

GLOBAL SENSITIVITY ANALYSIS OF NONLINEAR CHEMICAL KINETIC EQUATIONS USING LIE GROUPS: I. DETERMINATION OF ONE-PARAMETER GROUPS

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Abstract

We introduce one-parameter groups of transformations that effect wide-ranging changes in the rate constants and input/output fluxes of homogeneous chemical reactions involving an arbitrary number of species in reactions of zero, first and second order. Each one-parameter group is required to convert every solution of such elementary rate equations into corresponding solutions of a one-parameter family of altered elementary rate equations. The generators of all allowed one-parameter groups are obtained for systems with N species using an algorithm which exactly determines their action on the rate constants, and either exactly determines or systematically approximates their action on the concentrations. Compounding the one-parameter groups yields all many-parameter groups of smooth time-independent transformations that interconvert elementary rate equations and their solutions.

1. Introduction

The response of kinetic systems over extensive regions of their physical parameter space – the space of rate constants and input/output fluxes – is of wide interest in many different contexts. For example, chemical system modelling can involve solving large numbers of coupled rate equations with considerable uncertainties in many values of the rate constants. In other problems some of the system parameters (e.g. input fluxes of chemical species) may actually be controlled, but determining the optimum choice of parameter values would require exploring a large domain of

control-parameter space. Conventional gradient-based local sensitivity analysis techniques [1] have limited applicability in problems of this type. In addition, fully statistically-based approaches [2] do not allow for an analysis of the structure of the parameter space. Other methodologies [3] based on repeated sampling of points in the parameter space suffer from the same problem and often require an impractical amount of computational labor.

In two previous papers, an alternative approach to sensitivity analysis, using Lie transformation groups, was introduced as a method for investigating the consequences of large changes in parameters in kinetic equations [4,5]. The present paper extends this effort into the realm of nonlinear kinetics.

The thrust of this work is the development of a systematic procedure that yields mappings which transform solutions of a system of kinetic equations through the hyperdimensional space defined by all rate constants, chemical species, and time. Here we will not, however, consider transformations of the time variable. We also do not allow the transformed rate constants to be explicit functions of the concentration variables.

The mappings are achieved by the application of operators $T(a) = \exp(aU)$ of one-parameter groups, where a is a real parameter and U is a group generator of Lie type. This generator is a first-order differential operator which may act on all physical parameters and variables of the kinetic system. Symbolizing concentrations by x_i and rate constants by k_μ , the generator here takes the form

$$U = \sum h_i(x, k) \partial / \partial x_i + \sum g_\mu(k) \partial / \partial k_\mu . \quad (1.1)$$

Here, x represents the set of x_i and k represents the set of k_μ . Henceforth, \mathbf{x}, \mathbf{k} represent vectors with components x_i and k_μ in a Euclidean space of x, k . The operator of finite transformations $T(a) = \exp(aU)$ acts as follows:

On a rate constant k_μ :

$$T(a)k_\mu = \bar{k}_\mu = K_\mu(\mathbf{k}; a); K_\mu(\mathbf{k}; 0) = k_\mu . \quad (1.2a)$$

On the concentration x_i of species i :

$$T(a)x_i = \bar{x}_i = X_i(\mathbf{x}, \mathbf{k}; a); X_i(\mathbf{x}, \mathbf{k}; 0) = x_i . \quad (1.2b)$$

Figure 1.1 depicts the type of mapping being considered.

As indicated in eqs. (1.2), assigning the group parameter a the value zero gives the identity transformation. As a is shifted from zero by infinitesimal and then finite amounts, changes in \mathbf{k} and \mathbf{x} develop which are at first infinitesimal, and then become increasingly profound. For a fixed value of the parameter a , $T(a)$ acts on the moving vector $\mathbf{x}(t)$ to give the transformed vector $\bar{\mathbf{x}}(t) = \mathbf{X}(\mathbf{x}(t), \mathbf{k}; a)$. It thus transforms the curve in concentration space described by $\mathbf{x}(t)$ into a new curve depict-

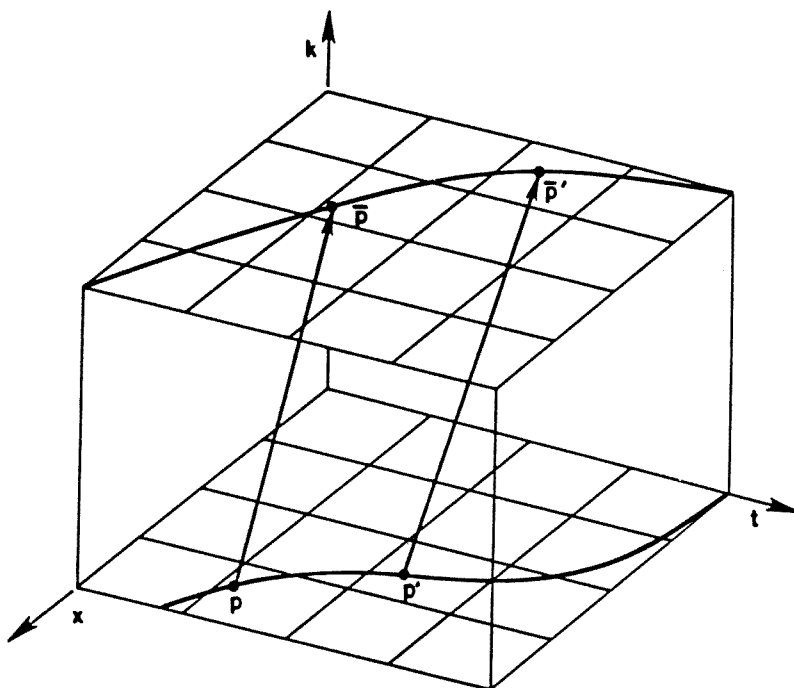


Fig. 1.1. The mappings in x, k, t space. The mappings $P \rightarrow \bar{P}$ represent the concentration changes $x \rightarrow \bar{x}$ and the changes in rate constants $k \rightarrow \bar{k}$, while the time t is held fixed. As \bar{k} is not a function of x or t , the trajectory $P \rightarrow P'$ is mapped into a trajectory $\bar{P} \rightarrow \bar{P}'$ that lies in a hyperplane of constant \bar{k} .

