

**GLOBAL SENSITIVITY ANALYSIS OF NONLINEAR CHEMICAL
KINETIC EQUATIONS USING LIE GROUPS:
II. SOME CHEMICAL AND MATHEMATICAL PROPERTIES
OF THE TRANSFORMATION GROUPS**

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Abstract

This paper establishes a number of properties of transformation groups that map elementary kinetic equations into new elementary kinetic equations with altered rate constants. The chemical significance of the transformations is assessed by applying them to systems involving two reacting species. There are then twelve one-parameter groups of mappings. Some mappings may be used to study the effects of changes in input/output fluxes on concentrations and their compensation by changes in other rate constants. A number of mappings transform nonlinear kinetics into approximately linear kinetics valid in regions larger than those obtained by standard methods. In some cases, the linearization is globally exact. Some mappings create lumped concentration variables and may be used to systematically reduce the number of manifest concentration variables in nonlinear, as well as linear, kinetic equations. The global mappings may be characterized by the functions of rate constants and functions of concentrations that they leave invariant. Although they produce large changes in rate constants and concentrations, none of these mappings change the topology of concentration phase plots as they map a phase plot determined by one set of initial conditions and rate constants into that determined by transformed initial conditions and rate constants. Metrical properties of the concentration maps generally depend upon the accuracy with which the group generators are approximated: systematic methods for their improvement are sketched.

1. Introduction

This paper is devoted to the assessment of key chemical and mathematical properties of the transformations determined in the preceding paper [1], hereafter referred to as I. To this end, we begin by considering kinetic systems with two constituents, present in concentrations x_1 and x_2 . Using the same notation for rate constants used in I, we will thus begin with transformations of the equations

$$\begin{aligned} dx_1/dt &= k_{10} + k_{11} x_1 + k_{12} x_2 + k_{111} x_1 x_1 + k_{112} x_1 x_2 + k_{122} x_2 x_2 \\ dx_2/dt &= k_{20} + k_{21} x_1 + k_{22} x_2 + k_{211} x_1 x_1 + k_{212} x_1 x_2 + k_{222} x_2 x_2 . \end{aligned} \quad (1.1)$$

Section 2 applies a particular transformation of I to an exactly solvable pair of nonlinear kinetic equations with unstable solutions — a kinetic scheme used by Frank [2] as a model demonstrating the possibility of spontaneously developing optical activity in an initially achiral solution. Section 3 uses this same transformation to exactly linearize Frank's nonlinear rate equations and thereby leads to an indirect solution of them. Section 4 then considers a variety of transformations of these same rate equations and demonstrates that all the $T(a)$ of I act on Frank's equations to give transformed equations which possess unstable solutions.

Section 5 illustrates the application of the transformations of I to a kinetic system in which the linearizing transformation is not exact because the dependence of the group generator upon species concentrations has only been approximately determined. Unlike the usual methods of linearization which are accurate to $O(x^2)$, the linearization is accurate to $O(x^3)$. Section 6 is concerned with topological properties of the mappings in concentration space carried out by the transformations $T(a)$ of I. Two systems are defined to have qualitatively similar kinetics if their phase trajectories are topologically equivalent. It is shown that all the $T(a)$ of I convert phase curves into topologically equivalent phase curves. With this fact in hand, in section 7 it is shown how one may use the $T(a)$ to determine lumped concentration variables whose evolution is qualitatively similar to that of selected species of interest, yet governed by much simpler kinetic schemes. The $T(a)$ are also used to determine finite transformations of input/output fluxes that compensate for large changes in rate constants due to, for example, large temperature changes.

In section 8, the group generators established in I are used to determine functions of the rate constants that are left invariant by the transformations $T(a)$. This gives a global characterization of the mappings $x \rightarrow \bar{x} = T(a)x$, $k \rightarrow \bar{k} = T(a)k$, all of which make large changes in phase curves while leaving the topology of the phase curves unchanged. Section 9 determines the many-parameter groups whose transformations leave invariant the topology of the phase curves of a two-species system. Section 10 sets forth a method for improving the approximation to the transformed concentrations $\bar{x} = T(a)x$ one obtains when the generator U of $T(a)$ is approximate.

Section 11 sets forth an algorithm for improving the approximate generators used throughout the paper.

The final section, section 12, summarizes the results of this paper and I, and indicates directions for further investigation.

2. Solution of a set of nonlinear kinetic equations by transformation

To illustrate our transformation procedure, we use operators determined in I to change the value of the coefficients of the quadratic terms in the equations

$$dx_1/dt = px_1 + qx_1x_2 = k_{11}x_1 + k_{112}x_1x_2 \quad (2.1)$$

$$dx_2/dt = px_x + qx_1x_2 = k_{22}x_2 + k_{212}x_1x_2 .$$

Frank, and later Hochstim, used these equations with $p > 0$, $q < 0$ to model the chemical kinetics of a process in which an initially racemic mixture of two optical isomers with concentrations $x_1(t)$, $x_2(t)$ can spontaneously become optically active [2,3]. Although our purpose here is not a study of optical activity, reference to this interpretation will aid in understanding the transformations being used.

Perusing table 2.2 in I, we see that $T_{112}(\delta a)$ will change k_{212} to $k_{212} + \delta a k_{11}$, and that $T_{212}(\delta a)$ will change k_{112} to $k_{112} + \delta a k_{11}$. However, U_{112} and U_{212} do not commute; when a is finite, applying $T_{212}(a)$ to eqs. (2.1) after $T_{112}(a)$ gives a different result than applying $T_{112}(a)$ after $T_{212}(a)$. Neither sequence treats the two differential equations in the same manner. This leads us to use the generator $U = U_{112} + U_{212}$ in the operator $T(a) = \exp aU$ to change k_{112} and k_{212} . Using table 2.2 of I to evaluate the action of $\exp(\delta aU) = 1 + \delta a(U_{112} + U_{212})$ on x and k , we find that all k_{im} which vanish in (2.1) do not have their value changed, so we may drop many terms from $U_{112} + U_{212}$, specializing the generator to

$$U = x_1x_2 \partial/\partial x_1 + x_1x_2 \partial/\partial x_2 + k_{22} \partial/\partial k_{112} + k_{11} \partial/\partial k_{212} . \quad (2.2)$$

Evaluating $[V, U]$, one finds that this Lie generator exactly commutes with the evolution operator V for (2.1). If a is the group parameter in the transformation, one obtains for the transformed equations:

$$d\bar{x}_1/dt = p\bar{x}_1 + (q + ap)\bar{x}_1\bar{x}_2 \quad (2.3a)$$

$$d\bar{x}_2/dt = p\bar{x}_2 + (q + ap)\bar{x}_1\bar{x}_2 .$$

In producing this result, we have considered the concentrations x_i to simply take on new values \bar{x}_i . On the other hand, we have explicitly indicated that $\bar{q} = q + ap$. This

highlights the effect of the transformation in changing the kinetic equation by changing rate constants. However, the explicit effect of the transformation on the species concentrations is also of importance. One finds by integrating equations (2.13) of I that $\exp(aU)$ acts on x to give, when $x_1 \neq x_2$:

$$\bar{x}_1 = \frac{x_1(x_1 - x_2)}{x_1 - x_2 \exp(aD)}, \quad (2.3b)$$

$$\bar{x}_2 = \frac{x_2(x_1 - x_2) \exp(aD)}{x_1 - x_2 \exp(aD)},$$

with

$$x_1 \neq x_2 \exp(aD), \quad (2.3c)$$

$$D = x_1 - x_2 = \bar{x}_1 - \bar{x}_2.$$

Note that for a given range of x_1 and x_2 , we have limited the range available to the parameter a so as to ensure that the finite transformation is 1:1 within the space of real x_1, x_2 , i.e. that $-\infty < x_1, x_2 < \infty$.

If $x_1 = x_2$, then one obtains

$$\bar{x}_1 = \frac{x_1}{1 - ax_1}, \quad \bar{x}_2 = \frac{x_2}{1 - ax_2}, \quad ax_1 \neq 1, \quad ax_2 \neq 1. \quad (2.3d)$$

It is not necessary to solve eqs. (2.3) above for the x to obtain the inverse transformation: because of the group property, the results will be the same as that obtained simply by changing a to $-a$ and interchanging the barred and unbarred variables. Thus, if $x_1 \neq x_2$:

$$x_1 = \frac{\bar{x}_1(\bar{x}_1 - \bar{x}_2)}{\bar{x}_1 - \bar{x}_2 \exp(-aD)}, \quad x_2 = \frac{\bar{x}_2(\bar{x}_1 - \bar{x}_2) \exp(-aD)}{\bar{x}_1 - \bar{x}_2 \exp(-aD)}. \quad (2.3e)$$

If $x_1 = x_2$, the inverse transformation is

$$x_1 = \frac{\bar{x}_1}{1 + a\bar{x}_1}, \quad x_2 = \frac{\bar{x}_2}{1 + a\bar{x}_2}. \quad (2.3f)$$

3. Linearization of the kinetics generating spontaneous optical activity

Returning to (2.3a), we note that if one sets $a = -q/p$ the coefficient of the quadratic terms in (2.3a) vanishes. This observation enables us to rather easily obtain

solutions of the original kinetic equations (2.1) in terms of elementary functions, for one may immediately integrate the linear equations obtained when the coefficient of the quadratic terms in (2.3a) vanishes. The result is

$$\bar{x}_1 = \bar{x}_1(0)\exp(pt), \quad \bar{x}_2 = \bar{x}_2(0)\exp(pt). \tag{3.1}$$

(Note that \bar{x}_1, \bar{x}_2 remain finite for all finite times so that the denominators in (2.3e) can only vanish as t approaches infinity.) Then, using the inverse transformations, one transforms the linearized equations back to the original nonlinear equations and thereby transforms (3.1) into their exact solution which, if $x_1(t_0) \neq x_2(t_0)$, is found to be

$$\begin{aligned} x_1(t) &= \frac{C_1(C_1 - C_2)\exp(pt)}{C_1 - C_2 \exp([q/p] [C_1 - C_2] \exp [pt])} \\ x_2(t) &= \frac{C_2(C_1 - C_2)\exp(pt)\exp([q/p] [C_1 - C_2] \exp [pt])}{C_1 - C_2 \exp([q/p] [C_1 - C_2] \exp [pt])}, \end{aligned} \tag{3.2a}$$

where $C_i = \bar{x}_i(0)$. If $x_1(t_0) = x_2(t_0)$, then (2.3c) implies $C_1 = C_2 = C$, and the solutions of (2.1) are given by

$$x_1(t) = x_2(t) = \frac{C \exp(pt)}{1 - (q/p)C \exp(pt)}. \tag{3.2b}$$

These solutions agree with those obtained analytically by Frank using standard methods [2].

Note that the values of x_1 and x_2 at $t = 0$ are

$$\begin{aligned} x_1(0) &= \frac{C_1(C_1 - C_2)}{C_1 - C_2 \exp([q/p] [C_1 - C_2])} \\ x_2(0) &= \frac{C_2(C_1 - C_2)\exp([q/p] [C_1 - C_2])}{C_1 - C_2 \exp([q/p] [C_1 - C_2])}, \end{aligned} \tag{3.2c}$$

when $x_1(0) \neq x_2(0)$. When the initial concentrations are equal, one has

$$x_1(0) = x_2(0) = \frac{C}{1 - (q/p)C}. \tag{3.2d}$$

Equations (2.1) have equilibrium (i.e. critical) points at $(0, 0)$ and $(-p/q, -p/q)$. As (x_1, x_2) approaches the unstable equilibrium point at $(-p/q, -p/q)$, the denomi-

nators in (3.2b) approach zero and x_1 and x_2 become infinite. Note, however, that it is impossible for any of the solutions to reach these equilibrium values from any other concentrations in any finite time.

