The Mathematical Structure of Chemical Kinetics in Homogeneous Single-Phase Systems

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I. Introduction

There has recently been some renewed interest in formalizing the theory of chemically reacting systems. WEI & PRATER [1], for example, presented an exhaustive analysis of the dynamics of closed chemical systems with linear constitutive laws under conditions of constant volume and temperature. More general studies of the mathematical structure of chemical systems include those of ARIS [2, 3, 4], SELLERS [5], WEI [6, 7], SHAPIRO & SHAPLEY [8], COLEMAN & GURTIN [14], and BOWEN [15, 16]. In particular, WEI [6] proposed a set of axioms to characterize more general chemical systems. In doing so he lumped together conditions that result from the properties of constitutive equations (or chemical reaction rate expressions) with those that result from particular constraints imposed on the system. Thus he restricted his attention to systems constrained in such a way that the state of the system is determined completely by the amounts of the various chemical species. Systems constrained at constant temperature and volume or constant enthalpy and pressure, for example, would be in this category, but one constrained so as to lose heat at a rate proportional to its temperature would not. In addition, he assumed that the system is constrained so as to posess a Lyapunov function, a condition which will be seen to be still more restrictive. To clarify the situation it is necessary to study first the properties of the constitutive relations without regard to the boundary conditions and other constraints peculiar to a particular problem, and then, subsequently, to see how these properties govern the dynamic behavior of constrained systems.

In carrying out the above task, we will, however, restrict our attention to those systems which posess certain commonly encountered properties. Thus we assume our materials to be isotropic homogeneous single phases without memory. In addition, we assume that the processes of homogenization and chemical reaction are strictly dissipative, and that the Onsager relation is satisfied at thermodynamic equilibrium points.

One form of constitutive law which is of special interest is that of polynomial rate expressions (see [4, 7]). The restrictions imposed on these by the above requirements are studied in a separate section where, in particular, it is shown what properties such an expression must have to be derivable from the law of mass action.

2. Thermodynamics

The thermodynamic properties of our system may be described completely by one of the characteristic functions. For convenience we choose the Helmholtz free energy per unit volume, $a(T, c)$, as a function of temperature, T, and concentration $c=(c_1, c_2, \ldots, c_N)$, where N is the number of chemical species present. Here the concentration c_1 is defined as the number of moles of the i^{th} species per unit volume. The following thermodynamic identities are useful:

$$\frac{\partial a}{\partial T}=-s, \tag{2.1}$$

$$\frac{\partial a}{\partial c}=\mu, \tag{2.2}$$

$$P=\langle\mu, c\rangle-a \tag{2.3}$$

where s is the entropy density, μ is the vector of chemical potentials, and P is the pressure. The bracket $\langle\,,\rangle$ here denotes inner product:

$$\langle x, y\rangle=\sum_{i=1}^{N} x_i y_i .$$

An important restriction on the function $a(T, c)$ is provided by the assumption that the process of homogenization is spontaneous or, in other words, that our single-phase system will be stable. This requirement can be expressed in various ways (see, for example, CALLEN [9]), but in our case the necessary and sufficient conditions become

$$\frac{\partial^2 a}{\partial T^2}<0 \tag{2.4}$$

and that the $N\times N$ partial Hessian matrix J be positive definite, where

$$J=\left\|\frac{\partial^2 a}{\partial c_i \partial c_j}\right\|. \tag{2.5}$$

Or, in other words, $a(T, c)$ is a strictly concave function of T at each fixed c and a strictly convex function of c at each fixed T.

One consequence of (2.5) is that the transformation $(T, c)\to(T, \mu)$ is one-to-one, so that (T, μ) is also a complete coordinate system for the intensive thermodynamic variables. To see this, suppose, on the contrary, that at a particular temperature, T, there are two points, c and c'', where $\mu=\mu^0$. Then the function g, where

$$g(T, c)=a(T, c)-\langle\mu^0, c\rangle$$

satisfies

$$\frac{\partial g}{\partial c}=\mu-\mu^0$$

and

$$\left\|\frac{\partial^2 g}{\partial c_i \partial c_j}\right\|=J .$$

Expanding g in a Taylor series about the point $\mathbf{c}'$, and using the Cauchy form of the remainder, we see that

$$g(\mathbf{c}'')-g(\mathbf{c}')=\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{\partial^2 g}{\partial c_i\partial c_j}\bigg|_{\mathbf{c}^*}(c_i''-c_i)(c_j''-c_j)$$

where $\mathbf{c}^*$ lies somewhere on the line connecting $\mathbf{c}'$ and $\mathbf{c}''$. Since the matrix J is positive-definite, it follows that $g(\mathbf{c}'')>g(\mathbf{c}')$ unless $\mathbf{c}''=\mathbf{c}'$. On the other hand, the expansion can be taken about $\mathbf{c}''$, in which case $g(\mathbf{c}'')<g(\mathbf{c}')$, unless $\mathbf{c}'=\mathbf{c}''$. The two requirements together imply that $\mathbf{c}'=\mathbf{c}''$.

A further requirement for the function $a(T, \mathbf{c})$ is provided by Henry's law, which states that as $c_i\to 0$, $\mu_i(T, \mathbf{c})\sim RT\ln c_i$. This may be stated more precisely by defining the activity coefficient, $\gamma_i(T, \mathbf{c})$, as

$$\gamma_i(T,\mathbf{c})\equiv\frac{1}{c_i}e^{\mu_i(T,\mathbf{c})/RT} \tag{2.6}$$

where R is the gas constant. The statement of Henry's law then becomes that $\gamma_i(T, \mathbf{c})$ is continuous and positive at points where $c_i=0$. While equation (2.6) is really quite a strong condition (it provides a means for measuring R, for example), its main use for our purposes is to show that each component of $\boldsymbol{\mu}$ is unbounded from below (*i.e.*, $\mu_i\to -\infty$ as $c_i\to 0$).

Another consequence of this principle is that as all the components of $\mathbf{c}$ approach zero simultaneously, the function $\boldsymbol{\mu}(T, \mathbf{c})$ approaches the form

$$\begin{aligned}\mu_i&=RT\ln\{\gamma_i(T,\mathbf{0})\,c_i\}\\&=\mu_i^*(T)+RT\ln c_i\end{aligned} \tag{2.7}$$

where $\mu_i^*(T)=RT\ln\{\gamma_i(T,0)\}$. Equation (2.7) may be taken as the defining relationship for an ideal gaseous solution.