ing an altered evolution of chemical concentrations. By changing the value of the parameter a , one is able to convert an initial evolution curve into a one-parameter family of evolution curves. Thus, in fig. 1.1 the upper curve may be considered as one member of a family of transformed curves, a curve obtained by giving the group parameter a specific value. The value of the group parameter a can be assigned by the investigator, but it is neither a rate constant nor a concentration. Its chemical significance is determined by the functions K_i and X_μ in (1.2). This significance, and that of the generator U , can be assessed by investigating the action of the operator of the infinitesimal transformation $T(\delta a)$.

Letting $a \rightarrow \delta a$, one has

$$\exp(aU) \rightarrow \exp(\delta a U) \sim 1 + \delta a U. \quad (1.3)$$

Thus, for an infinitesimal transformation,

$$\bar{x}_i = x_i + \delta a U x_i = x_i + \delta a h_i(x, k); \quad \bar{k}_\mu = k_\mu + \delta a U k_\mu = k_\mu + \delta a g_\mu(k). \quad (1.4)$$

Consequently, if one defines δx_i as $\bar{x}_i - x_i$ and δk_μ as $\bar{k}_\mu - k_\mu$ in (1.4) one has

$$\delta x_i = \delta a h_i(x, k), \quad \delta k_\mu = \delta a g_\mu(k). \quad (1.5)$$

It follows that $T(\delta a)$ changes the concentration x_i by an amount $\delta a h_i$ that may depend upon all concentrations x and rate constants k . Similarly, the transformation changes the rate constant k_μ by an amount $\delta a g_\mu$ that may depend upon all rate constants k . As an example, consider the generator

$$U = k_{11} x_1 \partial/\partial x_1 + 2\partial/\partial k_{01} \quad (1.6)$$

and its action on a system involving a single species obeying the rate equation

$$dx_1/dt = k_{10} + k_{11} x_1 + k_{111} x_1^2. \quad (1.7)$$

This generator determines a shift in the concentration x_1 by an amount $\delta x_1 = k_{11} x_1 \delta a$, i.e. a shift proportional to the product of the concentration and the second-order rate constant. This determines a consequent shift in dx_1/dt by an amount $d(k_{11} x_1 \delta a)/dt = \delta a k_{11} dx_1/dt$. It also determines a shift $\delta k_{10} = 2 \delta a$ in the flux k_{10} . The generator does not affect either k_{11} or k_{111} .

Now, if it were true that the shifted concentration obeyed the same rate equation with the shifted value of k_{10} , the generator (1.6) could be of use in investigations of the consequences of changing the rate of supply or removal of the reagent. The operator $T(a) = \exp(aU)$ could then be used to determine the relation between changes in the flux and changes in the concentration x , the extent of both changes being determined by the value of the parameter a . However, the U of (1.6) was chosen at random and can not be expected at each value of t to convert $x(t)$ into $\bar{x}(t)$ that obey the altered rate equation.

If the U of (1.6) had the property that $UF = 0$, where

$$F = (k_{10} + k_{11} x_1 + k_{111} x_1^2), \quad (1.8)$$

then $\exp(aU)$ acting on the right-hand side of (1.7) would leave it unchanged, i.e. not change the reaction rate. This is because

$$\exp(aU)F = (1 + aU + \frac{1}{2}aUaU + \dots)F \quad (1.9a)$$

would then give

$$F + 0 + 0 + \dots = F. \quad (1.9b)$$

This is not, however, the restriction we wish to impose.

The restrictions we impose upon the $T(a)$, and hence the U 's, so as to obtain chemical information from them are as follows: Each $T(a)$ will be required to have a unique action on all k, x , in an elementary kinetic equation, map contiguous values of k_μ and x_i into contiguous values of \bar{k}_μ and \bar{x}_i , and give \bar{k} and \bar{x} that also satisfy elementary kinetic equations (cf. section 2 below). In addition, we shall require that all the variables a, x, k are real. Taken together, these requirements ensure that the transformation $T(a)$ maps solutions of the set of kinetic equations

$$dx_i/dt = k_{i0} + k_{ij}x_j + k_{ijj'}x_jx_{j'} \quad (1.10a)$$

into solutions of the set of transformed equations

$$d\bar{x}_i/dt = \bar{k}_{i0} + \bar{k}_{ij}\bar{x}_j + \bar{k}_{ijj'}\bar{x}_j\bar{x}_{j'} \quad (1.10b)$$

They impose restrictions on the form of the generators U sufficient to ensure that the U may be determined algorithmically. Because of this, one has available a systematic method for investigating the manner in which changes in rate constants are associated with changes in species concentrations and their time evolution. These restrictions are not equivalent to requiring that $T(a)$ leave reaction rates dx_i/dt invariant.

In the next section, we outline an algorithm for determining the allowed Lie generators U and use it to completely determine the terms in the generators which govern the transformation of rate constants of kinetic systems with an arbitrary number of species. The remaining terms in the generators, governing the transformation of species concentrations, are approximated by power series whose zero-, first-, and second-order terms we determine.