It follows immediately from (2.3c) that if, when we start our clock ($t = 0$), the concentrations C_1 and C_2 of x_1 and x_2 are small but not identical, then

$$x_1(t) - x_2(t) = (C_1 - C_2)\exp(pt). \quad (3.3)$$

Thus, if any fluctuation in the concentrations of the D and L isomers leads to a momentary difference in these concentrations, this difference may grow exponentially with time. As Frank [2] first pointed out, because such fluctuations are to be expected on statistical grounds, a reaction system with kinetic equations (2.1), though started off with equal concentrations of D and L isomers, can lead to a preponderance of one isomer over the other. As will be seen in the following section, the methods we have developed enable one to systematically determine all other two-species elementary kinetic schemes which lead to the same result. However, we do not here provide methods for making a corresponding examination of systems where local concentration fluctuations and diffusion are involved. The interested reader is referred to the paper by Hochstim [3], who incorporated diffusion in the kinetics (2.1) and investigated the fluctuation dynamics of the system, as is necessary in any realistic theory of the spontaneous generation of optical activity by chemical means.

4. Distortions of kinetics generating spontaneous optical activity

The chemically significant feature of the kinetics in the previous two sections is the instability of solutions in which the concentrations of D and L isomers are equal: if these concentrations momentarily become unequal at time t_0 , then thereafter

$$x_1(t) - x_2(t) = \{x_1(t_0) - x_2(t_0)\}\exp(t - t_0)p. \quad (4.1)$$

It is instructive to see what the invariance transformations do to the kinetic equations (2.1) and to the time evolution of this difference. To avoid confusion with the transformation of the previous section, we shall in this section write

$$\tilde{k} = T(a)k, \quad k = T(-a)\tilde{k}, \quad \tilde{x} = T(a)x, \quad x = T(-a)\tilde{x}. \quad (4.2)$$

We first consider the exact invariance transformations T_{10} , T_{11} , T_{12} . Letting $x = T_{10}(-a)\tilde{x} = (x_1 - a, x_2)$, we find using table 2.2 of I that

$$\tilde{k}_{10} = -ak_{11}, \quad \tilde{k}_{12} = -ak_{112}, \quad \tilde{k}_{22} = k_{22} - ak_{212}, \quad (4.3a)$$

while all other k 's are unchanged. Also,

$$\tilde{x}_1 - \tilde{x}_2 = (C_1 - C_2) \exp(pt) + a. \quad (4.3b)$$

Thus, $T_{10}(-a)$ converts the Frank equations into

$$\dot{\tilde{x}}_1 = -ap + p\tilde{x}_1 - aq\tilde{x}_2 + q\tilde{x}_1\tilde{x}_2, \quad \dot{\tilde{x}}_2 = (p - aq)\tilde{x}_2 + q\tilde{x}_1\tilde{x}_2. \quad (4.4)$$

It is evident from (4.3b) that these new equations also possess unstable solutions in the same sense as do eqs. (3.1).

Next, let $(x, k) = T_{11}(-a)(\tilde{x}, \tilde{k})$. Using table 2.2 of I, one finds

$$\tilde{x}_1 = x_1 e^a, \quad \tilde{x}_2 = x_2 \quad (4.5)$$

and

$$\dot{\tilde{x}}_1 = p\tilde{x}_1 + q\tilde{x}_1\tilde{x}_2, \quad \dot{\tilde{x}}_2 = p\tilde{x}_2 + e^{-aq}\tilde{x}_1\tilde{x}_2.$$

Thus, for these equations one has

$$\tilde{x}_1 - \tilde{x}_2 = (C_1 \exp(a) - C_2) \exp(pt). \quad (4.6)$$

Applying $T_{12}(-a)$, one obtains

$$\tilde{x}_1 - \tilde{x}_2 = x_1 - x_2 - ax_2. \quad (4.7)$$

which grows exponentially as t becomes large. The transformed kinetic equations are

$$\dot{\tilde{x}}_1 = p\tilde{x}_1 + q(1 + a)\tilde{x}_1\tilde{x}_2 - q(a + a^2)\tilde{x}_2^2, \quad \dot{\tilde{x}}_2 = p\tilde{x}_2 + q\tilde{x}_1\tilde{x}_2 - aq\tilde{x}_2^2. \quad (4.8)$$

We turn next to the action of transformations that only leave the kinetic equations approximately invariant.

Using table 2.2 of I to determine the action of $T_{111}(-a)$, one finds:

$$\tilde{x}_1 = \frac{x_1}{1 - ax_1}, \quad \tilde{x}_2 = \tilde{x}_2 \quad (4.9)$$

$$\tilde{x}_1 - \tilde{x}_2 = \left\{ \frac{C_1}{1 - aC_1 \exp(pt)} - C_2 \right\} \exp(pt)$$

and that

$$\tilde{k}_{111} = ak_{11} = ap. \quad (4.10)$$

The corresponding differential equations are

$$\begin{aligned}\dot{\tilde{x}}_1 &= p\tilde{x}_1 + ap\tilde{x}_1^2 + q\tilde{x}_1\tilde{x}_2 + O(x^3) \\ \dot{\tilde{x}}_2 &= p\tilde{x}_2 + q\tilde{x}_1\tilde{x}_2 + O(x^3).\end{aligned}\tag{4.11}$$

$T_{112}(-a)$ gives

$$\begin{aligned}\tilde{x}_1 &= x_1 e^{ax_2}, \quad \tilde{x}_2 = x_2, \\ \tilde{x} - \tilde{x}_2 &= \{C_1 \exp(aC_2 \exp(pt)) - C_2\} \exp(pt)\end{aligned}\tag{4.12}$$

and

$$\tilde{k}_{112} = k_{112} + ak_{22} = q + ap.\tag{4.13}$$

The transformed differential equations are

$$\begin{aligned}\dot{\tilde{x}}_1 &= p\tilde{x}_1 + (q + ap)\tilde{x}_1\tilde{x}_2 + O(x^3) \\ \dot{\tilde{x}}_2 &= p\tilde{x}_2 + q\tilde{x}_1\tilde{x}_2 + O(x^3).\end{aligned}\tag{4.14}$$

Finally, $T_{122}(-a)$ yields the transformed solutions

$$\tilde{x}_1 = x_1 - ax_2^2, \quad \tilde{x}_2 = x_2, \quad \tilde{k}_{122} = a(2k_{22} - k_{11}) = ap,\tag{4.15}$$

so that

$$\tilde{x}_1 - \tilde{x}_2 = (C_1 - C_2) \exp(pt) + aC_2^2 \exp(2pt)\tag{4.16}$$

depicts the time evolution of concentration differences for the resulting solutions of the equation

$$\begin{aligned}\dot{\tilde{x}}_1 &= p\tilde{x}_1 + q\tilde{x}_1\tilde{x}_2 + ap\tilde{x}_2^2 + O(x^3) \\ \dot{\tilde{x}}_2 &= p\tilde{x}_2 + q\tilde{x}_1\tilde{x}_2 + O(x^3).\end{aligned}\tag{4.17}$$

It will be noted that although these various transformations lead to equations with little self-evident relationship to the Frank equations, all the solutions have the property that they develop exponential growth of the difference between concentrations. By acting successively with the twelve different transformations of table 2.2 of I, one obtains from the Frank equations a twelve-parameter family of kinetic

equations, all of which possess similarly unstable solutions. In sections 6 and 7, we will establish the exact sense in which this property of our transformations is a general one.

5. Transformations of Lotka–Volterra systems

The example of sections 2 and 3 is somewhat misleading because the kinetic system possesses no separatrix in the phase plane and because we were able to use an exact invariance transformation to linearize the rate equations. In this section, we investigate the more typical example provided by the rate equations of Lotka and Volterra [4,5]. They can always be reduced to the special case [6]

$$\dot{x}_1 = p(x_1 - x_1 x_2), \quad \dot{x}_2 = -q(x_2 - x_1 x_2), \tag{5.1}$$

which has critical points at (0,0) and (1,1). If one rewrites these about the second singular point by making the substitution

$$x_1 = y_1 + 1, \quad x_2 = y_2 + 1,$$

then they become

$$\dot{y}_1 = p(-y_2 - y_1 y_2), \quad \dot{y}_2 = -q(-y_1 - y_1 y_2). \tag{5.2}$$

In this section we will, for simplicity, consider $p = q = 1$.

As we wish to allow the k_{im} to vary, we consider (5.1) to be a special case of the equations

$$\dot{x}_1 = k_{11} x_1 + k_{112} x_1 x_2, \quad \dot{x}_2 = k_{22} x_2 + k_{212} x_1 x_2, \tag{5.3}$$

with $k_{11} = 1, k_{112} = -1, k_{22} = -1, k_{212} = 1$.

Similarly, (5.2) is a special case of the equations

$$\dot{y}_1 = k_{12} y_2 + k_{112} y_1 y_2, \quad \dot{y}_2 = k_{21} y_1 + k_{212} y_1 y_2, \tag{5.4}$$

with $k_{12} = -1 = k_{112}, k_{21} = 1 = k_{212}$.

Comparing eqs. (5.3) with eqs. (2.1), we find that the generator U of (2.2) is the generator of a transformation that will linearize (5.3). However, in this case the equations are only approximately invariant under the transformation: Evaluating $[V, U]$, one obtains as the remainder a $W^{(2)}$ term with components

$$(w_1, w_2) = (-2x_1^2 x_2, 2x_1 x_2^2). \tag{5.5}$$

This remainder is of higher order in x than that obtained in the standard local linearization which simply neglects terms of $O(x^2)$.

We shall henceforth use the term *regional* to denote an approximation, such as this linearization, whose error terms are of order x^3 or greater.

Equations (5.4) may be linearized in a manner similar to that used for eqs. (5.3). Using table 2.2 of I, one finds that to linearize (5.4) it is necessary to make use of all the generators quadratic in x . Utilizing the infinitesimal transformations as before, one finds that a transformation with generator

$$U_{111} + U_{122} - U_{122} - U_{211} + U_{212} + U_{222} \quad (5.6)$$

will have the desired effect. Because many of the k 's that are zero do not have their values altered by the T_{ijk} , the generator (5.6) may be simplified to

$$U = (y_1^2 + y_1 y_2 - y_2^2) \partial / \partial y_1 + (y_2^2 + y_1 y_2 - y_1^2) \partial / \partial y_2 \\ + (k_{12} - 2k_{21}) \partial / \partial k_{112} + (k_{21} - 2k_{12}) \partial / \partial k_{212} . \quad (5.7)$$

Evaluating $[V, U]$, one finds that in the remainder

$$w_1 = k_{112} y_1^3 + k_{212} y_1^2 y_2 - (k_{112} + 2k_{212}) y_1 y_2^2 + k_{112} y_2^3 \\ w_2 = k_{212} y_1^3 - (2k_{112} + k_{212}) y_1^2 y_2 + k_{112} y_1 y_2^2 + k_{212} y_2^3 . \quad (5.8)$$

Acting with $\exp(aU)$ on the equations, they are, respectively, converted into

$$\dot{\bar{x}}_1 = k_{11} x_1 + (k_{112} + ak_{22}) \bar{x}_1 \bar{x}_2 + O(x^3) \\ \dot{\bar{x}}_2 = k_{22} x_2 + (k_{212} + ak_{11}) \bar{x}_1 \bar{x}_2 + O(x^3) \quad (5.9)$$

and

$$\dot{\bar{y}}_1 = k_{12} \bar{y}_2 + (k_{112} - 3ak_{21}) \bar{y}_1 \bar{y}_2 + O(y^3) \\ \dot{\bar{y}}_2 = k_{21} \bar{y}_1 + (k_{212} - 3ak_{12}) \bar{y}_1 \bar{y}_2 + O(y^3) . \quad (5.10)$$

The effect of the error terms will be discussed in sections 10 and 11.