Since the concept of an ideal gaseous solution is much used in chemical reaction theory, we pause for a moment to consider equation (2.7) in more detail. The characteristic function $a(T, \mathbf{c})$ for a system that obeys (2.7) for all $\mathbf{c}$ can be shown to be

$$a(T,\mathbf{c})=\langle\boldsymbol{\mu}^*(T),\mathbf{c}\rangle-RT\langle\mathbf{1},\mathbf{c}\rangle+RT\langle\mathbf{c},\ln\mathbf{c}\rangle \tag{2.8}$$

where $\mathbf{1}$ is the vector $(1, \ldots, 1)$ and $\ln \mathbf{c}$ is the vector $(\ln c_1, \ldots, \ln c_N)$. Because of (2.4), the function $\boldsymbol{\mu}^*(T)$ is not arbitrary but must satisfy

$$\left\langle\frac{d^2\mu^*}{dT^2},\mathbf{c}\right\rangle<0$$

for all $\mathbf{c}$. This is only possible if

$$\frac{d^2\mu_i^*}{dT^2}<0,\qquad i=1,\ldots,N. \tag{2.9}$$

The matrix $J=\left\|\frac{\partial\mu_i}{\partial c_j}\right\|$ for (2.8) is

$$J_{ij}=\frac{RT}{c_i}\delta_{ij}, \tag{2.10}$$

which is clearly positive-definite. Thus the particular $a(T, c)$ given by (2.8) satisfies all the requirements.

An additional property of (2.8) is that μ is unbounded, so that its range for each T is the whole N-dimensional real space. This situation is generally true for non-ideal systems also and will be assumed here.

3. Constitutive Laws of Chemical Change

As stated previously, all intensive thermodynamic properties of our system are unique functions of the coordinates (T, c). We will assume that chemical reaction rates are functions of the same coordinates or, in other words, that the system posesses no memory (or hidden variable). Thus we denote the vector of generation rates per unit volume by $f(T, c)$, which is to say that the number of moles of the i^{th} species produced by chemical reaction per unit time per unit volume is $f_i(T, c)$. Because the mapping $(T, c) \to (T, \mu)$ is one-to-one, we may alternatively describe the reaction effects by a function of (T, μ):

$$r(T, \mu) \equiv f(T, c).$$

The most obvious condition required of chemical rate expressions is that of mass balance, which requires that the reaction rate vector be always orthogonal to the vector of molecular weights:

$$\langle w, f(T, c)\rangle \equiv 0, \quad \text{all } T, c \tag{3.1}$$

where $w = (w_1, \dots, w_n)$ and w_i is the molecular weight of the i^{th} component. These are strictly positive:

$$w_i > 0, \quad i = 1, 2 \dots N. \tag{3.2}$$

In addition, the reaction rate will be constrained by other stoichiometric conditions, so that the range of $f(T, c)$ will be contained in some subspace, $\mathscr{R}$, of R^N which was termed by ARIS [2] the "reaction subspace". Thus defining $\mathscr{R}$ to be the smallest subspace containing the range of $f(T, c)$, we may state the mass balance condition by requiring that $\mathscr{R}^{\perp}$ contain at least one vector with all positive components.

The structure of the reaction subspace has been studied in some detail by ARIS [2, 3], BOWEN [15] and SELLERS [5]. In the present work, however, we use only the property of $\mathscr{R}$ given above. The content of the second law of thermodynamics for chemical systems is expressed by the standard entropy inequality:

$$\langle \mu, r(T, \mu)\rangle \leqq 0. \tag{3.3}$$

We will assume here that the inequality is strict whenever $r(T, \mu) \neq 0$, or, in the terminology of COLEMAN & GURTIN [14], that chemical systems are strictly dissipative. It may be noted that expressing the reaction rate in terms of the coordinate system (T, μ) makes condition (3.3) rather easy to test.

BOWEN [16] has considered a more general situation in which the chemical reaction rate also depends on the temperature gradient and the strain rate, in which case (3.3) must be replaced by a more complicated expression. Since we are dealing only with isotropic systems, without memory, however, (3.3) is adequate.

One more condition which we shall impose in chemical rate expressions is the Onsager reciprocity relationship. It is usual to express this in terms of independent fluxes and affinities, but in our case it is more convenient to use an equivalent form: that the matrix B, where

$$B = \left\| \frac{\partial r_i}{\partial \mu_j} \right\|, \tag{3.4}$$

is symmetric at equilibrium. Here we require equilibrium in the classical sense of vanishing affinity, or, expressed another way,

$$\boldsymbol{\mu} \in \mathscr{R}^{\perp}. \tag{3.5}$$

Thus we do not require (3.4) to hold at points referred to by BOWEN [20] as weak equilibrium points, where

$$\begin{aligned} &\boldsymbol{r}(T, \boldsymbol{\mu}) = 0, \\ &\boldsymbol{\mu} \notin \mathscr{R}^{\perp}. \end{aligned} \tag{3.6}$$

We may alternatively express (3.4) in terms of the matrix

$$F = \left\| \frac{\partial f_i}{\partial c_j} \right\|$$

using

$$B = F J^{-1}. \tag{3.7}$$

4. Axiomatic Structure

The foregoing considerations may now be summarized by a set of definitions and axioms. We let R^N denote the N-dimensional real Euclidean space with inner product $\langle\,,\rangle$ (*i.e.*, if $\boldsymbol{x}, \boldsymbol{y} \in R^N$, $\langle \boldsymbol{x}, \boldsymbol{y} \rangle = \sum_{i=1}^{N} (x_i\, y_i)$. Let $\mathscr{C} = \{\boldsymbol{c}\colon\ \boldsymbol{c} \in R^N, c_i \geqq 0;\ i = 1, \ldots, N\}$ be the set of all concentration vectors, and let $\mathscr{T} = \{T\colon\ T \in R^1, T > 0\}$ be the set of all temperatures.