2. Derivation of approximate invariance operators: Their action

Let a set of kinetic equations be given as

$$\dot{\mathbf{x}} = \mathbf{r}(\mathbf{x}, \mathbf{k}),$$

with

$$\dot{\mathbf{x}} = d\mathbf{x}/dt; \quad -\infty < t, x_i, \dot{x}_i < \infty$$

$$\mathbf{r} = (r_1, r_2, \dots)$$

$$r_i = k_{i0} + k_{ij}x_j + k_{ijj'}x_jx_{j'}, \quad j' \geq j,$$

$$i, j, j' = 1, 2, \dots; \quad -\infty < k_\mu < \infty. \quad (2.1)$$

The evolution operator of this system is then $\exp(tV)$, with

$$V = \mathbf{r} \cdot \nabla_{\mathbf{x}}, \quad \nabla_{\mathbf{x}} = (\partial/\partial x_1, \partial/\partial x_2, \dots). \tag{2.2a}$$

That is,

$$\bar{\mathbf{x}} = \exp(tV)\mathbf{x} = \mathbf{X}(x, k; t) \tag{2.2b}$$

is the vector that \mathbf{x} evolves into after a time interval t .

Define the operator $\exp(aU)$ of a one-parameter Lie group of transformations with real parameter a , ($-\infty < a < \infty$) and generator U of the form

$$U = \mathbf{h} \cdot \nabla_{\mathbf{x}} + \mathbf{g} \cdot \nabla_{\mathbf{k}},$$

where

$$\begin{aligned} \mathbf{h} &= (h_1, h_2, \dots), \quad h_i = h_{i0} + h_{ij}x_j + h_{ijj'}x_jx_{j'} + \dots \\ h_{ijj'} &= h_{ij'j}, \text{ etc.} \\ \mathbf{g} \cdot \nabla_{\mathbf{k}} &= \sum g_{im} \partial/\partial k_{im}, \quad m = 0, j, jj' \dots \end{aligned} \tag{2.3}$$

Here, and in the remainder of the paper, we use the index m in h_{im} , k_{im} and g_{im} to signify any of the values $0, j, jj' \dots$.

The coefficients h_{im} may in general be allowed to be explicit functions of t , \mathbf{x} , \mathbf{k} . The coefficients g_{im} are not allowed to depend upon \mathbf{x} or t but can depend upon \mathbf{k} . In ref. [4] it was shown that with these restrictions the action of $\exp(aU)$ on the variables \mathbf{x} and \mathbf{k} is to give a set of transformed variables $\bar{\mathbf{x}}$ and $\bar{\mathbf{k}}$ in which the $\bar{\mathbf{k}}$ have fixed values that do not change with time, while the $\bar{\mathbf{x}}$ are, like the \mathbf{x} , running variables whose values change with time. On transformation, the new values of the k_{im} depend upon the old values, but not upon \mathbf{x} or t : geometrically, the space of the k_{im} is an invariant subspace of the space of $\mathbf{x}, t, \mathbf{k}$. The k_{im} are allowed to take on any real values, and in particular may take on the special value zero without altering the general form of the equations given in (2.1).

It was also shown in ref. [4] that the transformed equations will be of the same general form, (2.1), with \mathbf{x} replaced by $\bar{\mathbf{x}}$ and \mathbf{k} replaced by $\bar{\mathbf{k}}$ if and only if

$$W \equiv [V, U] + \partial U/\partial t = 0. \tag{2.4}$$

In this paper, we shall require that the h_{im} are time independent so that here $\partial U/\partial t$ is zero. W is then easily seen to be of the form

$$W = \mathbf{w} \cdot \nabla_{\mathbf{x}} ,$$

with

$$\mathbf{w} = (w_1, w_2 \dots)$$

and

$$w_i = w_{i0} + w_{ij}x_j + w_{ijj'}x_jx_{j'} + \dots \tag{2.5}$$

For (2.4) to hold in the time-independent case, it is necessary that each of the coefficients w_{im} vanish identically. For reasons explained below, we shall at first approximate \mathbf{h} by the terms explicitly listed in (2.3) and only require that the coefficients given explicitly in (2.5) vanish. The resulting quadratic approximation to the generators U will later be improved by methods discussed in the succeeding paper II. Each w_{im} in (2.4) is a bilinear function of the k_{im} and h_{im} , and is linear in the g_{im} . Our first problem is to determine the h_{im} and the g_{im} .

Before determining the generators in which \mathbf{h} is quadratically approximated, it is helpful to understand the effect of allowing \mathbf{h} to depend upon polynomials of arbitrary degree in the x_i . To this end, we classify the contributions to U, V, W according to their degree in x . We write

$$\mathbf{r} = \mathbf{r}^{(0)} + \mathbf{r}^{(1)} + \mathbf{r}^{(2)}, \tag{2.6}$$

where $\mathbf{r}^{(p)}$ is a homogeneous polynomial of degree p in x , and we write

$$V^{(p-1)} = \mathbf{r}^{(p)} \cdot \nabla_{\mathbf{x}}$$

to indicate that the corresponding contribution to the generator is of one degree less. Then

$$\begin{aligned} V &= (\mathbf{r}^{(0)} + \mathbf{r}^{(1)} + \mathbf{r}^{(2)}) \cdot \nabla_{\mathbf{x}} = V^{(-1)} + V^{(0)} + V^{(1)} \\ U &= (\mathbf{h}^{(0)} + \mathbf{h}^{(1)} + \mathbf{h}^{(2)} + \mathbf{h}^{(3)} + \dots) \cdot \nabla_{\mathbf{x}} + \mathbf{g} \cdot \nabla_{\mathbf{k}} \\ &= U^{(-1)} + U^{(0)} + U^{(1)} + U^{(2)} + \dots + \mathbf{g} \cdot \nabla_{\mathbf{k}}, \\ W &= [U, V] = W^{(-1)} + W^{(0)} + W^{(1)} + W^{(2)} + \dots \end{aligned} \tag{2.7}$$