Setting $a = -1$ in (5.9) and $a = -1/3$ in (5.10), one obtains linear equations whose solutions are, respectively,

$$\bar{x}_1 = C_1 \exp(t), \quad \bar{x}_2 = C_2 \exp(-t) \quad (5.11)$$

and

$$\begin{aligned}\bar{y}_1 &= C_1 \cos(t) - C_2 \sin(t) \\ \bar{y}_2 &= C_2 \cos(t) + C_1 \sin(t).\end{aligned}\tag{5.12}$$

Using the inverse transformations developed in section 2, one converts (5.11) into approximate solutions of the Lotka–Volterra equations. One finds, as before,

$$\begin{aligned}x_1(t) &= \frac{\bar{x}_1(\bar{x}_1 - \bar{x}_2)}{\bar{x}_1 - \bar{x}_2 \exp\{-a(\bar{x}_1 - \bar{x}_2)\}}, \\ \text{or if } x_1 &= x_2, \quad \frac{\bar{x}_1}{1 + a\bar{x}_1} \\ x_2(t) &= \frac{\bar{x}_2(\bar{x}_1 - \bar{x}_2) \exp\{-a(\bar{x}_1 - \bar{x}_2)\}}{\bar{x}_1 - \bar{x}_2 \exp\{-a(\bar{x}_1 - \bar{x}_2)\}}, \\ \text{or if } x_1 &= x_2, \quad \frac{\bar{x}_2}{1 + a\bar{x}_2},\end{aligned}\tag{5.13}$$

where \bar{x}_1 and \bar{x}_2 are given by (5.11) in the vicinity of the origin. The range of a must be restricted to ensure that the transformations are 1 : 1 on the reals.

In the vicinity of (1, 1), one uses the transformation with generator U given in (5.7) to obtain the transformed variables. We may take advantage of the fact that the commutator of any two of the generators composing this U either vanishes or is of order y^3 . As a result, to order y^3 we may write $\exp(aU)$ as a product $\exp(aU_{111})\exp(aU_{112}) \dots \exp(aU_{222})$. Proceeding in such a manner, we find

$$\begin{aligned}y_1 &= \frac{\bar{y}_1 + a\bar{y}_2^2}{1 + a(\bar{y}_1 + \bar{y}_2) + a^2(\bar{y}_1^2 + \bar{y}_2^2)} \\ y_2 &= \frac{\bar{y}_2 + a\bar{y}_1^2}{1 + a(\bar{y}_1 + \bar{y}_2) + a^2(\bar{y}_1^2 + \bar{y}_2^2)},\end{aligned}\tag{5.14}$$

with \bar{y}_1, \bar{y}_2 given as functions of t by (5.12). Note that y_1 and y_2 are single valued functions of \bar{y}_1, \bar{y}_2 and a for the allowed range of these variables. Hence, as \bar{y}_1 and \bar{y}_2 are cyclic functions of t , y_1 and y_2 must be cyclic in t . This has the consequence that the closed curves which are the phase plane plots of \bar{y}_1, \bar{y}_2 are mapped into closed phase curves of y_1, y_2 .

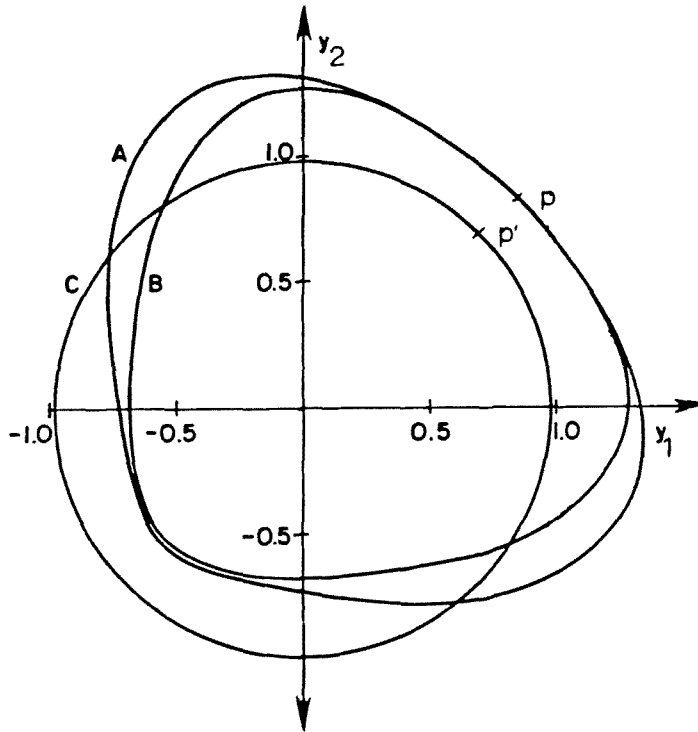


Fig. 5.1. Global approximation to a phase trajectory of the Lotka–Volterra equation. The trajectory B of the Lotka–Volterra equation is approximated by the trajectory A defined by (5.14). C is the reference circle defined by (5.12).

Because the U of (5.7) is only approximate, eqs. (5.14) do not yield exact solutions of the rate equations when a is assigned the prescribed value of $-1/3$. In fig. 5.1, an approximate phase trajectory (A) determined by (5.14) and (5.12) is compared with the trajectory (B) obtained by numerical integration of the Lotka–Volterra equations. The corresponding trajectory of the linearized equations is plotted in the figure as (C). In obtaining these trajectories, the initial point p was used to determine p' on the reference circle defined by (5.12). In section 10, a method is developed for improving the approximate trajectory in the region of any point of interest.

6. Transformation of phase trajectories: Topological invariants

A key feature of any kinetic system is the behaviour of its phase portrait [6–8]. (We shall use the term phase portrait when we are referring to trajectories in the vicinity of singular points in the phase space $\{x\}$.) As a result, it is important to

investigate the way in which these portraits are affected by the transformations we have obtained. To introduce this study, we carry out a standard investigation of the phase portraits of (1.1). When $q \neq 0$, the right-hand sides of the equations vanish for $x_1 = x_2 = 0$, and for $x_1 = x_{10} = -p/q$, $x_2 = x_{20} = -p/q$. Only the first critical point persists if $q = 0$. In the region of the critical point at the origin, the solutions of the equations are

$$x_1(t) = x_1(0) \exp(pt), \quad x_2(t) = x_2(0) \exp(pt) \quad (6.1)$$

and the phase portrait consists of trajectories fleeing the origin, an improper node, (Of course, on interpreting x_1 and x_2 as species concentrations, one sees that the trajectories on which either of these variables become negative have no direct chemical relevance.) The invariance transformations of section 2 merely distort these trajectories as they recede from the origin, but none of the transformations changes the topological classification of the portrait.

We next turn to an investigation of the phase portraits in the region of the second critical point at $(-p/q, -p/q)$. Letting $y = x - (-p/q, -p/q)$ and expressing the equations about this second critical point yields

$$dy_1/dt = -py_2 + qy_1 y_2, \quad dy_2/dt = -py_1 + qy_1 y_2. \quad (6.2)$$

The secular equation of the linear part of this system is

$$\text{Det} \begin{pmatrix} -\lambda & -p \\ -p & -\lambda \end{pmatrix} = 0 = \lambda^2 - p^2. \quad (6.3)$$

It will be noted that the roots are independent of q . Since these roots determine the phase portrait, it is evident that the portrait is independent of q whenever y is well defined, i.e. for $q \neq 0$. The portrait is that of a saddle point. Applying the transformations of table 2.2 of I to y_1 and y_2 , one finds, as in the previous case, that the topological classification of the portrait is unchanged.

The Lotka–Volterra system of section 5 has an unstable saddle point at the origin, and a stable center at $(1, 1)$. Thus, the portrait in the region of the first critical point and that in the region of the second critical point are of radically different topological type. (Although only the latter is of direct chemical interest, we shall for illustrative purposes consider them both.) Applying the transformations of table 2.2 of I to the variables x in eqs. (5.1) and the variables y in eqs. (5.2), one finds that neither phase portrait may be changed into the other or into a portrait of a different topological classification.

It is a difficult task to determine all possible phase portraits for just two elementary kinetic equations. One must first locate all stationary points $dx_1/dt = 0 = dx_2/dt$.

This is equivalent to investigating and classifying all possible intersections of the pair of conics defined by setting the right-hand sides of (1.1) to zero, which if they are not identical, may intersect at 4, 3, 2, 1 or no points. To then investigate the action of all the transformations in table 2.2 of I on each phase portrait is a task one would like to avoid. In the following paragraphs, we determine the effects of the transformations on the topological properties of all possible phase portraits without proceeding on a case by case basis, and without confining the system to a phase space of two dimensions.

In the examples of this and previous sections, we have seen transformations of kinetic equations that have preserved qualitative features of the solutions of the equations even though they may have greatly changed the concentrations and rate constants, and hence the equations themselves. All transformations of the equations introduced by Frank were found to preserve the instability of the solutions with equal concentrations of D and L isomers portrayed in the phase portrait of the untransformed system. All transformations of the cyclic solutions of the Lotka–Volterra equations in the region of their critical point gave rise to cyclic solutions, and all transformations of the non-cyclic solutions in the region of their critical point yielded non-cyclic solutions. None of the transformations in the examples altered the topological classification of a critical point.

Let us therefore address the question of whether it is true in general that our invariance transformations change phase trajectories in such a manner as to preserve the topological properties of the trajectories everywhere in the phase space.

First of all, we ask whether the operators $\exp(aU)$ always transform closed phase curves into closed phase curves, and open phase curves into open phase curves? The answer to this question is yes, for the following reasons. The polynomial form of the coefficient functions in the generators U ensures that the coefficients $h_i(x)$ are single valued differentiable, indeed analytic, functions, *and this is true even when the polynomials are only approximations to the exact h_i* . Now, at each point in the phase space the infinitesimal shift in x, k brought about by an infinitesimal transformation with parameter δa is given by $\delta a Ux, \delta a Uk$. Thus, at each point in phase space ($-\infty < x_i < \infty$ for all t), our infinitesimal transformations define a unique shift of the point, that is to say, they are local diffeomorphisms. We have not allowed finite transformations that shift x_i outside this same range. Since the finite transformations $T(a)$ are compounded of a succession of infinitesimal transformations $T(\delta a)$ such that $a = \int \delta a$, for each value of a they also determine unique motions of each point in x, k, t space as long as x, k, t remain real. Thus, first of all, for all a within the allowed range, the transformations carried out by the operators $\exp(aU)$, in addition to being unique and having a unique inverse, vary smoothly from point to point and carry contiguous regions in x, k, t space into contiguous regions, and discontinuous regions into discontinuous regions – that is to say, they are local diffeomorphisms of the space of x, k, t [7]. Second, because we do not allow values

of the group parameter which would transform any variable outside the reals, the transformations are global diffeomorphisms of the space of real x, k, t . In addition, the transformations are time independent so that they are diffeomorphisms of x, k space. Finally, the transformations are such that as x varies with t , k does not vary. It follows from this that as t progresses and a phase trajectory and its transformed image develop (a being held fixed), if it should happen that the phase point returns to its initial position, then its transformed image will also return to its corresponding initial position. Thus, a closed phase curve is mapped into a closed phase curve. In a similar way, one argues that because the transformations are t -independent diffeomorphisms of x, k, t space, they carry discontinuous regions of phase space into discontinuous regions, and hence transform open phase curves into open phase curves.