Definition 4.1. A chemical system consists of a pair of functions, $\{a, \boldsymbol{f}\}$:

$a\colon\ \mathscr{T} \times \mathscr{C} \to R^1$

$\boldsymbol{f}\colon\ \mathscr{T} \times \mathscr{C} \to R^N$

which satisfy the following axioms.

A0 (Regularity Conditions). $a(T, \boldsymbol{c})$ is continuous in $\mathscr{T} \times \mathscr{C}$ and has continuous second derivatives in the interior of $\mathscr{T} \times \mathscr{C}$. The function $\boldsymbol{\mu} = \frac{\partial a}{\partial \boldsymbol{c}}\colon\ \mathscr{T} \times \mathscr{C} \to R^N$ is onto R^N for each fixed $T \in \mathscr{T}$. The function $\boldsymbol{f}(T, \boldsymbol{c})$ has continuous first derivatives everywhere in $\mathscr{T} \times \mathscr{C}$.

A1 (Single-Phase Stability). For each $T \in \mathscr{T}$, $a(T, c)$ is a strictly convex function of c. Also, $a(T, c)$ satisfies $\frac{\partial^2 a}{\partial T^2} < 0$.

A2 (Mass Conservation). Let $\mathscr{R}$ be the smallest subspace of R^N containing the range of $f(T, c)$. Then $\mathscr{R}^\perp$ has an element with strictly positive components (*i.e.*, the vector of molecular weights).

A3 (Irreversibility). The function σ: $\mathscr{T} \times \mathscr{C} \to R^1$ given by $\sigma(T, c) = \langle \mu(T, c), f(T, c) \rangle$ is negative at any point (T, c) for which $f(T, c) \neq 0$.

A4 (Onsager Relation)*. Let $J(T, c) = \left\| \frac{\partial \mu_i}{\partial c_j} \right\| = \left\| \frac{\partial^2 a}{\partial c_i \partial c_j} \right\|$, and $F(T, c) = \left\| \frac{\partial f_i}{\partial c_j} \right\|$.

Then the matrix $B(T, c) = FJ^{-1}$ is symmetric at each point (T, c) where $\mu(T, c) \in \mathscr{R}^\perp$. (Note that J is positive-definite and, hence, invertible, because $a(T, c)$ is strictly convex in c at each T.)

In comparing the above set of axioms with those of WEI [6] one must bear in mind that his axioms refer not to the chemical system as defined here but to the dynamical system that results when one applies some set of constraints to it. One might, for example, assume the system to be constrained at constant temperature and volume, in which case the equation of change becomes

$$\dot{c} = f(T, c). \tag{4.1}$$

We may then compare the properties of the dynamical system (4.1) implied by axioms A0–A4 with the axioms of WEI. Thus A2 implies W1 (WEI's axiom 1) that mass be conserved. W2, the postulate that concentrations remain nonnegative, is implied by the part of A0 that states that $\mu(T, c)$ is onto R^N, together with A3 (this will be proved in the following section). WEI's regularity condition, W3, is weaker than A0, only requiring that $f(T, c)$ be continuous. We require the stronger condition so that A4 will make sense. The condition W4, detailed balance, actually implies A4. The reverse implication for the special case of mass-action kinetics will be demonstrated in Section 6. Finally W5, the existence of a Liapunov function, is, for the dynamical system (4.1), given by A3, since in this case

$$\dot{a} = \langle \mu, \dot{c} \rangle = \langle \mu(T, c), f(T, c) \rangle < 0$$

so that $a(T, c)$ is the required function.

There are many other sets of constraints for which this correspondence can be shown, including constant T and P, constant H and P, constant U and V, *etc.* If we consider a more general closed system, however, A3 no longer implies the existence of a Liapunov function, and, in general, no such function exists. In the next section we shall study the properties of various types of closed systems.

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* While the requirement that the matrix B be symmetric at equilibrium is strongly suggested by the ONSAGER-CASIMIR reciprocal relations for homogeneous systems as presented on pp. 123–124 of C. TRUESDELL, *Rational Thermodynamics*, McGraw-Hill, 1969, it cannot be derived directly from them unless they are strengthened so as to cover not only strictly linear systems but also *linear approximations* in the neighborhood of equilibrium.

In particular, we will show for which class of closed system A3 does, in fact, imply the existence of a Liapunov function.

Before proceeding, we first derive some of the elementary properties of chemical systems. Theorem 4.6 below was first discovered by BOWEN [16], and it is included here simply for completeness. His definition of strong equilibrium coincides with ours of thermodynamic equilibrium. The converse of this theorem, which has not appeared previously, will be demonstrated for the case of mass-action kinetics in Section 6.

Definition 4.2. A regular equilibrium point of the chemical system $\{a, f\}$ is a point $(T, c) \in \mathscr{T} \times \mathscr{C}$ for which $f(T, c) = \mathbf{0}$ and $F(T, c) = \left\| \frac{\partial f_i}{\partial c_j} \right\|$ has rank p, where p is the dimension of $\mathscr{R}$.

Theorem 4.3. *The mapping* $\mu_T = \frac{\partial a}{\partial c}: \mathscr{T} \times \mathscr{C} \to R^N$ *is one-to-one at each fixed* T. *See Section* 2.

Because of Theorem 3.3, we may use (T, μ) as independent variables:

$$r(T, \mu) = f(T, \mu_T^{-1}(\mu)).$$

This somewhat simplifies the following theorem:

Theorem 4.4. *Let* $\mathscr{E} = \mathscr{R}^{\perp}$. *Then* $f(T, c) = \mathbf{0}$ *for all* c *such that* $\mu(T, c) \in \mathscr{E}$ (i.e., $r(T, \mu) = \mathbf{0}$ *for all* $\mu \in \mathscr{E}$).

Proof. If $\mu \in \mathscr{E}$, then $\langle \mu, r(T, \mu) \rangle = \mathbf{0}$, since the range of r at fixed T is perpendicular to $\mathscr{E}$. By axiom A3, this implies that $r(T, \mu) = \mathbf{0}$.

Since the criterion $\mu \in \mathscr{E}$ is the usual thermodynamic condition of equilibrium, we propose the definition:

Definition 4.5. A thermodynamic equilibrium point of the chemical system $\{a, f\}$ is a point $(T, c) \in \mathscr{T} \times \mathscr{C}$ for which $\mu(T, c) \in \mathscr{E}$.