Now the commutator of $U^{(m)}$ and $V^{(n)}$ is of degree $m + n$, and the commutator of $\mathbf{k} \cdot \nabla_{\mathbf{g}}$ and $V^{(n)}$ is of degree n . Thus, the vanishing of W requires that

$$0 = W^{(-1)} = [U^{(-1)}, V^{(0)}] + [U^{(0)}, V^{(-1)}] + \mathbf{g} \cdot \nabla_{\mathbf{k}}(\mathbf{r}^{(0)} \cdot \nabla_{\mathbf{x}}) \quad (2.8a)$$

$$0 = W^{(0)} = [U^{(-1)}, V^{(1)}] + [U^{(0)}, V^{(0)}] + [U^{(1)}, V^{(-1)}] + \mathbf{g} \cdot \nabla_{\mathbf{k}}(\mathbf{r}^{(1)} \cdot \nabla_{\mathbf{x}}) \quad (2.8b)$$

$$0 = W^{(1)} = [U^{(0)}, V^{(1)}] + [U^{(1)}, V^{(0)}] + [U^{(2)}, V^{(-1)}] + \mathbf{g} \cdot \nabla_{\mathbf{k}}(\mathbf{r}^{(2)} \cdot \nabla_{\mathbf{x}}) \quad (2.8c)$$

$$0 = W^{(2)} = [U^{(1)}, V^{(1)}] + [U^{(2)}, V^{(0)}] + [U^{(3)}, V^{(-1)}] \quad (2.8d)$$

$$0 = W^{(p)} = [U^{(p-1)}, V^{(1)}] + [U^{(p)}, V^{(0)}] + [U^{(p+1)}, V^{(-1)}], \quad p > 3. \quad (2.8e)$$

Note that each of these equations stands for a set of separate equations $w_{im} = 0$, where w_{im} is the coefficient of

$$\partial/\partial x_i, x_j \partial/\partial x_i, x_j x_j, \partial/\partial x_i \dots \text{as } m = 0, j, jj' \dots \quad (2.9)$$

A key feature of the set of equations $w_{im} = 0$ is the fact that their rank is much less than their order, so that their solution contains many free parameters. If we do not allow cubic and higher degree polynomials in x into U and W , we find that the equations $w_{im} = 0$ for $W^{(-1)}$, $W^{(0)}$, $W^{(1)}$ are the set of simultaneous linear equations

$$\begin{aligned} \sum_p \{ h_{p0} k_{ip} - h_{ip} k_{p0} \} + g_{i0} &= 0, \quad i = 1, 2, \dots, n \\ \sum_p \{ h_{p0} (k_{ijp} + k_{ipj}) + h_{pj} k_{ip} - j_{ip} k_{pj} - (h_{ipj} + h_{ijp}) k_{p0} \} + g_{ij} &= 0 \\ i, j &= 1, 2, \dots, n \\ \sum_p \{ h_{pj} (k_{ipk} + k_{ikp}) + h_{pk} (k_{ipj} + k_{ijp}) - h_{ip} (k_{pjk} + k_{pkj}) + (h_{pjk} + h_{pkj}) k_{ip} \\ - (h_{ipk} + h_{ikp}) k_{pj} - (h_{ipj} + h_{ijp}) k_{pk} \} + g_{ijk} + g_{ikj} &= 0 \\ i, j, k &= 1, 2, \dots, n. \end{aligned} \quad (2.10)$$

In this “quadratic” approximation, each component of \mathbf{g} is uniquely determined by a single equation if one chooses \mathbf{r} to be a one-term homogeneous polynomial. Since the general solution of the equation is an arbitrary linear combination of these special solutions, one may make this choice without any loss of generality. In this linear combination, the coefficients may be arbitrary functions of the k_{im} . We shall say that the generators U_m in a collection are “independent” if no linear combination of them

$$\sum c_m U_m$$

is identically equal to zero when the coefficients c_m in the linear combination are not functions of x .

The remaining sections of this paper will make use of the quadratic approximation to the generators and the approximation to (2.8) obtained by dropping all $W^{(p)}$ with p greater than 1. We shall term this twofold approximation the "quadratic approximation". In paper II, we will investigate more accurate approximations to the generators and show that the quadratic approximation is of great utility.

In the two-species case, we obtain twelve equations $w_{im} = 0$ from the quadratic approximation to (2.8). Their general solution is a linear combination of twelve independent special solutions. Each special solution fixes a generator U , listed in table 2.1. The generators whose h 's are of zero or first order in x are exact solutions of (2.3).

Inspecting table 2.1, the reader will note that we have chosen the U_{im} to be of the form (here, g^{i0} is the g vector of U_{i0} , etc.)

$$\begin{aligned} U_{i0} &= \partial/\partial x_i + g^{i0} \cdot \nabla_k, & U_{ij} &= x_j \partial/\partial x_i + g^{ij} \cdot \nabla_k \\ U_{ijj'} &= x_j x_{j'} \partial/\partial x_i + g^{ijj'} \cdot \nabla_k. \end{aligned} \quad (2.11)$$

That is, eqs. (2.10) allow one to choose the action of each U upon the species concentrations and then determine the action on the kinetic coefficients that is required to leave the kinetic equations invariant up through terms quadratic in the concentrations.