It is evident from this discussion that our transformations allow us to determine changes in rate constants that will leave an initially oscillatory reaction oscillatory and an initially non-oscillatory reaction non-oscillatory. Any transformation compounded of transformations $\exp(aU')$, each of whose generators are of the form

$$U' = \sum c_m(k)U_m, \quad (6.4)$$

will have this property when acting on the x_i if the U_m are those determined in section 2, and the c_m are smooth functions of k .

In the usual topological classification of phase portraits and phase curves, the direction of motion as t increases is also a topological invariant. Hence, we next investigate whether any of our changes in rate constants invert the direction of motion along a phase curve.

Inspecting table 2.2 of I, one finds that none of its transformations can have such an effect. The underlying reason for this is perhaps most clearly seen with the aid of fig. 6.1, which purports to depict a solution curve in x_1, x_2, t space and its projections onto x_1, x_2 phase space, together with another curve in this phase space. Suppose that at times t_1 and t_2 the points P_1 and P_2 are marked on a trajectory of growing concentrations. Suppose that for a given value a' of the group parameter it were to happen that $\exp(aU)$ were to map P_1 into P'_1 — and that for the same value of the group parameter, P_2 is carried into P'_2 , a point where \bar{x}_1 and \bar{x}_2 have smaller values than at P'_1 . The arrows are drawn in to indicate how, as one increases the group parameter from 0 to a' , the transformed points move away from the original trajectory. It will be noted that these lines cross at some intermediate value of a . However, if this were to happen, then for larger values of a the transformation would have to carry the point of crossing into both P'_1 and P'_2 — and the inverse transformation would have to carry the point to both P_1 and P_2 . Because our generators U have single valued functions for their coefficients, the infinitesimal transformations are everywhere unique and all this is impossible. In short, it is impossible to convert the first phase trajectory into the second using any of our $T(a)$.

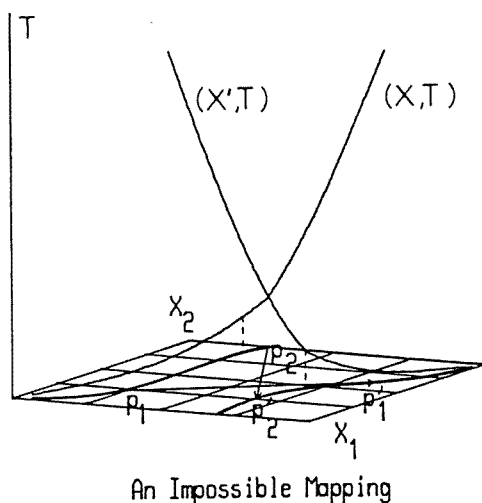


Fig. 6.1. An impossible mapping. Two curves $x(t)$ can not be mapped into one another by any of the transformations considered in this paper if one depicts concentrations that increase with time and the other depicts concentrations that decrease with time at the same time.

The argument just given evidently fails if the phase space is more than two dimensional, for then the lines $P_1 P_1'$ and $P_2 P_2'$ need not intersect. In such cases, we may consider an initial phase trajectory which develops in one direction as t increases, and a nearby phase trajectory obtained from the first by a transformation with operator $T(a)$ — a trajectory which by hypothesis evolves in the opposite direction. If two such curves exist we can, from arguments of continuity in the group parameter a , conclude that between them lie two similar curves that are connected by an infinitesimal transformation $T(\delta a)$ and that between these two curves lies a curve along which points do not move with t . Thus, along this intermediate curve all \dot{x}_i vanish. We now prove that in the region of this intermediate curve, T cannot change any of the rates \dot{x}_i . The effect upon x_i of the infinitesimal transformation with generator U is to convert x_i to $\bar{x}_i = x_i + \delta a h_i(x)$. This induces a transformation of dx_i/dt to

$$d\bar{x}_i/dt = \frac{d}{dt}(x_i + \delta a h_i(x)) = \dot{x}_i + \delta a \sum \dot{x}_j \partial h_i / \partial x_j. \quad (6.5)$$

As \dot{x}_i and all the other \dot{x}_j vanish on the intermediate curve, we see that in its infinitesimal neighbourhood T cannot change any of the \dot{x} 's and so cannot change the direction of motion along any trajectory. It follows from continuity in the group parameter a that T is unable to transform any trajectory into a trajectory developing oppositely in time.

The observations so far made in this section may be subsumed in the general observation that because our transformations are, for each allowed value of the group parameter a , diffeomorphisms of the space of x, k that keep dk/dt zero, they transform phase trajectories into topologically equivalent phase trajectories [7].

It is important to note that because even our approximate invariance transformations are local and global diffeomorphisms, all the above statements hold true even for them. Of course, when one uses approximate invariance transformations, one converts exact solutions into approximate solutions and hence, usually, converts exact phase trajectories of one kinetic system into approximate phase trajectories of another. Nevertheless, increasing the accuracy of the approximation by increasing the number of terms in the power series approximation to the $h_i(x)$ will not alter the topology of the target curve, which is completely determined by the topology of the untransformed solution curve. *Thus, for all the transformations we allow, the evolution of the original system and the evolution of the transformed systems are qualitatively similar in a well-defined sense: their phase curves are topologically indistinguishable.* The topology of the phase curves is, in the standard sense which includes the direction of motion, an invariant of our transformations.

To sum up our observations to this point: the methodology and conceptions we have described enable one to establish well-defined qualitative relations, as well as quantitative relations, between the behaviour of kinetic systems with different rate constants. Because one may transform many rate constants to zero, the conceptions are also applicable to studies relating the global behaviour of systems with complex kinetics to the behaviour of systems with simpler kinetics – and vice versa.

7. Lumping and flux control

Both in the analysis and in the utilization of kinetic studies of complex reacting systems, one often tries to simplify the kinetic scheme by ‘lumping’ a number of reactions into one, thus submerging a part of the detailed elementary kinetics. For this goal, it is necessary that the reactions retained in the kinetic scheme proceed at least qualitatively, as they would if the submerged reactions were taken into account. Because we are assured that our transformations do not change the qualitative behaviour of a kinetic system, it is worthwhile to determine whether they can be used to determine lumpings. Sometimes a lumping is only possible because the initial concentrations satisfy some special relationship, and sometimes it is only possible because some kinetic coefficients are confined to some special range of values. While the methods developed in this article can be of help in studying both these situations, here we wish only to deal with the use of the methods in the global analysis of kinetic systems. That is to say, we are here concerned only with the consequences of large changes in kinetic coefficients and with consequences that are independent of initial concentrations.

To exemplify our approach to lumping, we begin by considering the inverse process, that of sophisticating one member of a set of rate equations — an equation that happens to involve only one species. Consider the general elementary kinetic scheme involving only one species:

$$\dot{x}_1 = g_{10} + g_{11} x_1 + g_{111} x_1^2 . \quad (7.1)$$

We may suppose that while this reaction is proceeding, another reaction involving x_2 is also proceeding independently. Now the concentration x_1 necessarily evolves in a non-oscillatory manner. Acting on (7.1) with any of the twelve transformations $T(a)$ of table 2.2 of I will give a one-parameter family of two-component kinetic systems in which \bar{x}_1 's evolution is also non-oscillatory. Acting with each of the twelve transformations in succession will give a twelve-parameter family of such kinetic systems.

The lumped variable \bar{x}_1 resulting from these transformations will in general be a complicated function of x_1 and the other concentrations, but as the group parameters become smaller and smaller, it will come closer and closer to being x_1 . Even though \bar{x}_1 makes large excursions and the kinetic coefficients may be greatly altered, the evolution of \bar{x}_1 for all members of this twelve-parameter family of reactions is globally, i.e. topologically, equivalent to that of the lumped system (7.1). All this is to say that \bar{x}_1 will behave qualitatively as though it were x_1 .

Consider now the process involved in eliminating a concentration variable from a kinetic equation using transformations $x_1, x_2 \rightarrow \bar{x}_1, \bar{x}_2$. It might appear at first sight that with a twelve-parameter family of lumping transformations available, one could lump away just about any variable in a reaction without changing the topology of the phase trajectories. In this connection, an example involving the lumping of three species into two may be revealing. Consider the reactions



and suppose that A is being supplied at rate k_0 while C is being supplied at rate k_3 . Let us try to transform away the intermediate species in the final reaction. Assigning the index i antilexically, the associated kinetic equations are

$$\begin{aligned} \dot{x}_3 &= k_0 + 2k_{-1} x_2 - k_1 x_3 x_3 = k_{30} + k_{32} x_2 + k_{333} x_3 x_3 \\ \dot{x}_2 &= -k_{-1} x_2 - 2k_{-2} x_1 + k_1 x_3 x_3 - 2k_2 x_2 x_2 \\ &= k_{22} x_2 + k_{21} x_1 + k_{233} x_3 x_3 + k_{222} x_2 x_2 \\ \dot{x}_1 &= k_3 - k_{-2} x_1 + k_2 x_2 x_2 = k_{10} + k_{11} x_1 + k_{122} x_2 x_2 . \end{aligned} \quad (7.3)$$

We wish to carry out a transformation $x \rightarrow \bar{x}$, $k \rightarrow \bar{k}$ which will eliminate \bar{x}_2 from the last reaction. Perusing table 2.1 of I and taking into account the fact that a number of k 's vanish in the intermediate and final reactions, we see that U_{12} is the only generator available for this purpose. Table 2.2 then indicates that

$$\bar{k}_{122} = k_{122} + ak_{222}, \quad \bar{k}_{12} = a(k_{22} - k_{11}) - a^2k_{21}. \quad (7.4)$$

Thus, on setting $a = -k_{122}/k_{222} = k_2/-k_2 = -1$ we can transform k_{122} to zero — but we will also, in general, create a nonzero k_{12} . Again perusing table 2.1 of I, we find that we can not find another transformation that will eliminate the unwanted \bar{k}_{12} . It follows that we can only attain our desired end if it should happen that the value of a which makes \bar{k}_{122} vanish also makes \bar{k}_{12} vanish. This will happen only if

$$(k_{122}/k_{222})k_{21} + k_{22} - k_{11} = -(k_{-2} + k_{-1}) = 0. \quad (7.5)$$

As untransformed rate constants can not be negative, it is evident (7.5) can only be satisfied if we can replace the k 's by some negative \bar{k} 's by means of some further transformation. Perusing tables 2.1 and 2.2 of I, one finds that a candidate for such a transformation is provided by $T_{111}(b)$. It acts on k_{11} to give $k_{11} + 2bk_{10}$ so that the term in (7.5) which must vanish becomes $-(k_{-2} + k_{-1} + 2bk_3)$. Thus, by setting $b = -(k_{-1} + k_{-2})/2k_3$, the lumping becomes possible. The only other effect of $T_{111}(b)$ on the final reaction is to convert x_1 to $x_1/(1 + bx_1)$. Applying T_{111} after T_{12} , the lumped concentration variable will be $\bar{x}_1 = (x_1 + ax_2)/(1 + b\{x_1 + ax_2\})$. The other concentrations x_2 and x_3 are unaffected. The kinetics of the final reaction will become

$$\begin{aligned} \dot{\bar{x}}_1 &= k_{10} + \bar{k}_{11}\bar{x}_1 + \bar{k}_{111}\bar{x}_1\bar{x}_1 \\ \bar{k}_{11} &= k_{11} + 2bk_{10} + ak_{21}, \quad \bar{k}_{111} = ak_{11} + a^2k_{12} + bk_{21}. \end{aligned} \quad (7.6)$$