Then we have the theorem

Theorem 4.6. *Any regular equilibrium point is also a thermodynamic equilibrium point.*

Proof. Suppose (T, c^0) is a regular equilibrium point, and $\mu^0 = \mu^0(T, c^0)$. Then $r(T, \mu^0) = f(T, c^0) = \mathbf{0}$, and $\sigma = \langle \mu^0, r(T, \mu^0) \rangle = \mathbf{0}$. By axiom A3, σ is always non-positive, so it must be a local maximum at (T, μ^0). Since μ ranges over all of R^N (by A1), this implies that

$$d\langle \mu, r(T, \mu) \rangle = 0 \quad \text{at} \quad (T, \mu^0)$$

for fixed T, or that

$$\langle d\mu, r(T^0, \mu^0) \rangle + \langle \mu^0, B\, d\mu \rangle = 0 \tag{4.2}$$

where $B = \left\| \frac{\partial r_i}{\partial \mu_j} \right\| = F J^{-1}$. Since (4.2) must be zero for arbitrary $d\mu$, μ^0 must be a left null vector of $B(T, \mu^0)$. Since J^{-1} is non-singular, μ^0 must be also a left null vector of F. The elements of $\mathscr{E} = \mathscr{R}^{\perp}$ will be left null vectors of F, and, because of Definition 4.2, the dimension of the null space is just the dimension of $\mathscr{R}^{\perp}$. Thus $\mathscr{E} = \mathscr{R}^{\perp}$ is the left null space of F, and $\mu^0 \in \mathscr{E}$.

The existence of equilibrium points is shown by the following theorem:

Theorem 4.7. *At any fixed temperature, T, there is a C^1-differentiable submanifold of thermodynamic equilibrium points in $\mathscr{C}$ whose dimension is equal to that of $\mathscr{E}=\mathscr{R}^{\perp}$.*

Proof. Let $P_{\mathscr{R}}$: $R^N \to \mathscr{R}$ be the orthogonal projection onto $\mathscr{R}$. Then the set of thermodynamic equilibrium points consists of the solutions to the equation $P_{\mathscr{R}} \circ \boldsymbol{\mu}(T, \boldsymbol{c}) = \mathbf{0}$. Consider the left-hand side at a fixed temperature as a mapping from $\mathscr{C}$ into $\mathscr{R}$. The Jacobian of this mapping has rank p, since $\left\| \frac{\partial \mu_i}{\partial c_j} \right\| = J$ is non-singular, and the mapping itself is of class C^1. Thus, by the implicit function theorem [12] we prove the assertion. Because of A2 the dimension of $\mathscr{E}$ is non-zero.

In connection with Section 6, it will be useful to express the requirements of Definition 4.1 in terms of the function $\boldsymbol{r}(T, \boldsymbol{\mu})$ rather than $\boldsymbol{f}(T, \boldsymbol{c})$. In this case axioms A2–A4 no longer involve the function $\boldsymbol{a}(T, \boldsymbol{c})$. Thus we may make the additional definition:

Definition 4.8. A function $\boldsymbol{r}(T, \boldsymbol{\mu})$ will be called a valid chemical rate expression if it satisfies the following conditions:

A′ 0 $\boldsymbol{r}(T, \boldsymbol{\mu})$: $\mathscr{T} \times R^N \to R^N$ has continuous first derivatives.

A′ 2 Let $\mathscr{R}$ be the smallest subspace of R^N containing the range of $\boldsymbol{r}(T, \boldsymbol{\mu})$. Then $\mathscr{R}^{\perp}$ has an element with strictly positive components.

A′ 3 The function σ: $\mathscr{T} \times R^N \to R^1$ given by $\sigma(T, \boldsymbol{\mu}) = \langle \boldsymbol{\mu}, \boldsymbol{r}(T, \boldsymbol{\mu}) \rangle$ is negative at any point $(T, \boldsymbol{\mu})$ where $\boldsymbol{r}(T, \boldsymbol{\mu}) \neq \mathbf{0}$.

A′ 4 The matrix $B(T, \boldsymbol{\mu}) = \left\| \frac{\partial r_i}{\partial \mu_j} \right\|$ is symmetric whenever $\boldsymbol{\mu} \in \mathscr{R}^{\perp}$. Here we note that A1 no longer appears.

5. Trajectories of Closed Systems

There is a class of dynamical systems connected with chemical systems. These are constructed by imposing certain constraints on the state variables. Contained in this class is the subclass of closed systems, which satisfy the differential equation

$$\dot{\boldsymbol{n}} = V \boldsymbol{r}(T, \boldsymbol{\mu}) = V \boldsymbol{f}(T, \boldsymbol{c}) \tag{5.1}$$

where $\boldsymbol{n}$ is the vector of mole numbers $(= V\boldsymbol{c})$ and V is the system volume. We assume that $V \in \mathscr{V}$, where $\mathscr{V} = \{V\colon V \in R^1, V > 0\}$. This may be written

$$\dot{\boldsymbol{c}} = \boldsymbol{f}(T, \boldsymbol{c}) - \boldsymbol{c} \frac{\dot{V}}{V}. \tag{5.2}$$

Equation (5.2) does not define the system completely, however. In addition, we must introduce equations for the time variation of T and V:

$$\begin{aligned} \dot{V} &= g(T, V, \boldsymbol{c}, t), \\ \dot{T} &= h(T, V, \boldsymbol{c}, t), \end{aligned} \tag{5.3}$$

where t is the time and h and g are scalar functions. Combining (5.3) with (5.2), we have the set

$$\begin{aligned} \dot{c} &= f(T, c) - c \cdot \frac{1}{V} g(T, V, c, t), \\ \dot{V} &= g(T, V, c, t), \\ \dot{T} &= h(T, V, c, t) \end{aligned} \tag{5.4}$$

which will determine the system's trajectories. Equation (5.4) may be taken as the definition of a closed system.

Definition 5.1. A closed system associated with a chemical system $\{a, f\}$ is a dynamical system whose trajectories are given by (5.4) for some pair of functions $g(T, V, c, t)$ and $h(T, V, c, t)$.