This procedure generalizes to systems of three or more species. As a result, one can easily obtain analogously exact and quadratically approximated invariance generators U for kinetic systems (2.1) involving an arbitrary number of species. In the general case, the generators obtained with the aid of eqs. (2.10) are:

$$\begin{aligned} U_{i0} &= \partial/\partial x_i - \sum_j k_{ij} \partial/\partial k_{j0} - \sum_{m \neq i} k_{jmi} \partial/\partial k_{jm} - 2 \sum_j k_{jii} \partial/\partial k_{ji} \\ U_{ii} &= x_1 \partial/\partial x_i + k_{i0} \partial/\partial k_{i0} + \sum_{j \neq i} k_{ij} \partial/\partial k_{ij} - k_{iii} \partial/\partial k_{iii} \\ &+ \sum_{j, m \neq i} k_{ijm} \partial/\partial k_{ijm} - \sum_{j \neq i} k_{ji} \partial/\partial k_{ji} \\ &- 2 \sum_{j \neq i} k_{jii} \partial/\partial k_{jii} - \sum_{m, j \neq i} k_{jim} \partial/\partial k_{jim}. \end{aligned}$$

For $j \neq i$:

Table 2.1
Generators of invariance transformations

Generator		g												
h_1	h_2	g_{10}	g_{11}	g_{12}	g_{111}	g_{112}	g_{122}	g_{20}	g_{21}	g_{22}	g_{211}	g_{212}	g_{222}	
U_{10}	1	0	$-k_{11}$	$-2k_{111}$	$-k_{112}$	0	0	$-k_{21}$	$-2k_{211}$	$-k_{212}$	0	0	0	
U_{11}	x_1	0	k_{10}	k_{12}	$-k_{111}$	0	k_{122}	0	$-k_{21}$	0	$-2k_{211}$	$-k_{212}$	0	
U_{12}	x_2	0	k_{20}	$(k_{22} - k_{11})$	k_{211}	$(k_{212} - 2k_{111})$	$(k_{222} - k_{112})$	0	0	$-k_{21}$	0	$-2k_{211}$	$-k_{212}$	
U_{111}	x_1^2	0	0	0	k_{11}	$2k_{12}$	0	0	0	0	$-k_{21}$	0	0	
U_{112}	$x_1 x_2$	0	0	k_{10}	k_{21}	k_{22}	k_{12}	0	0	0	0	$-k_{21}$	0	
U_{122}	x_2^2	0	0	$2k_{20}$	0	$2k_{21}$	$(2k_{22} - k_{11})$	0	0	0	0	0	$-k_{21}$	
U_{20}	1	$-k_{12}$	$-k_{112}$	$-2k_{122}$	0	0	0	$-k_{22}$	$-k_{212}$	$-2k_{222}$	0	0	0	
U_{21}	x_1	0	$-k_{12}$	0	$-k_{112}$	$-2k_{122}$	0	k_{10}	$(k_{11} - k_{22})$	k_{12}	$(k_{111} - k_{221})$	$(k_{112} - 2k_{222})$	k_{122}	
U_{22}	x_2	0	0	$-k_{12}$	0	$-k_{112}$	$-2k_{122}$	k_{20}	k_{21}	0	k_{211}	0	$-k_{222}$	
U_{211}	x_1^2	0	0	0	$-k_{12}$	0	0	0	$2k_{10}$	0	$(2k_{11} - k_{22})$	$2k_{12}$	0	
U_{212}	$x_1 x_2$	0	0	0	0	$-k_{12}$	0	0	k_{20}	k_{10}	k_{21}	k_{11}	k_{12}	
U_{222}	x_2^2	0	0	0	0	0	$-k_{12}$	0	0	$2k_{20}$	0	$2k_{21}$	k_{22}	

$$\begin{aligned}
U_{ij} &= x_j \partial / \partial x_i + k_{j0} \partial / \partial k_{i0} + k_{ji} \partial / \partial k_{ii} + (k_{jj} - k_{ii}) \partial / \partial k_{ij} \\
&+ \sum_{m \neq i, j} k_{jm} \partial / \partial k_{im} - \sum_{m \neq i} k_{mi} \partial / \partial k_{mj} + k_{jii} \partial / \partial k_{iii} \\
&+ (k_{jij} - 2k_{iii}) \partial / \partial k_{iij} + (k_{jji} - k_{iij}) \partial / \partial k_{ijj} \\
&+ \sum_{m \neq i, j} k_{jim} \partial / \partial k_{iim} + \sum_{m \neq i, j} (k_{jjm} - k_{iim}) \partial / \partial k_{ijm} \\
&- 2 \sum_{m \neq i} k_{mii} \partial / \partial k_{mij} - \sum_{m, n \neq i} k_{min} \partial / \partial k_{mjn} \\
U_{iii} &= x_1 x_i \partial / \partial x_i + 2k_{i0} \partial / \partial k_{ii} + k_{ii} \partial / \partial k_{iii} \\
&+ 2 \sum_{j \neq i} k_{ij} \partial / \partial k_{iij} - \sum_{j \neq i} k_{ji} \partial / \partial k_{jii}. \tag{2.12}
\end{aligned}$$

For $j \neq i$:

$$\begin{aligned}
U_{iij} &= x_i x_j \partial / \partial x_i + k_{j0} \partial / \partial k_{ii} + k_{i0} \partial / \partial k_{ij} + \sum k_{jm} \partial / \partial k_{iim} + 2k_{ij} \partial / \partial k_{ijj} \\
&+ \sum_{m \neq i, j} k_{im} \partial / \partial k_{ijm} - \sum_{m \neq i} k_{mi} \partial / \partial k_{mij} \\
U_{ijj} &= x_j x_j \partial / \partial x_i + 2k_{j0} \partial / \partial k_{ij} + 2k_{ji} \partial / \partial k_{iij} + (2k_{jj} - k_{ii}) \partial / \partial k_{ijj} \\
&+ 2 \sum_{m \neq i, j} k_{jm} \partial / \partial k_{ijm} - \sum_{m \neq i} k_{mi} \partial / \partial k_{mjj}. \tag{2.13}
\end{aligned}$$

For i, j, j' all different:

$$\begin{aligned}
U_{ijj'} &= x_j x_{j'} \partial / \partial x_i + k_{j0} \partial / \partial k_{ij'} + k_{j'0} \partial / \partial k_{ij} + k_{jj'} \partial / \partial k_{ij'j'} \\
&+ k_{j'j} \partial / \partial k_{ijj} + \sum_{m \neq j'} k_{jm} \partial / \partial k_{imj'} \\
&+ \sum_{m \neq j} k_{j'm} \partial / \partial k_{ijm} - \sum_m k_{mi} \partial / \partial k_{mjj'}. \tag{2.14}
\end{aligned}$$

In this list, the generators U_{i0} , U_{ii} , and U_{ij} exactly satisfy the determining eqs. (2.8). The generators U_{iii} , $U_{ijj'}$, and U_{ijj} satisfy (2.8) in quadratic approximation.