Lumped concentration variables are also of use in another setting, in which one wishes the lumped variables to behave qualitatively like the original concentrations. It is a common experience that heat produced in the course of a chemical reaction may affect reaction rates (and, as a result, product composition) by changing unimolecular rate constants k_{ij} and bimolecular rate constants k_{ijk} . One commonly controls such reactions by adjusting cooling rates and by adjusting concentrations and rates of supply of reagents. For reactions involving two species, the extent to which time-independent reaction fluxes and concentration changes may be so used can be determined with the aid of table 2.1 of I. Perusing the table, one sees that only the generators U_{i0} and U_{ij} have nonzero values of g_{10} and g_{20} . Thus, only transformations using them can adjust the fluxes k_{10} and k_{20} . The most general allowed generator available for such purposes is a linear combination of these six generators of the form

$$U = \sum c_m(\mathbf{k}) U_m . \quad (7.7)$$

Using table 2.1 of I one finds that an infinitesimal transformation with this generator has the following effect on the flux k_{10} and the rate constants $k_{1\mu}$:

$$\begin{aligned} \delta k_{10} &= \delta a \{-c_{10} k_{11} + c_{11} k_{10} + c_{12} k_{20} - c_{20} k_{12}\} \\ \delta k_{11} &= \delta a \{-2c_{10} k_{111} + c_{12} k_{21} - c_{20} k_{112} - c_{21} k_{12}\} \\ \delta k_{12} &= \delta a \{-c_{10} k_{112} + c_{11} k_{12} + c_{12}(k_{22} - k_{11}) - 2c_{20} k_{122} - c_{22} k_{12}\} \\ \delta k_{111} &= \delta a \{-c_{11} k_{111} + c_{12} k_{211} - c_{21} k_{121}\} \\ \delta k_{112} &= \delta a \{c_{12}(k_{212} - 2k_{111}) - 2c_{21} k_{112} - c_{22} k_{112}\} \\ \delta k_{122} &= \delta a \{c_{11} k_{122} + c_{12}(k_{222} - k_{112}) - 2c_{22} k_{122}\} . \end{aligned} \quad (7.8)$$

The associated changes in concentrations are

$$\begin{aligned} \delta x_1 &= \delta a \{c_{10} + c_{11} x_1 + c_{12} x_2\} \\ \delta x_2 &= \delta a \{c_{20} + c_{21} x_1 + c_{22} x_2\} . \end{aligned} \quad (7.9)$$

A similar set of relations can be written for the flux k_{20} and rate constants $k_{2\mu}$. To negate the effects of infinitesimal temperature-driven changes in the ten unimolecular and bimolecular rate constants, we may try to choose the six constants $c_{1\mu}$ and $c_{2\mu}$ so that all δk 's except δk_{10} and δk_{20} vanish. If such c 's can be found, then they will determine associated shifts in fluxes δk_{10} and δk_{20} and concentrations δx_1 and δx_2 . Under these circumstances, the transformed kinetic equations will read

$$\begin{aligned} \dot{\bar{x}}_1 &= \bar{k}_{10} + k_{11} \bar{x}_1 + k_{12} \bar{x}_2 + k_{111} \bar{x}_1 \bar{x}_1 + k_{112} \bar{x}_1 \bar{x}_2 + k_{122} \bar{x}_2 \bar{x}_2 \\ \dot{\bar{x}}_2 &= \bar{k}_{20} + k_{21} \bar{x}_1 + k_{22} \bar{x}_2 + k_{211} \bar{x}_1 \bar{x}_1 + k_{212} \bar{x}_1 \bar{x}_2 + k_{222} \bar{x}_2 \bar{x}_2 . \end{aligned} \quad (7.10)$$

Here, the k 's without overbars have the value taken on at the original ambient temperature, the change in the actual temperature-dependent k 's having been absorbed in the indicated changes in x_1 , x_2 , k_{10} , k_{20} indicated by overbars. When the \bar{x}_i are expressed in terms of the untransformed variables, the \bar{x}_i are seen to be lumped concentration variables if c_{12} , c_{21} , respectively, are nonzero. Otherwise, \bar{x}_1 , \bar{x}_2 are simply altered values of x_1 , x_2 .

Clearly, all this will only be possible in special cases — cases which may be determined using this linear analysis. When the linear analysis using infinitesimal

transformations establishes that compensation is possible, the corresponding finite transformations may be used to determine the shifts in fluxes and concentrations required to compensate for finite temperature-driven shifts in rate constants.

When this is possible, eqs. (7.10) state that the reaction with altered fluxes and concentration variables will proceed with the same unimolecular and bimolecular rate constants as did the original reaction at ambient temperature. If c_{12} and c_{21} are zero, one will have been able to accomplish this simply by changing fluxes and real world concentrations.

We also call attention to the fact that in the general case the determination of lumpings that will eliminate intermediates from consideration also begins with the determination of an appropriate infinitesimal transformation by specifying an appropriate linear combination of base generators. Once this has been determined – by solving a set of linear equations – one can determine the corresponding finite transformations. In proceeding from the infinitesimal to the finite transformations in these lumping analyses that fix a generator U , one may directly use the operator $\exp(aU)$ or a succession of different T 's, each involving one of the base generators in U and a particular choice of parameter that may be determined with the aid of table 2.2 of I or an extension of it that deals with a larger number of variables x_i and k_μ .

8. Invariant functions of kinetic coefficients

As the parameter a varies, the operators $\exp(aU)$ change the values of the kinetic coefficients \mathbf{k} and the representative points in \mathbf{k} space move along a definite path, as indicated in fig. 8.1 for a three-dimensional \mathbf{k} space. The functional form of these paths is most usefully characterized by stating the functions $F(\mathbf{k})$ that are left invariant as the point moves along the path. Setting each $F(\mathbf{k})$ equal to a constant defines a surface in the space of kinetic coefficients, and the intersection of all these surfaces defines a line in this space – a path specified by the transformation. The constant value to be assigned to each $F(\mathbf{k})$ is determined by the initial values of the k 's. In the figure, it is supposed that both curves are determined by the same two generators U so that only the differing values of the constants C distinguishes them.

We now turn to the problem of determining the functions F . Let $F(\mathbf{k})$ be a function left invariant by the transformations $\exp(aU)$. Then, expanding the exponential, one has

$$\{1 + aU + (aU)^2/2 + \dots\} F = F. \quad (8.1)$$

The necessary and sufficient condition that this holds for all values of a is

$$UF = 0. \quad (8.2)$$

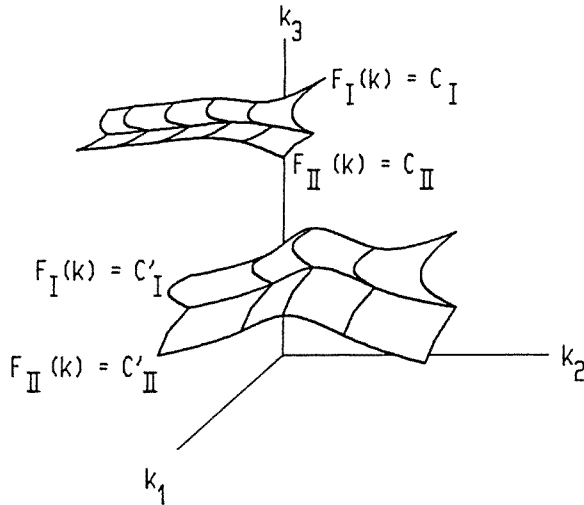


Fig. 8.1. Invariant surfaces and curves defined by invariant functions of rate constants. The functions F_I and F_{II} , when set equal to the constants C , here define two-dimensional surfaces in a three-dimensional space of rate coefficients. These surfaces intersect in a line. Changing the values of the constants C changes the surfaces and their intersection.

For a given U , this is a first-order partial differential equation for F . By the usual theory of such equations, it is equivalent to a set of first-order ordinary differential equations [9]

$$\frac{\delta k_{10}}{g_{10}} = \frac{\delta k_{20}}{g_{20}} \dots = \frac{\delta k_{222}}{g_{222}} . \quad (8.3)$$

Consider, for example, the case of the transformation with generator

$$\begin{aligned} U_{11} = & x_1 \partial/\partial x_1 + k_{10} \partial/\partial k_{10} + k_{12} \partial/\partial k_{12} - k_{111} \partial/\partial k_{111} \\ & - k_{122} \partial/\partial k_{122} - k_{21} \partial/\partial k_{21} - 2k_{211} \partial/\partial k_{211} - k_{212} \partial/\partial k_{212} . \end{aligned} \quad (8.4)$$

Here, the equations (8.3) have as solutions a basic set of invariant functions

$$\begin{aligned} & k_{10}/k_{12}, \quad k_{11}, \quad k_{111} \cdot k_{12}, \quad k_{112}, \quad k_{122}/k_{12} \\ & k_{20}, \quad k_{21} \cdot k_{12}, \quad k_{22}, \quad k_{211} \cdot k_{12}^2, \quad k_{212} \cdot k_{12}, \quad k_{222} . \end{aligned} \quad (8.5)$$

Any function of these base functions is, of course, also an invariant function.

Table 8.1(a)
Invariants of the transformations

T_{10}	k_{111}	k_{112}	k_{122}	k_{211}	k_{212}	k_{222}
T_{11}	k_{11}	k_{20}	k_{22}	k_{112}	k_{222}	k_{10}/k_{12}
T_{12}	k_{20}	k_{21}	k_{211}	$k_{11} + k_{22}$	$k_{10} k_{21} + k_{20} k_{221}$	$2k_{111} + k_{212}$
T_{111}	k_{10}	k_{12}	k_{20}	k_{21}	k_{22}	k_{122}
T_{112}	k_{10}	k_{20}	k_{21}	k_{22}	k_{211}	k_{222}
T_{122}	k_{10}	k_{11}	k_{20}	k_{21}	k_{22}	k_{111}

Table 8.1(b)
Invariants of the transformations

T_{10}	$(k_{11})^2 - 4k_{10} k_{111}$	$(k_{21})^2 - 4k_{20} k_{211}$	$2k_{12} k_{111} - k_{11} k_{112}$	$2k_{211} k_{22} - k_{21} k_{212}$	$k_{212} k_{12} - k_{112} k_{22}$
T_{11}	$k_{111} k_{12}$	k_{122}/k_{12}	$k_{21} k_{12}$	$k_{211}/(k_{12})^2$	k_{212}/k_{12}
T_{12}	$(k_{212})^2 - k_{211} k_{222}$	$k_{11} k_{22} - k_{12} k_{21}$	$k_{11} k_{211} - k_{21} k_{111}$	$k_{111} k_{212} - k_{112} k_{211}$	$(k_{11})^2 - 4k_{10} k_{111}$
T_{111}	k_{212}	k_{222}	$k_{10} k_{112} - k_{11} k_{12}$	$k_{11} k_{21} - 2k_{10} k_{211}$	$k_{10} k_{11} - k_{20} k_{12}$
T_{112}	$2k_{10} k_{122} - (k_{12})^2$	$k_{111} + k_{212}$	$k_{20} k_{112} - k_{11} k_{22}$	$k_{11} k_{21} - k_{20} k_{111}$	$k_{11} k_{12} - 2k_{12} k_{22} + 2k_{20} k_{122}$
T_{122}	k_{211}	k_{212}	$k_{12} k_{21} - k_{20} k_{112}$	$k_{112} + k_{222}$	