We now consider some general properties of closed system trajectories. It will be useful to describe these through the coordinate set $(T, V, \boldsymbol{n}) = (T, V, Vc)$, since the equations of change, (5.4), are then somewhat simpler:

$$\begin{aligned} \dot{\boldsymbol{n}} &= Vf(T, \boldsymbol{n}/V), \\ \dot{V} &= g(T, V, \boldsymbol{n}/V, t), \\ \dot{T} &= h(T, V, \boldsymbol{n}/V, t). \end{aligned} \tag{5.5}$$

In particular, the projections of these trajectories into the point set $\mathcal{N} = \{\boldsymbol{n}: \boldsymbol{n} = V\boldsymbol{c}; c \in \mathscr{C}, V \in \mathscr{V}\}$ will be considered. Note that $\mathcal{N}$ is just the positive orthant of R^N. We introduce the definition, due to WEI & PRATER [1].

Definition 5.2. A reaction simplex is the intersection of a hyperplane, perpendicular to the space $\mathscr{E}$, with the set $\mathcal{N}$.

The point set defined in this way is, in fact, a simplex, because the space $\mathscr{E}$ contains a positive element (by A2), so that the intersection of each such hyperplane with the positive orthant is bounded. These simplices have the following important property:

Theorem 5.3. *Each reaction simplex is an invariant set of the closed system (*i.e., *a trajectory that begins in a given simplex remains in it).*

Proof. Because of (5.1), $\dot{\boldsymbol{n}}$ is always in $\mathscr{R} = \mathscr{E}^{\perp}$. Thus the projection of $\boldsymbol{n}$ onto $\mathscr{E}$ along $\mathscr{R}$ does not change with time. Now as a particular component of $\boldsymbol{n}$, say n_i, goes to zero with the others held constant, then $c_i \to 0$. Because of A1, $\mu_i \to -\infty$, and because of A3, $\lim_{c_i \to 0} f_i(T, c) \geqq 0$. Thus the trajectory will never leave the positive orthant once it is inside. This completes the proof.

Theorem 5.4. *For any reaction simplex $\mathscr{S} \subset \mathcal{N}$, and for each pair (T, V), there is one and only one point $\boldsymbol{n} \in \mathscr{S}$ for which $(T, c) = (T, \boldsymbol{n}/V)$ is a thermodynamic equilibrium point.*

Proof. Consider the function $a(T, \boldsymbol{c}) = a(T, \boldsymbol{n}/V)$ varying over $\mathcal{S}$. Since V is fixed, the point $\boldsymbol{c} = \boldsymbol{n}/V$ will trace out a simplex in $\mathcal{C}$. Because of A1, $a(T, \boldsymbol{c})$ has a stationary point in $\mathcal{C}$, and because it is convex, a global minimum in $\mathcal{C}$. It has, thus, a minimum over the simplex in $\mathcal{C}$. Because $\mu_i = \dfrac{\partial a}{\partial c_i} \to -\infty$ as $c_i \to 0$, this minimum is not on a boundary. Thus there is a point in the simplex for which a is stationary with respect to directions in $\mathcal{S}$, i.e., $\dfrac{\partial a}{\partial \boldsymbol{c}} = \boldsymbol{\mu}$ is $\perp$ to $\mathcal{R}$, or $\boldsymbol{\mu} \in \mathcal{E}$. Since a is convex and $\mathcal{S}$ is linear, this point is unique.

We shall require the following lemma which, though slightly different from the commonly available Liapunov theorems, can be proved on very similar lines (see, for example, [17]).

Lemma 5.5. *Consider a dynamical system whose state, $\boldsymbol{x}$, is a vector in R^q, and with trajectories given by*

$$\dot{\boldsymbol{x}} = \varphi(\boldsymbol{x}).$$

Suppose that there is an invariant set $\mathcal{X}$ that is compact, that $\varphi(\boldsymbol{x})$ is continuous in $\mathcal{X}$ and that there exists a (Liapunov) function $\Psi(\boldsymbol{x})$, with continuous first derivatives in $\mathcal{X}$ for which

$$\dot{\Psi}(\boldsymbol{x}) = \sum_{i=1}^{q} \frac{\partial \Psi}{\partial x_i} \dot{x}_i = \sum_{i=1}^{q} \frac{\partial \psi}{\partial x_i} \varphi_i(\boldsymbol{x})$$

is negative at every point for which $\varphi(\boldsymbol{x}) \neq \boldsymbol{0}$. Then

(i) The set $\mathcal{Z} = \{\boldsymbol{x}\colon\ \varphi(\boldsymbol{x}) = \boldsymbol{0},\ \boldsymbol{x} \in \mathcal{X}\}$ is nonempty.

(ii) Every trajectory whose starting point is in $\mathcal{X}$ remains eventually in every neighborhood of $\mathcal{Z}$ (i.e., for every open set $\mathcal{U}$ containing $\mathcal{Z}$, there exists a time θ such that $\boldsymbol{x} \in \mathcal{U}$ for all $t > \theta$).

(iii) $\lim\limits_{t \to \infty} |\dot{\boldsymbol{x}}| = 0$ *along every trajectory starting in $\mathcal{X}$.*

Proof. Since $\Psi(\boldsymbol{x})$ is continuous over a compact set, it must have a minimum on the set. At this point, $\dot{\Psi} \geqq 0$ along any trajectory remaining in $\mathcal{X}$. Thus $\varphi(\boldsymbol{x}) = \boldsymbol{0}$ at this point, and hence, $\dot{\Psi} = 0$ at the point. Further, $\dot{\Psi}(\boldsymbol{x}) = 0$ if $\boldsymbol{x} \in \mathcal{Z}$.

