$th reaction pair</td>
</tr>
<tr>
<td>$s$</td>
<td>dimension of the stoichiometric subspace</td>
</tr>
<tr>
<td>$S$</td>
<td>stoichiometric subspace</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$V$</td>
<td>species space</td>
</tr>
<tr>
<td>$V^+$</td>
<td>positive orthant of $V$</td>
</tr>
<tr>
<td>$\overline{V^+}$</td>
<td>nonnegative orthant of $V$</td>
</tr>
<tr>
<td>$\gamma_i$</td>
<td>$i$th complex in a mechanism</td>
</tr>
</tbody>
</table>

**Greek symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon$</td>
<td>rate constant in Figure 1.7 (moles$^{-2}$-time$^{-1}$-vol.$^{-1}$)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>deficiency of a mechanism ($\equiv n - \ell - s$)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>time</td>
</tr>
</tbody>
</table>