Table 8.1(c)
Invariants of the transformations

T_{20}	k_{111}	k_{112}	k_{122}	k_{211}	k_{212}	k_{222}
T_{21}	k_{10}	k_{12}	k_{122}	$k_{11} + k_{22}$	$(k_{20}k_{12} + k_{10}k_{112})$	$2k_{222} + k_{112}$
T_{22}	k_{11}	k_{10}	k_{22}	k_{111}	k_{212}	k_{20}/k_{21}
T_{211}	k_{20}	k_{22}	k_{10}	k_{12}	k_{11}	k_{222}
T_{212}	k_{10}	k_{20}	k_{12}	k_{11}	k_{122}	k_{111}
T_{222}	k_{20}	k_{21}	k_{10}	k_{12}	k_{11}	k_{211}

Table 8.1(d)
Invariants of the transformations

T_{20}	$(k_{22})^2 - 4k_{20}k_{222}$	$(k_{12})^2 - 4k_{10}k_{122}$	$2k_{21}k_{222} - k_{22}k_{221}$	$2k_{122} - k_{12}k_{121}$	$k_{121}k_{21} - k_{212}k_{11}$
T_{21}	$(k_{112})^2 - k_{122}k_{111}$	$k_{11}k_{22} - k_{12}k_{21}$	$k_{22}k_{122} - k_{12}k_{222}$	$k_{222}k_{111} - k_{212}k_{122}$	$k_{22}k_{21} - 2k_{21}k_{11} + 2k_{10}k_{211}$
T_{22}	$k_{222}k_{21}$	k_{211}/k_{21}	$k_{12}k_{21}$	$k_{122}/(k_{21})^2$	k_{112}/k_{21}
T_{211}	k_{122}	k_{112}	$k_{12}k_{21} - k_{10}k_{212}$	$k_{212} + k_{111}$	$k_{22}k_{21} - 2k_{21}k_{11} + 2k_{10}k_{211}$
T_{212}	$2k_{20}k_{211} - (k_{21})^2$	$k_{222} + k_{112}$	$k_{10}k_{212} - k_{22}k_{21}$	$k_{22}k_{12} - k_{10}k_{222}$	$k_{20}k_{22} - k_{10}k_{21}$
T_{222}	k_{112}	k_{111}	$k_{20}k_{212} - k_{22}k_{21}$	$k_{22}k_{12} - 2k_{20}k_{122}$	$(k_{22})^2 - 4k_{20}k_{222}$

The reader will note on inspecting table 2.2 of I that the invariant functions (8.5) can also be constructed by eliminating the group parameter a from the finite transformations. If it should happen that k_{12} were zero, one would avoid introducing k_{12} by combining the transformed k 's in a different manner than indicated in (8.5).

In table 8.1, we list a basis of independent functions $F(k)$ left invariant by each of the generators in table 2.1 of I. Any two sets of values of the kinetic coefficients that give the same values for one or more of these sets of functions will yield reaction systems whose global behaviour is qualitatively the same in the sense defined in section 7. A set of eleven such basis functions $F(k)$ may be similarly determined for any linear combination of generators one chooses.

As an example of the utilization of these functions, we consider the functions determined by the translation operator $T_{10}(-a)T_{20}(-b) = T(-a, -b)$. This operator acts on (x_1, x_2) to give $(\bar{x}_1, \bar{x}_2) = (x_1 - a, x_2 - b)$. At the same time, it shifts a number of rate constants $k_{i\mu}$ to $\bar{k}_{i\mu}$. $T(-a, -b)$ thereby determines homeomorphisms of x, k space that convert a given set of initial concentration values (x_1^0, x_2^0) (and running values (x_1, x_2)), and a given rate equation $\dot{x} = r(x, k)$ into a new set of concentrations obeying a new set of rate equations. For each value of a, b , the new initial concentrations $(\bar{x}_1^0, \bar{x}_2^0)$ evolve along a phase trajectory $(\bar{x}_1(t), \bar{x}_2(t))$ topologically equivalent to that of the initial phase trajectory $(x_1(t), x_2(t))$. Thus, by acting on a system with initial concentrations evolving along a phase trajectory of given topology, the transformation converts it into a two-parameter family of initial concentrations and phase trajectories of identical topology but belonging to different rate equations. (Any of the values (x_1, x_2) on the initial trajectory can of course be considered initial concentrations.) Inserting the initial values of the k_μ into the functions of table 8.1, one obtains initial values of the invariant functions. Setting the corresponding functions of the \bar{k}_μ equal to these initial values, one obtains the equations that determine the relations among the \bar{k}_μ that must subsist to ensure that the altered kinetic equations should have topologically identical trajectories originating from the transformed concentrations.

9. Group properties

So far, we have not dealt with important questions concerning the totality of transformations in table 2.2 of I. For example, are the different one-parameter groups of transformations in the table all subgroups of a single many-parameter group? Are there other time-independent transformations with generators quadratic in x , which will also leave the kinetic equations (2.1) invariant?

The first of these questions is also the logically prior one, because if the transformations do not together comprise a group, it can be shown that they give rise to further transformations which leave eqs. (1.1) invariant. Now, for the transformations to be those of a many-parameter group it is necessary and sufficient that their generators close under commutation:

$$[U_i, U_j] = \sum c_{ij}^k U_k . \tag{9.1}$$

In the previous paper I, we established that the commutation relations of invariance generators which leave the k subspace invariant are the same as the commutation relations of the full generators which act in the space of k and x . (That is to say, the structure constants c_{ij}^k are the same in both instances.) Because we have chosen the functions $h_i(x)$ to be independent of the k 's, it is also true that the commutation relations of that portion of the generators which acts on the x 's — the $h \cdot \nabla_x$ — are also the same as the commutation relations of the full generators. This enables us to use Lie's classification of all the transformation groups of the plane (here the plane of x_1, x_2) to determine all possible Lie groups obtainable from the generators in table 2.1 of I. These are set forth in table 9.1.

Table 9.1
U's that generate many-parameter Lie groups

I.	$U_{10}, U_{20}, U_{11}, U_{12}, U_{21}, U_{22}, U_{111} + U_{212}, U_{222} + U_{112}$ (projective group of the plane [20])
II.	(i) $U_{10}, U_{20}, U_{11}, U_{21}, U_{22}, U_{211}, U_{111} + U_{212}$ (ii) $U_{20}, U_{10}, U_{22}, U_{12}, U_{11}, U_{122}, U_{222} + U_{112}$
III.	(i) $U_{10}, U_{20}, U_{11} + U_{22}, U_{21}, U_{211}, U_{111} + 2U_{212}$ (ii) $U_{20}, U_{10}, U_{22} + U_{11}, U_{12}, U_{122}, U_{222} + 2U_{112}$
IV.	(i) $U_{10}, U_{11}, U_{12}, U_{112}, U_{20}, U_{22}$ (ii) $U_{20}, U_{22}, U_{21}, U_{212}, U_{10}, U_{11}$
V.	(i) $U_{10}, U_{12}, U_{122}, U_{20}, U_{22}, 2U_{11} + U_{122}$ (ii) $U_{20}, U_{21}, U_{211}, U_{10}, U_{11}, 2U_{22} + U_{211}$
VI.	(i) $U_{10}, U_{20}, U_{11}, U_{22}, U_{21}, U_{211}$ (ii) $U_{20}, U_{10}, U_{22}, U_{11}, U_{12}, U_{122}$
VII.	$U_{10}, U_{20}, U_{11}, U_{12}, U_{21}, U_{22}$ (general linear group of the plane [20])
VIII.	$U_{10}, U_{20}, U_{12}, U_{21}, U_{11} - U_{22}$ (special linear group of the plane [20])
IX.	(i) $U_{10}, U_{11}, U_{22}, U_{122} + U_{112}$ (ii) $U_{20}, U_{22}, U_{11}, U_{211} + U_{212}$
X.	(i) $U_{10}, 2U_{11} + U_{22}, U_{111} + U_{212}$ (ii) $U_{20}, 2U_{22} + U_{11}, U_{222} + U_{112}$
XI.	(i) $U_{10}, U_{11}, U_{12}, U_{122}$ (ii) $U_{20}, U_{22}, U_{21}, U_{211}$
XII.	(i) U_{10}, U_{12}, U_{122} (ii) U_{20}, U_{21}, U_{211}
XIII.	(i) U_{10}, U_{11}, U_{111} (ii) U_{20}, U_{22}, U_{222} (group of the line [20])

Note: Many of the groups whose generators are listed above contain subgroups not listed, e.g. in XIII (i), U_{10} and U_{11} generate a two-parameter group.

It will be noted that no one of the many-parameter groups in this table contains all the generators in table 2.1 of I. The largest group is the first listed, a ten-parameter group that is a form of the projective group of the plane. If one takes the commutators of the generators in this group with the remaining linearly independent generators available from table 2.1 of I, then one obtains new generators not in table 2.1. However, in the generators the h_i are of third degree in x . No further linearly independent generators exist in which the h are of less than third degree and g is nonzero.

10. Errors in finite transformations resulting from use of approximate generators

The generators used in section 5 to approximately linearize the Lotka–Volterra equations are typical generators in the sense that they are generators of transformations that only approximately leave invariant a set of kinetic equations. Expanding the finite transformation operator $\exp(aU)$ in powers of the group parameter a , one sees that as a consequence one would have to expect that the effect of $\exp(aU)$ on the differential equation, its solutions, and functions of its solutions, would only be accurate through $O(ax^2)$. In particular, eq. (5.2) is linearized only through $O(y^2)$. However, one is interested in having the transformation $\exp(aU)$ act at every point on a given solution curve – not just near the origin.

In sections 3 and 5, we have used critical points in phase space as origins of coordinates. One can just as well choose a point on or near a trajectory as the origin and thereby ensure that in the region of such a point, the error in the coefficients $h_i(x)$ in U is minimal. This allows one to determine trajectories in the region of any point P that are accurate through second order in displacements from P . If, using P as origin, one proceeds as in sections 3, 5 and transforms the system of interest into a system with known analytic solutions, one can use the inverse transformation to obtain analytic approximations to trajectories in the region of P . From a more general standpoint, expansions about P will allow accurate investigations of solution behaviour near P when one varies k 's.

To illustrate the method, we use it to improve the approximate Lotka–Volterra trajectory obtained in section 5. There, the analytic reference solution was obtained by transforming away the quadratic terms in the rate equations using an operator $\exp(aU)$. Since the group generators are accurate to $O(y^3)$, this gave a set of rate equations linear to $O(y^3)$, the origin being the singular point. The linear equations were solved, and their solution transformed into an approximate solution of the Lotka–Volterra equation (5.3) by action of $\exp(-aU)$.

To improve the solutions obtained in this way, one may proceed as follows:

- (i) Determine the general form of the generator of the transformation that linearizes the nonlinear equations in the region of a point P on the actual trajectory of interest – e.g. the point whose coordinates are initial values of the species concentrations.

- (ii) Determine the finite transformation that carries out the linearization.
- (iii) Obtain and solve the linearized equations.
- (iv) Transform the solution of the linearized equation into the required solution of the nonlinear equation.