Since $\Psi(\boldsymbol{x})$ has a minimum and $\dot{\Psi}(\boldsymbol{x})$ is non-positive, it is clear that for a given trajectory, $\boldsymbol{x}(t)$, $\dot{\Psi}(\boldsymbol{x}(t)) \to 0$ as $t \to \infty$. Thus for any $\varepsilon > 0$, there exists a θ such that $|\dot{\Psi}(\boldsymbol{x}(t))| < \varepsilon$ for all $t > \theta$. We must show, in addition, that for any open set $\mathcal{U}$ containing $\mathcal{Z}$, there is an $\varepsilon > 0$ such that $\boldsymbol{x} \in \mathcal{U}$ if $|\dot{\Psi}(\boldsymbol{x})| < \varepsilon$. Suppose, on the contrary, that there is a sequence of points in $\mathcal{X}$, $\{\boldsymbol{x}_n\}$, such that $|\dot{\Psi}(\boldsymbol{x}_n)| < 1/n$ and $\boldsymbol{x}_n \notin \mathcal{U}$. Then, since $\mathcal{X}$ is compact and $\mathcal{U}$ is open, the sequence has a convergent subsequence, with limit $\boldsymbol{x}_0 \notin \mathcal{U}$. Since $\dot{\Psi}(\boldsymbol{x}) = \sum\limits_{i=1}^{q} \dfrac{\partial \Psi}{\partial x_i} \varphi_i(\boldsymbol{x})$ is continuous, $\dot{\Psi}(\boldsymbol{x}_0) = 0$, and thus, $\boldsymbol{x}_0 \in \mathcal{Z} \circ \mathcal{U}$, a contradiction.

Finally, since $\varphi(\boldsymbol{x})$ is continuous, for any $\varepsilon > 0$ there exists an open set $\mathcal{U} \supset \mathcal{Z}$ such that $|\varphi(\boldsymbol{x})| < \varepsilon$ for all $\boldsymbol{x} \in \mathcal{U}$. Then by the previous statement $\lim\limits_{t \to \infty} |\varphi(\boldsymbol{x}(t))| = \boldsymbol{0}$. Note that $\dot{\boldsymbol{x}} = \varphi(\boldsymbol{x})$.

Theorem 5.6. *A closed system at constant temperature and volume has a unique thermodynamic equilibrium point in each reaction simplex. If there are no "weak" equilibrium points, every trajectory originating in the simplex converges to this point.*

Proof. By Theorem 5.4, the unique thermodynamic equilibrium point exists, and $a(T, c)$ is stationary there. Since $a(T, c)$ is strictly convex at fixed T, it is also a minimum at this point. Because of (4.7) and A3,

$$\frac{da}{dt} = \left\langle \boldsymbol{\mu}, \frac{dc}{dt} \right\rangle = \langle \boldsymbol{\mu}, \boldsymbol{f} \rangle < 0 .$$

Since the reaction simplex is compact (since it is of finite dimension, closed and bounded), and since a and f have the appropriate continuity properties (A0), the requirements of Lemma 4.5 are fulfilled. In this case, the set $\mathscr{X}$ consists of only one point, say, $\boldsymbol{n}^*$, and condition (ii) of Lemma 4.5 implies

$$\lim_{t \to \infty} \boldsymbol{n}(t) = \boldsymbol{n}^*$$

for any trajectory originating in the simplex.

We may extend Theorem 4.6 to many other closed systems. A particularly useful class of closed systems includes those for which the constraints may be rearranged to the form

$$\begin{aligned} V &= V(\boldsymbol{n}), \\ T &= T(\boldsymbol{n}) \end{aligned} \tag{5.6}$$

where $V(\boldsymbol{n})$ and $T(\boldsymbol{n})$ are continuous functions of $\boldsymbol{n}$. The essential feature of such systems is that the constraints applied to the chemical system in forming the closed system are integrable. The fact that these integral relationships may be rearranged to the form (5.6) is simply a useful regularity condition. By analogy with mechanical systems whose constraints are integrable, we refer to such systems as holonomic:

Definition 5.7. A holonomic closed system is a closed system whose dynamical equations may be rearranged to the form

$$\begin{aligned} \dot{\boldsymbol{n}} &= V\boldsymbol{f}(T, \boldsymbol{n}/V), \\ V &= g(\boldsymbol{n}), \\ T &= h(\boldsymbol{n}) \end{aligned}$$

(*i.e.*, to the form $\dot{\boldsymbol{n}} = \varphi(\boldsymbol{n})$) where g and h are positive continuous functions of $\boldsymbol{n}$ over the reaction simplex determined by the starting point.

An example of a non-holonomic system is one confined at constant volume, but that exchanges heat with a cooling coil at constant temperature through a constant resistance. In this case, it is necessary to know the whole history of the trajectory to calculate the instantaneous value of temperature.

One property of holonomic closed systems is given by this modification of a theorem due to Wei [6]:

Theorem 5.8. *A holonomic closed system has at least one thermodynamic equilibrium point in each reaction simplex.*

Proof. Since the system is holonomic, T and V are continuous functions of $\boldsymbol{n}$ in a given reaction simplex. By Theorem 5.4, there is a point $\boldsymbol{n}^*(T, V)$ in the simplex for each T and V that is a thermodynamic equilibrium point. The function $\boldsymbol{n}^*(T, V)$ will be continuous from $\mathcal{T}\times\mathcal{V}$ into the simplex $\mathcal{S}$ because of the continuity of $a(T, \boldsymbol{c})$. Thus there is a continuous mapping of $\mathcal{S}$ into $\mathcal{S}$, given by $\boldsymbol{n}^*(T(\boldsymbol{n}), V(\boldsymbol{n}))$. Since $\mathcal{S}$ is a closed p-cell, Brouwers' fixed-point theorem [10] states there is at least one fixed point of the mapping $\boldsymbol{n}^*(\boldsymbol{n})$ that is clearly a thermodynamic equilibrium point of the closed system.

Another subclass of closed systems is that which is adiabatic. An adiabatic closed system is one for which the entropy S, where

$$S = -V\frac{\partial a}{\partial T} \tag{5.7}$$

satisfies

$$\dot{S} = -\frac{1}{T}\langle \boldsymbol{\mu}, \dot{\boldsymbol{n}}\rangle. \tag{5.8}$$

From (5.7), the definition of S, we have

$$dS = -V\frac{\partial^2 a}{\partial T^2}dT + \left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T}\right]dV - \left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, d\boldsymbol{n}\right\rangle. \tag{5.9}$$

Combining (5.9) with (5.1), (5.2), and (5.8), an alternative definition of an adiabatic closed system is obtained:

$$\dot{\boldsymbol{c}} = \boldsymbol{f} - \boldsymbol{c}\frac{\dot{V}}{V},$$

$$\dot{T} = \frac{\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T} - \frac{\boldsymbol{\mu}}{T}, \boldsymbol{f}\right\rangle}{-\frac{\partial^2 a}{\partial T^2}} - \frac{\left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T}\right]}{-\frac{\partial^2 a}{\partial T^2}}\frac{\dot{V}}{V} \tag{5.10}$$

where $\dot{V} = g(T, V, \boldsymbol{c}, t)$ remains arbitrary. If an adiabatic system is also holonomic, then the following theorem applies:

Theorem 5.9. *Any trajectory of a holonomic adiabatic closed system remains eventually in every neighborhood of the equilibrium point set.*

Proof. If the system is holonomic, T and V are functions of $\boldsymbol{n}$ in a given reaction simplex. Then the entropy, S, is also a function of $\boldsymbol{n}$. By (5.8),

$$\dot{S} = -\frac{V}{T}\langle \boldsymbol{\mu}, \boldsymbol{f}\rangle \tag{5.11}$$

and by A3, $\dot{S} > 0$ unless $\boldsymbol{f} = \boldsymbol{0}$. The derivatives of S are continuous by A0. Thus $-S$ serves as the function Ψ in Lemma 5.5, which then establishes Theorem 5.9. Note again that the reaction simplex is compact.

Clearly, Theorem 5.9 depends only on the exactness of the differential form $-\frac{1}{T}\langle \boldsymbol{\mu}, d\boldsymbol{n}\rangle$ under the constraints of the closed system. The physical significance of this differential form is that it is the differential of the total entropy of the system plus surroundings due to the chemical reaction. In cases where this form is exact, we may define a "total entropy" S^* by the expression $dS^* = -\frac{1}{T}\langle \boldsymbol{\mu}, d\boldsymbol{n}\rangle$. This leads us to the following definition.

Definition 5.10. A completely holonomic closed system is a holonomic closed system for which the differential form $-\frac{1}{T(\boldsymbol{n})}\langle \boldsymbol{\mu}(T(\boldsymbol{n}), \boldsymbol{n}/V(\boldsymbol{n})), d\boldsymbol{n}\rangle (= dS^*)$ is exact, and to the theorem.

Theorem 5.11. *Any trajectory of a completely holonomic closed system remains eventually in every neighborhood of the equilibrium point set.*

Proof. Same as for Theorem 5.9, with S replaced by S^*.

The class of completely holonomic closed systems may be characterized by the following theorem:

Theorem 5.12. *The constraints of any completely holonomic closed system may be expressed in one of the following forms:*

(*i*)
$$\begin{cases} T = \text{constant} \\ V = \text{constant}, \end{cases}$$

(*ii*)
$$\begin{cases} T = \text{constant} \\ P = P(V), \end{cases}$$

(*iii*)
$$\begin{cases} S^0 = S^0(T) \\ V = \text{constant}, \end{cases}$$

(*iv*)
$$\begin{cases} S^0 = \varphi_T(T, V) \\ P = -\varphi_V(T, V) \end{cases}$$

where φ *is some function of* (T, V), *and* φ_T, φ_V *are its derivatives with respect to* T *and* V, *respectively. The function* S^0 *is defined as* $S^* - S$ (i.e., $TdS^0 = -TdS - \langle \boldsymbol{\mu}, d\boldsymbol{n}\rangle$). *In any adiabatic case,* $S^0 =$ constant.

Proof. Since the constraints are completely holonomic, S^*, and hence S^0, will be functions of the state of the system. From the identity

$$dU = TdS - PdV + \langle \boldsymbol{\mu}, d\boldsymbol{n}\rangle \tag{5.12}$$

we see that

$$dU = -TdS^0 - PdV. \tag{5.13}$$

Applying a Legendre transformation on T gives

$$d\varphi = S^0\, dT - PdV \tag{5.14}$$

where

$$\varphi = U + TS^0.$$

Clearly φ must be a function of state, and this is only possible if one of the four conditions above is satisfied.

The four possible forms can be condensed into one,

$$\begin{aligned} S^0 &= \varphi_T(T, V), \\ P &= -\varphi_V(T, V), \end{aligned} \tag{5.15}$$

by introducing the convention that if $\varphi_T = 0$, then T=constant, and if $\varphi_V = 0$, then V=constant. This is consistent with the definition $\varphi = U + TS^0$, and results in the expression

$$S^* = S + \frac{1}{T}[\varphi - U] \tag{5.16}$$

for the Liapunov function S^*. In using (5.16), one must be careful to adjust φ by an additive constant so that $\varphi = U + TS^0$ is satisfied.

Once the function $\varphi(T, V)$ in Theorem 5.12 is specified, the equations of change, (5.4), may be derived. Thus, from the definitions of P and S^0, and from (iv) above,

$$\begin{aligned} \dot{P} &= -\varphi_{TV}\,\dot{T} - \varphi_{VV}\,\dot{V} = \frac{1}{V}\langle J\boldsymbol{c}, \dot{\boldsymbol{n}}\rangle - \frac{1}{V}\langle J\boldsymbol{c}, \boldsymbol{c}\rangle\,\dot{V} + \left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T}\right]\dot{T}, \\ \dot{S}^0 &= \varphi_{TT}\,\dot{T} + \varphi_{TV}\,\dot{V} = -\frac{1}{T}\langle \boldsymbol{\mu}, \dot{\boldsymbol{n}}\rangle - \dot{S}, \\ \dot{S} &= -V\frac{\partial^2 a}{\partial T^2}\,\dot{T} + \left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T}\right]\dot{V} - \left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \dot{\boldsymbol{n}}\right\rangle. \end{aligned} \tag{5.17}$$