3. Finite transformations

As mentioned earlier, corresponding to each generator U there is an operator $\exp(aU)$ of finite transformations. One way to determine the effect of this upon each variable x_i, k_μ is to expand the exponential in powers of aU , carry out the indicated actions and sum the resulting series, which sometimes terminates, has evident recursiveness, or is recognizable as the MacLaurin expansion of a simple function. Often, a more practical method is to integrate the set of equations [4] :

$$\delta a = \frac{\delta x_1}{h_1} = \frac{\delta x_2}{h_2} \dots = \frac{\delta k_{10}}{g_{10}} = \frac{\delta k_{20}}{g_{20}} = \frac{\delta k_{11}}{g_{11}} \dots = \frac{\delta k_{2jj'}}{g_{2jj'}} \dots \quad (3.1)$$

When the h are of the form we have chosen, the necessary integrations can all be carried out analytically.

Note that the only concentration altered by $T_{im}(a) = \exp(aU_{im})$ is x_i . One finds using (3.1):

$$\begin{aligned} T_{i0}(a)x_i &= x_i + a, & T_{ii}(a)x_i &= x_i e^a, \\ T_{ij}(a)x_i &= x_i + ax_j, \quad j \neq i, & T_{iii}(a)x_i &= x_i/(1 - ax_i) \\ T_{ijj}(a)x_i &= x_i e^{ax_j}, \quad j \neq i, & T_{ijj'}(a)x_i &= x_i + ax_j x_{j'}, \quad i \neq j, j'. \end{aligned} \quad (3.2)$$

The effect of each of the finite transformation operators on the kinetic parameters k_{im} are listed in table 2.2. As an example, one finds from table 2.2 that T_{10} acting on k_{10} gives $\bar{k}_{10} = k_{10} - ak_{11}$.

Because $T_{10}(a)$ and $T_{20}(b)$ leave \dot{x}_1 and \dot{x}_2 invariant, their action on the kinetic equations can be determined by replacing x_1 by $x_1 + a$, or x_2 by $x_2 + b$, in r and determining the coefficients $c_{ijj'}$ of the various powers $x_j x_{j'}$ of the concentrations in the equation for \dot{x}_i . Then one finds $\bar{k}_{ijj'} = c_{ijj'}$. Because T_{10} and T_{20} carry out translations of x while leaving the kinetic equations invariant in the generalized sense that the quadratic polynomic form of r is preserved, we shall term them "invariant translation" operators.

In all the generators other than the U_{i0} , the operator $\partial/\partial x_i$ is premultiplied by either x_i or x_j . As a consequence, these generators vanish at the origin of x . Because of this, the corresponding operators of finite transformations T cannot move a point at the origin. If one lets U be a linear combination of the generators in table 2.1, the finite transformations may be obtained by solving eqs. (3.1) *de novo*.

Before concluding this paper, we would call attention to some geometrical properties of our transformations. First note that the evolution generator V is a special type of U with $g = 0$, and that the corresponding operator of finite trans-

Table 2.2(a)
Finite transformations of k

	\bar{k}_{i_0}	\bar{k}_{i_1}	\bar{k}_{i_2}	$\bar{k}_{i_{11}}$	$\bar{k}_{i_{12}}$	$\bar{k}_{i_{22}}$
T_{10}	$k_{i_0} - ak_{i_1} + a^2 k_{i_{11}}$	$k_{i_1} - 2ak_{i_{11}}$	$k_{i_2} - ak_{i_{12}}$	$k_{i_{11}}$	$k_{i_{12}}$	$k_{i_{22}}$
T_{11}	$e^a k_{i_0}$	k_{i_1}	$e^a k_{i_2}$	$e^{-a} k_{i_{11}}$	$k_{i_{12}}$	$e^a k_{i_{22}}$
T_{12}	$k_{i_0} + ak_{i_20}$	$k_{i_1} + ak_{i_21}$	$k_{i_2} - a^2 k_{i_21} + a(k_{i_22} - k_{i_{11}})$	$k_{i_{11}} + ak_{i_{211}}$	$k_{i_{112}} - 2a^2 k_{i_{211}} + a(k_{i_{212}} - 2k_{i_{111}})$	$k_{i_{122}} + a(k_{i_{222}} - k_{i_{112}}) + a^2(k_{i_{111}} - k_{i_{212}}) + a^3 k_{i_{211}}$
T_{111}	k_{i_0}	$k_{i_1} + 2ak_{i_10}$	k_{i_2}	$k_{i_{11}} + ak_{i_{11}} + a^2 k_{i_10}$	$k_{i_{112}} + 2ak_{i_12}$	$k_{i_{122}}$
T_{112}	k_{i_0}	$k_{i_1} + ak_{i_20}$	$k_{i_2} + ak_{i_10}$	$k_{i_{11}} + ak_{i_21}$	$k_{i_{112}} + ak_{i_22}$	$k_{i_{122}} + ak_{i_12} + \frac{1}{2}a^2 k_{i_10}$
T_{122}	k_{i_0}	k_{i_1}	$k_{i_2} + 2ak_{i_20}$	$k_{i_{11}}$	$k_{i_{112}} + 2ak_{i_21}$	$k_{i_{122}} + a(2k_{i_22} - k_{i_{11}})$