Let the new center of expansion of (5.2) be at a point P with coordinates (α, β) and define

$$y_1^\alpha = y_1 - \alpha, \quad y_2^\beta = y_2 - \beta \quad (10.1a)$$

and

$$T_{10}(-\alpha, -\beta) = \exp(-\alpha U_{10} - \beta U_{20}), \quad y^{\alpha\beta} = T_{10}(-\alpha - \beta)y = (y_1^\alpha, y_2^\beta). \quad (10.1b)$$

The action of $T_{10}(-\alpha, -\beta)$ on eqs. (5.2) gives

$$\begin{aligned} dy_1^\alpha/dt &= k_{10}^{\alpha\beta} + k_{11}^{\alpha\beta} y_1^\alpha + k_{12}^{\alpha\beta} y_2^\beta + k_{112}^{\alpha\beta} y_1^\alpha y_2^\beta \\ dy_2^\beta/dt &= k_{20}^{\alpha\beta} + k_{21}^{\alpha\beta} y_1^\alpha + k_{22}^{\alpha\beta} y_2^\beta + k_{212}^{\alpha\beta} y_1^\alpha y_2^\beta, \end{aligned} \quad (10.2a)$$

where

$$\begin{aligned} k_{10}^{\alpha\beta} &= \alpha\beta k_{112} + \beta k_{12}, & k_{11}^{\alpha\beta} &= \beta k_{112}, \\ k_{12}^{\alpha\beta} &= k_{12} + \alpha k_{112}, & k_{112}^{\alpha\beta} &= k_{112}, \\ k_{20}^{\alpha\beta} &= \alpha\beta k_{212} + \alpha k_{21}, & k_{21}^{\alpha\beta} &= k_{21} + \beta k_{212}, \\ k_{22}^{\alpha\beta} &= \alpha k_{21}, & k_{212}^{\alpha\beta} &= k_{212}. \end{aligned} \quad (10.2b)$$

We seek an invariance generator

$$U = \mathbf{h}(y^{\alpha\beta}) \cdot \nabla_{y^{\alpha\beta}} + \mathbf{g} \cdot \nabla_{\mathbf{k}^{\alpha\beta}} \quad (10.3)$$

and a value of a such that $\exp(aU)$ acts on $y^{\alpha\beta}$ and $\mathbf{k}^{\alpha\beta}$ to transform the $k_{112}^{\alpha\beta}$ and $k_{212}^{\alpha\beta}$ terms to zero, leaving only terms of $O((y^{\alpha\beta})^0)$, $O(y^{\alpha\beta})$, and $O((y^{\alpha\beta})^3)$ and higher. One may suppose that such a generator is of the form $\sum c_\mu U_\mu$. We first determine the c_μ that would be required if the nonlinearity were infinitesimal. To do this, we multiply $k_{112}^{\alpha\beta}$ and $k_{212}^{\alpha\beta}$ by an infinitesimal ϵ and determine the c_μ by requiring that $(1 + \delta aU)$ annihilate $\epsilon k_{112}^{\alpha\beta}$ and $\epsilon k_{212}^{\alpha\beta}$ while leaving $k_{111}^{\alpha\beta}$, $k_{122}^{\alpha\beta}$, $k_{211}^{\alpha\beta}$ and $k_{222}^{\alpha\beta}$ all zero.

Inspecting table 2.1 of I, one finds that in the sum one need only consider the six generators U_{ijj} , that generate nonlinear transformations of the concentrations. Considered as functions of y_1^α, y_1^β , all these generators vanish at $y_1^\alpha = 0 = y_2^\beta$. It follows that $\bar{y}_1^\alpha, \bar{y}_2^\beta$ also vanish at the origin, which is thus an invariant point of the transformation. Table 2.2 of I shows the transformed rate constants \bar{k}_{i0} and \bar{k}_{ij} depend linearly on both group parameters and rate constants. Consequently, $\exp(U)$ has the same effect on the k_{0i} and k_{ij} as does $(1 + U)$, so that setting $\epsilon = \delta a$ allows one to use $(1 + U)$ to obtain the same linearized equation as would be obtained using $\exp(U)$. It cannot, however, be concluded that $(1 + U)$ generally acts on the concentration variables to give transformed variables that are good approximations to those obtained by the action of $\exp(U)$.

For $(1 + \delta a U)$ to kill $\epsilon k_{ijj}^{\alpha\beta}$, the c_μ must satisfy the following set of linear equations:

$$\begin{aligned}
 0 &= \delta a (c_{111} k_{11}^{\alpha\beta} + c_{112} k_{21}^{\alpha\beta} - c_{211} k_{12}^{\alpha\beta}) \\
 -\epsilon k_{112}^{\alpha\beta} &= \delta a (c_{111} 2k_{12}^{\alpha\beta} + c_{112} k_{22}^{\alpha\beta} + c_{122} 2k_{21}^{\alpha\beta} - c_{212} k_{12}^{\alpha\beta}) \\
 0 &= \delta a (c_{112} k_{12}^{\alpha\beta} + c_{122} (2k_{22}^{\alpha\beta} - c_{222} k_{12}^{\alpha\beta})) \\
 0 &= \delta a (-c_{111} k_{21}^{\alpha\beta} + c_{211} (2k_{11}^{\alpha\beta} - k_{22}^{\alpha\beta}) + c_{212} k_{21}^{\alpha\beta}) \\
 -\epsilon k_{212}^{\alpha\beta} &= \delta a (-c_{112} k_{21}^{\alpha\beta} + c_{211} 2k_{12}^{\alpha\beta} + c_{212} k_{11}^{\alpha\beta} + c_{222} 2k_{21}^{\alpha\beta}) \\
 0 &= \delta a (-c_{122} k_{21}^{\alpha\beta} + c_{212} k_{12}^{\alpha\beta} + c_{222} k_{22}^{\alpha\beta})
 \end{aligned} \tag{10.4}$$

To further particularize the discussion, we approximate a trajectory of the Lotka–Volterra equations (5.1) through the point (0.922, -0.491). Translating the origin to this point, the Lotka–Volterra equations become

$$\begin{aligned}
 \dot{y}_1^\alpha &= 0.9437 + 0.491 y_1^\alpha - 1.922 y_2^\beta - y_1^\alpha y_2^\beta \\
 \dot{y}_2^\beta &= 0.4693 + 0.509 y_1^\alpha + 0.922 y_2^\beta + y_1^\alpha y_2^\beta .
 \end{aligned} \tag{10.5}$$

To linearize these, we first use (10.4) to determine the parameters a_{ijk} in the linearizing operator $1 + \Sigma a_{ijk} U_{ijk}$, and find them to be

$$\begin{aligned}
 a_{111} &= -0.3289, \quad a_{112} = -0.1067, \quad a_{122} = 0.4829 \\
 a_{211} &= 0.1123, \quad a_{212} = -0.3422, \quad a_{222} = -0.4467 .
 \end{aligned} \tag{10.6}$$

The approximately linearized equations, obtained using $1 + \sum a_{ijk} U_{ijk}$, are

$$\begin{aligned}\dot{\bar{y}}_1^\alpha &= 0.9437 + 0.1170 \bar{y}_1^\alpha - 1.0511 \bar{y}_2^\beta + O(y^3) \\ \dot{\bar{y}}_2^\beta &= 0.4693 + 0.7161 \bar{y}_1^\alpha + 0.1615 \bar{y}_2^\beta + O(y^3).\end{aligned}\tag{10.7}$$

If one writes the finite transformation T in the form

$$T = T_{222} [T_{212} [T_{211} [T_{122} [T_{112} [T_{111}]]]]]],\tag{10.8}$$

one finds that T linearizes (10.5), yielding (10.7), when the group parameters are

$$\begin{aligned}a_{111} &= -0.0123, \quad a_{112} = -0.7473, \quad a_{122} = 1.6794 \\ a_{211} &= 0.2792, \quad a_{212} = -0.6817, \quad a_{222} = -0.1248.\end{aligned}\tag{10.9}$$

There are several ways to obtain these values. We calculated them by taking advantage of the fact that when the k_{i0} vanish, T acts linearly on the k_{ijj} , and so began with initial approximations to the a 's which we obtained by solving (10.4). We then simultaneously increased k_{10} and k_{20} in five stages. At each stage, the a 's that zeroed the k_{ijj} to 1 part in 10^4 were determined by Newton's method. This required two steps at each stage, and yielded final values of the a 's that zero the k_{ijj} to within 1 part in 10^5 .

The solution of (10.7) passing through $\bar{y}^\alpha = 0 = \bar{y}^\beta$ at $t = 0$ obtained on neglecting terms $O(y^3)$ is

$$\begin{aligned}\bar{y}_1^\alpha &= -0.8349 + 0.8349 \cos(0.8673 t) \\ &\quad + 0.9549 \sin(0.8673 t) \exp(0.1384 t) \\ \bar{y}_2^\beta &= 0.8049 + (-0.8049 \cos(0.8673 t) \\ &\quad + 0.6695 \sin(0.8673 t) \exp(0.1384 t).\end{aligned}\tag{10.10}$$

Acting on $(\bar{y}_1^\alpha, \bar{y}_2^\beta)$, the inverse transformation T^{-1} gives (y_1^α, y_2^β) . In fig. 10.1, the resulting phase trajectory is compared with the exact trajectory and with the trajectory generated by dropping the quadratic terms in (10.5), and then solving the resulting linear equation. The errors in the trajectory obtained by transformation arise via third-order errors in the linearized equations. The errors in the other trajectory arise from second-order errors in the linearized equations.

It should be noted that the phase trajectory of (5.2) passing through the point P with coordinates $(y_1, y_2) = (0.922, -0.491)$ is a closed curve. However, when the translated equation (10.5) is linearized by dropping its bimolecular terms,

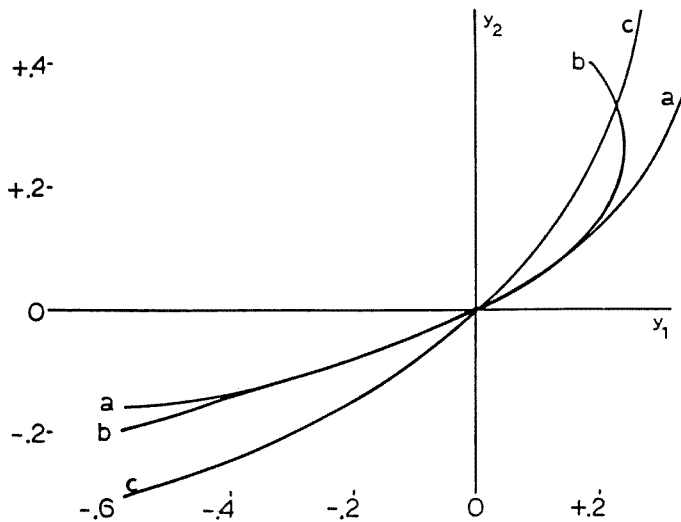


Fig. 10.1. Regional approximation to a phase trajectory of the Lotka – Volterra equation. Curve *a* is an exact trajectory of (10.5). Curve *b* is its regional approximation defined by (10.8, 10.9, 10.10). Curve *c* is the approximation to curve *a* determined by the usual linearization of (10.5).

all its phase curves are open ones. The linearization is not an invariant one in our generalized sense (cf. I), and has as a consequence not left the topology of its phase curves invariant. The same is true of the regional linearization method: (10.7) has only open curves for phase trajectories because our generators are insufficiently accurate to ensure that the approximate linearization carried out by T is a sufficiently good approximation to an invariance transformation. The open phase trajectories of (10.7) are then of course mapped into open phase trajectories by the transformation inverse to (10.8) because the transformation is a diffeomorphism. These topological errors could of course have been avoided had we linearized equations (5.2) in the way we did in section 5, and then translated the resulting equations to the new origin. This, however, makes it more difficult to obtain a close approximation to the phase curves at points far from the singular point at the origin. The method illustrated here is designed for that purpose.

11. Higher approximations to generators

All our considerations so far have involved generators obtained by quadratic approximation. In this section, we will determine higher approximations to the generators and investigate the ways in which their use modifies results obtained from the quadratic approximation. It will be remembered that the quadratic approxi-

mation to the U was obtained by solving eqs. (2.8a), (2.8b) together with the approximation to (2.8c) obtained by setting $U^{(2)}$ to zero. We begin this section by relaxing the approximation that $U^{(2)} = 0$ in (2.8c), and thereby solve the full set of equations implied by (2.8a, b, c). Inspecting (2.8), one sees that this completely determines the k terms in the U . Thus, the approximation we are about to discuss fixes the g 's and therefore for each U completely determines the transformation of the kinetic coefficients carried out by $\exp(aU)$.

We start with an example and determine the modifications to the U_{122} of table 2.1 of I that one obtains by removing the approximation $U^{(2)} = 0$ when solving (2.8a, b, c) of I. Equations (2.8a, b) are not altered and one obtains from (2.8c) the six determining equations

$$\begin{aligned}
 (g_{111}) - 3k_{10}h_{1111} - k_{20}h_{1112} &= 0 \\
 (g_{112} - 2k_{21}) - 2k_{10}h_{1112} - 2k_{20}h_{1122} &= 0 \\
 (g_{122} + k_{11} - 2k_{22}) - k_{10}h_{1122} - 3k_{20}h_{1222} &= 0 \\
 (g_{211}) - 3k_{10}h_{2111} - k_{20}h_{2112} &= 0 \\
 (g_{212}) - 2k_{10}h_{2112} - 2k_{20}h_{2122} &= 0 \\
 (g_{222} + k_{21}) - k_{10}h_{2122} - 3k_{20}h_{2222} &= 0.
 \end{aligned} \tag{11.1}$$

On setting $U^{(2)} = 0$, the terms in parentheses remain and are the terms used previously to determine the $U^{(-1)} + U^{(0)} + U^{(1)}$ approximation to U . To obtain corrections to the resulting U_{122} , one transfers these terms to the right-hand side of the equations and solves the resulting inhomogenous equations for the h_{ijkl} . The three equations for the h_{1jkl} and the three for the h_{2jkl} are independent and each set is of rank 3 if neither k_{10} nor k_{20} vanish. Consider this case first. Solving the equations, one finds that they yield the following U :

$$\begin{aligned}
 U &= U_{122} + (-K^3 x_1^3 + 3K^2 x_1^2 x_2 - 3Kx_1 x_2^2 + x_2^3) \\
 &\times (e_1 \partial/\partial x_1 + e_2 \partial/\partial x_2),
 \end{aligned} \tag{11.2}$$

where $K = k_{20}/k_{10}$. Here, e_1 and e_2 are arbitrary parameters. One may in fact re-express (11.2) in the form

$$U = U_{122} + e_1 U_{e_1} + e_2 U_{e_2} . \tag{11.3}$$

As U_{122} is reclaimed on setting e_1, e_2 to zero, U_{122} is itself a solution of the full set of equations $W_1 = 0$. Thus, U_{122} is one degree more accurate than might have been expected. It will also be noted that the operators U_{e_1} and U_{e_2} act only on x_1, x_2 and not upon the rate coefficients k . They are consequently of no interest in the context of this paper.

Next, consider the case $k_{10} = k_{20} = 0$. It is evident that each of the h_{ijk} may then be chosen arbitrarily, so that one obtains an eight-parameter family of generators:

$$U = U_{122} + \sum h_{ijkl} x_j x_k x_l \partial / \partial x_i . \tag{11.4}$$

As in the previous case, the additional generators have no effect upon the rate coefficients.

Next, consider the situation where k_{20} vanishes, while k_{10} does not. Then one finds

$$U = U_{122} + h_{1222} x_2^3 \partial / \partial x_1 + h_{2222} x_2^3 \partial / \partial x_2 . \tag{11.5}$$

When k_{10} vanishes and k_{20} does not, one finds

$$U = U_{122} + h_{1111} x_1^3 \partial / \partial x_1 + h_{2111} x_1^3 \partial / \partial x_2 . \tag{11.6}$$

In both cases, the h 's are arbitrary and are coefficients of new generators that have no effect on the rate constants. In short, in order to obtain corrections to U_{122} it is necessary to move on to eq. (2.8d) of I.

This discussion of "corrections" to U_{122} applies to the other U_{ijk} in a parallel manner. The terms in (11.1) not contained in parentheses are the same in each case. The terms contained in parentheses are different in each case, but vanish in the original approximation. Thus, the generators listed in table 2.1 of I and the finite transformations in table 2.2 of I are all unchanged when eqs. (2.8a, b, c) of I are solved in toto.

We next investigate the modifications of the $U^{(2)}$ that are required in order to satisfy (2.8d) of I. Equation (2.8d) may be written in matrix form as

$$0 = G^{(2)}H^{(2)} + G^{(1)}H^{(3)} + G^{(0)}H^{(4)} = (GH)^{(4)} . \tag{11.7}$$

Here, $G^{(n)}$ is a matrix whose entries contain $g^{(n)}$ coefficients and $H^{(n)}$ is a vector of $h^{(n)}$ coefficients. The product $(GH)^{(4)}$ is of the form

$$(GH)^{(4)} = \begin{bmatrix} [g^{(0)}] & [0] & [0] \\ [0] & [g^{(1)}] & [0] \\ [0] & [0] & [g^{(2)}] \end{bmatrix} \begin{bmatrix} [h^{(4)}] \\ [h^{(3)}] \\ [h^{(2)}] \end{bmatrix} . \tag{11.8}$$

From this, it is evident that on insertion into (11.8) of the $h^{(2)}$ and $h^{(3)}$ calculated by setting to zero the lower order w , one obtains a set of equations which determine the $h^{(4)}$ without modifying the lower order $h^{(n)}$. *It follows that the functions $g(k)$ in the generators obtained by solving (2.8a, b, c) of I are exact. Thus, the invariant functions listed in table 8.1 are exact.*

If one wishes to use transformations whose generators are linear combinations of those listed in table 2.1 of I, it becomes necessary to integrate eqs. (8.3) to determine the corresponding invariant functions of the rate constants. These also will remain unaltered by all further improvements in the generators obtained by solving eqs. (2.8) of I in higher orders of approximation.

An interesting property of the higher order approximations to the U 's is worth noting. Even when a set of U_r in table 2.1 of I close under commutation, it will not generally be true that the corresponding set of improved generators will close under commutation. The commutators will generally contain terms of higher degree in x than the original generators. However, one may write

$$U_n = {}^kU_r + {}^xU_r, \quad (11.9)$$

where kU_r acts only on the kinetic coefficients and xU_r acts only on the species concentrations. If the kU_r close under commutation, then the theorem of ref. [1] of I establishes that the U_r will obey the same commutation relations as the kU_r when they satisfy (2.8) of I exactly. Any failure of the approximate generators to obey these commutation relations is thus an artifact of approximation.

Finally, we consider the general problem of obtaining arbitrarily high-order approximations to a generator U . Referring back to eqs. (2.8) of I, one sees that the contribution to U of order $p+1$ in x is obtained from the contributions of order p and $p-1$ by solving linear equations exactly analogous to those depicted in (11.8) above. As in the case of the example of eqs. (11.1), one obtains solutions corresponding to generators with g vanishing as well as the desired improvement $U^{(p+1)}$ to the U of interest. This $U^{(p+1)}$ can then be used together with $U^{(p)}$ to obtain $U^{(p+2)}$ in an analogous fashion.

12. Conclusions

This paper has utilized basic methods of the theory of Lie groups admitted by ordinary differential equations to determine large-scale global mappings connecting systems with differing rate constants.

As we have illustrated, a key consequence of such large changes is their effect upon the topology of the phase trajectories of a system. As we knew that time-independent transformations of species concentrations and rate constants could preserve the topology of phase portraits if the transformations were sufficiently

restricted, in this paper we investigated time-independent transformations whose generators are analytic in the rate constants and approximated as analytic in the concentrations. This is more than sufficient to force the transformations to be local diffeomorphisms of the entire system space – the space of all real values of the concentrations and rate constants. By also restricting the range of the group parameter where necessary, we have ensured that all finite transformations are diffeomorphisms of the space of real x, k . In addition, because the generators are so chosen that the space of rate constants is an invariant subspace, the topology of trajectories in concentration space is preserved by the transformations. This has allowed us to determine the one-parameter groups of changes in rate constants for which the phase trajectories are qualitatively insensitive in a well defined topological sense. As we have been able to exactly determine the changes in rate constants that preserve the topology of these phase portraits, it is possible to give a quantitative treatment of these changes in rate constants without further elaboration.

Because the determining equations for the group generators could be solved algorithmically, we have been able to systematically determine all one-parameter transformation groups satisfying the imposed conditions.

We are not the first to realize the importance of topological considerations in chemical kinetics: we particularly call attention to the work of Bruce Clark and his coworkers [10], and to the work of Martin Feinberg [11].

Our work differs from that of these and other investigators because we have taken advantage of the fact that the process of determining the Lie generators of an invariance transformation can be made algorithmic. This now makes it possible to develop a systematic and general treatment of the consequences of large changes in rate constants upon the behaviour of kinetic systems.

We have not attempted to exactly determine the phase portraits themselves. There is a fundamental reason for this. Autonomous ordinary differential equations whose right-hand sides are analytic functions can have “chaotic” solutions. This has the consequence that the coefficients $h(x)$ in the generators U of this paper need not be analytic functions; they may, for example, be only infinitely differentiable functions. In practice, one may approximate infinitely differentiable functions by a series of analytic functions, but it would be a mistake to suppose that this approximation was of the same value in all regions of the phase space. Experience suggests that this, and related, mathematical complexity seldom expresses itself in the chaotic evolution of the reacting systems of common occurrence in the chemical laboratory and chemical industry. It may be of more common occurrence in biochemical systems. Whenever the evolution of a kinetic system is nonchaotic, the transformations introduced in this paper allow one to both qualitatively and quantitatively investigate the sensitivity of phase trajectories to gross changes in rate constants, and to determine those changes in rate constants which leave some quantitative property unchanged [12]. If the evolution is chaotic, further investigations are necessary.

In the interest of simplicity, we have also side-stepped three problems mathematically much less troublesome than that of chaotic evolution. We have not required that the group parameters a be so restricted so as to ensure that no “real world” concentration becomes negative. We have also not required that mass conservation be preserved when $T(a)$ acts on a kinetic system. There are no fundamental problems involved here; it is not difficult to impose the requirements in any particular case – the difficulty is simply that the variety of cases is immense and diverse. Finally, we have not dealt with problems that arise when many-parameter Lie groups, whose parameters are only restricted in range by the structural properties of the group, have further restrictions imposed by the requirement that the group action on a space of real variables yields only real variables. In our case, the difficulty appears when abstractly allowed parameter values carry points with finite coordinates to coordinates whose value is $\pm\infty$. A considerable simplification occurs if one proceeds as is done in the theory of projective transformations; this, however, changes the topology of the space of x, k and introduces conceptual elaborations that we consider to be inappropriate in an introductory work such as this.

A variety of applications can be envisioned for the time-independent transformations of this paper. Because so much of the analysis involves only linear algebra, the methods are applicable to systems involving many chemical species. Further applications to the linearization of kinetics and to lumping and control problems appear to hold particular promise. The methods we have introduced for determining the subspace of x, k containing phase space trajectories of a fixed topology are methods that are systematic and apply directly to systems involving an arbitrary number of reactants: they may be used to obtain a great deal of qualitative information about these systems. The use of the methods to obtain regional analytic approximations to solutions of nonlinear kinetic equations also appear promising.

We are currently extending Lie methods to reactions involving diffusion [13]. It is known that reaction-diffusion equations are invariant under a much larger class of transformations than those considered herein and in I; in the general case, it will be necessary to allow transformations that depend upon partial derivatives of arbitrary order [14].

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