Table 2.2(b)
Finite transformations of k

	\bar{k}_{i_0}	\bar{k}_{i_1}	\bar{k}_{i_2}	$\bar{k}_{i_{211}}$	$\bar{k}_{i_{212}}$	$\bar{k}_{i_{222}}$
T_{10}	$k_{i_20} - ak_{i_21} + a^2 k_{i_{211}}$	$k_{i_21} - 2ak_{i_{211}}$	$k_{i_22} - ak_{i_{212}}$	$k_{i_{211}}$	$k_{i_{212}}$	$k_{i_{222}}$
T_{11}	k_{i_20}	k_{i_21}	k_{i_22}	$e^{-2a} k_{i_{211}}$	$e^{-2a} k_{i_{212}}$	$k_{i_{222}}$
T_{12}	k_{i_20}	k_{i_21}	$k_{i_22} - ak_{i_21}$	$k_{i_{211}}$	$k_{i_{212}} - 2ak_{i_{211}}$	$k_{i_{222}} - ak_{i_{212}} + a^2 k_{i_{211}}$
T_{111}	k_{i_20}	k_{i_21}	k_{i_22}	$k_{i_{211}} - ak_{i_21}$	$k_{i_{212}}$	$k_{i_{222}}$
T_{112}	k_{i_20}	k_{i_21}	k_{i_22}	$k_{i_{211}}$	$k_{i_{212}} - ak_{i_21}$	$k_{i_{222}}$
T_{122}	k_{i_20}	k_{i_21}	k_{i_22}	$k_{i_{211}}$	$k_{i_{212}}$	$k_{i_{222}} - ak_{i_21}$

Table 2.2(c)
Finite transformations of k

	\bar{k}_{10}	\bar{k}_{11}	\bar{k}_{12}	\bar{k}_{111}	\bar{k}_{112}	\bar{k}_{122}
T_{20}	$k_{10} - ak_{12} + a^2 k_{122}$	$k_{11} - ak_{112}$	$k_{12} - 2ak_{122}$	k_{111}	k_{112}	k_{122}
T_{21}	k_{10}	$k_{11} - ak_{12}$	k_{12}	$k_{111} - ak_{112} + a^2 k_{122}$	$k_{112} - 2ak_{122}$	k_{122}
T_{22}	k_{10}	k_{11}	$e^{-a} k_{12}$	k_{111}	$e^{-a} k_{112}$	$e^{-2a} k_{122}$
T_{211}	k_{10}	k_{11}	k_{12}	$k_{111} - ak_{12}$	k_{112}	k_{122}
T_{212}	k_{10}	k_{11}	k_{12}	k_{111}	$k_{112} - ak_{12}$	k_{122}
T_{222}	k_{10}	k_{11}	k_{12}	k_{111}	k_{112}	$k_{122} - ak_{12}$

Table 2.2(d)
Finite transformations of k

	\bar{k}_{20}	\bar{k}_{21}	\bar{k}_{22}	\bar{k}_{211}	\bar{k}_{212}	\bar{k}_{222}
T_{20}	$k_{20} - ak_{22} + a^2 k_{222}$	$k_{21} - ak_{212}$	$k_{22} - 2ak_{222}$	k_{211}	k_{212}	k_{222}
T_{21}	$k_{20} + ak_{10}$	$k_{21} - a^2 k_{12} + a(k_{11} - k_{22})$	$k_{22} + ak_{12}$	$k_{211} + a(k_{111} - k_{212}) + a^2(k_{222} - k_{112}) + a^3 k_{122}$	$k_{212} + a(k_{112} - 2k_{222}) - 2a^2 k_{122}$	$k_{222} + ak_{122}$
T_{22}	$e^a k_{20}$	$e^a k_{21}$	k_{22}	$e^a k_{211}$	k_{212}	$e^{-a} k_{222}$
T_{211}	k_{20}	$k_{21} + 2ak_{10}$	k_{22}	$k_{211} + a(2k_{11} - k_{22})$	$k_{212} + 2ak_{12}$	k_{222}
T_{212}	k_{20}	$k_{21} + ak_{20}$	$k_{22} + ak_{10}$	$k_{211} + ak_{21} + \frac{1}{2}a^2 k_{20}$	$k_{212} + ak_{11}$	$k_{222} + ak_{12}$
T_{222}	k_{20}	k_{21}	$k_{22} + 2ak_{20}$	k_{211}	$k_{212} + 2ak_{21}$	$k_{222} + ak_{22} + a^2 k_{20}$

formations $\exp(aV)$ becomes the time evolution operator if a is replaced by t . Equations (3.1) then simply restate the kinetic equations (2.1). (Of course, V is supposed known, while in the analysis just completed we have *determined* the U 's allowed for a given V .) Now the operator $\exp(tV)$ evolves an initial point into a trajectory in the space of x, k without changing the k 's. Taken together, all these trajectories constitute a flow because the coefficients r_i in (2.1) everywhere define a unique infinitesimal transformation $\exp(\delta tV)$. Each operator $\exp(aU)$ whose U satisfies the determining eqs. (2.8) will take a point P on such a trajectory and displace it in a transverse direction, by changing both x and k , giving an image point \bar{P} . If, with the same value of a , $\exp(aU)$ acts on another point P' of the original trajectory, it will carry this

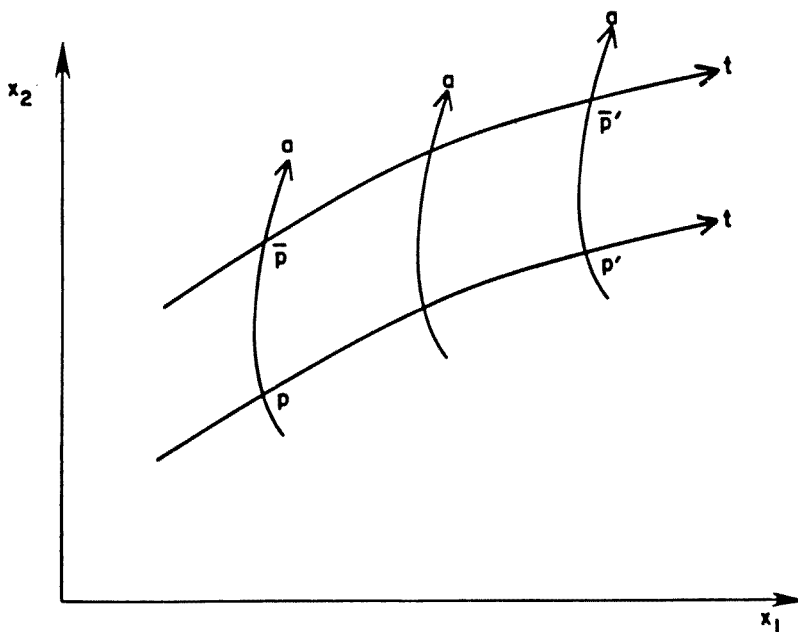


Fig. 2.1. Transformation flows $e^{aU}\mathbf{x}$ transverse to evolution flows $e^{tV}\mathbf{x}$. For each fixed value of the group parameter a , the transformation with generator U carries the evolving concentrations $x_i(t)$ into an altered set of evolving concentrations. The transformed concentrations obey a set of elementary kinetic equations with altered rate constants.

into an image point \bar{P}' . Because $\exp(\delta aU)$ everywhere defines a unique infinitesimal transformation and U is not proportional to V , the collection of all these trajectories produced by $\exp(aU)$ constitutes a flow transverse to the flow produced by the evolution operator. As indicated in fig. 2.1, the evolution operator will evolve the image point \bar{P} into a trajectory which will pass through \bar{P}' at the same time t that P is evolved into P' . The proof of this observation follows from the fact that in deriving (2.8) we have required that $\partial U/\partial t$ vanishes. Thus, (2.4) becomes

$$[U, V] = 0, \quad (3.3)$$

which implies that

$$\exp(tV) \exp(aU)(\mathbf{x}, \mathbf{k}) = \exp(aU) \exp(tV)(\mathbf{x}, \mathbf{k}). \quad (3.4)$$

When the generator U only approximately commutes with V , (3.4) will only hold approximately and the point obtained by transforming, then evolving, will not necessarily coincide with the point obtained by evolving, then transforming. This is the case for the generators $U_{ijj'}$, for example.

4. Conclusions

Inspection of eqs. (2.8) shows that if $U^{(-1)}$, $U^{(0)}$, and $U^{(1)}$ all vanish, then U does not act on the rate constants k . Thus, by determining all U with nonvanishing $U^{(-1)}$, $U^{(0)}$, $U^{(1)}$ whose $T(a)$ transform elementary rate equations into elementary rate equations, we have found *all* U generating one-parameter groups $\exp(aU)$ that transform elementary rate equations into elementary rate equations with different rate constants. The U_i and the U_{ij} have been determined exactly. In the $U_{ijj'}$, the functions governing the transformation of species concentrations have been determined to second order in the concentrations, and the functions governing the transformation of the rate constants have been exactly determined.

Throughout this and the following paper, two one-parameter groups are composed by allowing the second to act on the result obtained from the action of the first. Thus, if

$$x'_1 = \exp(bU_{112})x_1 = x_1 \exp(bx_2) \quad (4.1)$$

and

$$x'_2 = \exp(aU_{222})x_2 = x_2/(1 - ax_2), \quad (4.2)$$

then the effect of the transformation $\exp(bU_{112}) \exp(aU_{222})$ is to first shift the point with coordinates x_1, x_2 to the point with coordinates (x_1, x'_2) . It then moves this to the point with coordinates $(x'_1 = x_1 \exp(bx'_2), x'_2)$. Written as functions of the coordinates of the initial point, the coordinates of the final point are therefore

$$(x_1 \exp(b\{x_2/(1 - ax_2)\}), x_2/(1 - ax_2)). \quad (4.3)$$

From the one-parameter groups with operators $T_\alpha(a_\alpha) = \exp(a_\alpha U_\alpha)$, one may construct many-parameter groups $T_{\alpha\beta} \dots (a_\alpha, a_\beta, \dots) = \exp(a_\alpha U_\alpha) \exp(a_\beta U_\beta) \dots$ whenever

$$[U_\alpha, U_\beta] = \sum c_{\alpha\beta}^\nu U_\nu \quad (4.4)$$

for all α, β, ν . As all many-parameter groups may be obtained from one-parameter groups in this way, it may be concluded that our determination of the generators of all one-parameter groups that transform elementary rate equations into different elementary rate equations at once determines, exactly or approximately, all generators of many-parameter groups with this property. (In the following paper II, a list of such many-parameter groups is given for systems involving two chemical species.)

To conclude: In this paper, all generators of all one-parameter and all many-parameter groups of flows that transform elementary rate equations into elementary rate equations with different rate constants have been determined either exactly or approximately. A particularly simple generator basis has been chosen and the finite transformations obtained by exponentiating each generator have been determined.

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References

- [1] H. Rabitz, *Chem. Rev.* 87(1987)101.
- [2] R. Cukoer, H. Levine and K. Schuler, *J. Comp. Phys.* 26(1978)1.
- [3] C. Box, W. Hunter and J. Hunter, *Statistics for Experimenters* (Wiley, New York, 1978).
- [4] C. Wulfman and H. Rabitz, *J. Phys. Chem.* 90(1986)2264.
- [5] L.M. Hubbard, C. Wulfman and H. Rabitz, *J. Phys. Chem.* 90(1986)2273.
- [6] Cf., for example, A. Cohen, *An Introduction to the Lie Theory of One-Parameter Groups* (Heath, Boston, 1911).