Combining with (5.2), we have

$$\begin{aligned} \dot{\boldsymbol{c}} &= \boldsymbol{f} - \boldsymbol{c} \\ &\cdot \left\{ \frac{\left[-\frac{\partial^2 a}{\partial T^2} + \frac{\varphi_{TT}}{V}\right]\langle J\boldsymbol{c}, \boldsymbol{f}\rangle + \left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T} + \varphi_{TV}\right]\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T} - \frac{\boldsymbol{\mu}}{T}, \boldsymbol{f}\right\rangle}{\left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T} + \varphi_{TV}\right]^2 + \left[-V\frac{\partial^2 a}{\partial T^2} + \varphi_{TT}\right]\left[\frac{1}{V}\langle J\boldsymbol{c}, \boldsymbol{c}\rangle - \varphi_{VV}\right]} \right\}, \\ \dot{V} &= V\,\frac{\left[-\frac{\partial^2 a}{\partial T^2} + \frac{\varphi_{TT}}{V}\right]\langle J\boldsymbol{c}, \boldsymbol{f}\rangle + \left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T} + \varphi_{TV}\right]\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T} - \frac{\boldsymbol{\mu}}{T}, \boldsymbol{f}\right\rangle}{\left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T} + \varphi_{TV}\right]^2 + \left[-V\frac{\partial^2 a}{\partial T^2} + \varphi_{TT}\right]\left[\frac{1}{V}\langle J\boldsymbol{c}, \boldsymbol{c}\rangle - \varphi_{VV}\right]}, \\ \dot{T} &= \frac{\left[\langle J\boldsymbol{c}, \boldsymbol{c}\rangle - V\varphi_{VV}\right]\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T} - \frac{\boldsymbol{\mu}}{T}, \boldsymbol{f}\right\rangle - \left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T} + \varphi_{TV}\right]\langle J\boldsymbol{c}, \boldsymbol{f}\rangle}{\left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T} + \varphi_{TV}\right]^2 + \left[-V\frac{\partial^2 a}{\partial T^2} + \varphi_{TT}\right]\left[\frac{1}{V}\langle J\boldsymbol{c}, \boldsymbol{c}\rangle - \varphi_{VV}\right]}. \end{aligned} \tag{5.18}$$

It may easily be seen that all the commonly encountered thermodynamic constraints are included in Theorem 5.12, as well as many new ones. Thus the axioms of WEI do indeed apply to a wide range of cases.

In the case of constant temperature and volume, the Liapunov function S^* is just $-\frac{Va}{T}$. For this case, the function $S^*(\boldsymbol{n})$ is strictly concave, so that the thermodynamic equilibrium point is unique (Theorem 5.4). Thus the question arises as to under what other conditions $S^*(\boldsymbol{n})$ will be concave. A sufficient condition which, again, covers all the commonly encountered cases is given by

Theorem 5.13. *The Liapunov function, $S^*(\boldsymbol{n})$, of a completely holonomic closed system, is strictly concave if $\varphi(T, V)$ satisfies*

$$\varphi_{TT} \geqq V \frac{\partial^2 a}{\partial T^2},$$

$$\varphi_{VV} \leqq 0$$

where $\varphi(T, V)$ is the function that characterizes the system, as described in Theorem 5.12.

Proof. Since $dS^* = -\frac{1}{T} \langle \boldsymbol{\mu}, d\boldsymbol{n} \rangle$, the Hessian matrix is given by

$$\frac{\partial^2 S^*}{\partial n_i \partial n_j} = -\left(\frac{\partial \mu_i/T}{\partial n_j}\right)_{T,V,n_l} - \left(\frac{\partial \mu_i/T}{\partial V}\right)_{T,\boldsymbol{n}} \frac{\partial \hat{V}}{\partial n_j} - \left(\frac{\partial \mu_i/T}{\partial T}\right)_{V,\boldsymbol{n}} \frac{\partial \hat{T}}{\partial n_j} \tag{5.19}$$

where $\hat{V}(\boldsymbol{n})$ and $\hat{T}(\boldsymbol{n})$ are the functions that express the constraints (5.6). From (5.18), we see that

$$\begin{gathered}
\frac{\partial \hat{V}}{\partial n_j} = \frac{\left[-V \frac{\partial^2 a}{\partial T^2} + \varphi_{TT}\right] \frac{1}{V} (J\boldsymbol{c})_j + \left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c} \right\rangle - \frac{\partial a}{\partial T} + \varphi_{TV}\right] \left(\frac{\partial \mu_j}{\partial T} - \frac{\mu_j}{T}\right)}{\left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c} \right\rangle - \frac{\partial a}{\partial T} + \varphi_{TV}\right]^2 + \left[-V \frac{\partial^2 a}{\partial T^2} + \varphi_{TT}\right] \left[\frac{1}{V} \langle J\boldsymbol{c}, \boldsymbol{c} \rangle - \varphi_{VV}\right]}, \\
\frac{\partial \hat{T}}{\partial n_j} = \frac{\left[\frac{1}{V} \langle J\boldsymbol{c}, \boldsymbol{c} \rangle - \varphi_{VV}\right] \left(\partial \frac{\mu_j}{\partial T} - \frac{\mu_j}{T}\right) - \left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c} \right\rangle - \frac{\partial a}{\partial T} + \varphi_{TV}\right] \frac{1}{V} (J\boldsymbol{c})_j}{\left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c} \right\rangle - \frac{\partial a}{\partial T} + \varphi_{TV}\right]^2 + \left[-V \frac{\partial^2 a}{\partial T^2} + \varphi_{TT}\right] \left[\frac{1}{V} \langle J\boldsymbol{c}, \boldsymbol{c} \rangle - \varphi_{VV}\right]}.
\end{gathered} \tag{5.20}$$

Also, we have the identities

$$\begin{gathered}
\left(\frac{\partial \mu_i/T}{\partial n_j}\right)_{T,V,n'_k} = \frac{1}{TV} \frac{\partial \mu_i}{\partial c_j} = \frac{1}{TV} J_{ij} \\
\left(\frac{\partial \mu_i/T}{\partial V}\right)_{T,\boldsymbol{n}} = \frac{1}{T} \sum_k \frac{\partial \mu_i}{\partial c_k} \left(\frac{\partial c_k}{\partial V}\right)_{\boldsymbol{n}} = -\frac{1}{TV} (J\boldsymbol{c})_i \\
\left(\frac{\partial \mu_i/T}{\partial T}\right)_{v,\boldsymbol{n}} = \frac{1}{T} \left(\frac{\partial \mu_i}{\partial T} - \frac{\mu_i}{T}\right).
\end{gathered} \tag{5.21}$$

Substituting (5.20) and (5.21) into (5.19), we find, after rearrangement,

$$
\begin{aligned}
d^2 S^* &= \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\partial^2 S^*}{\partial n_i \partial n_j}\, d n_i\, d n_j \\
&= -\frac{1}{TD}\left\{ \frac{1}{V^2}\left[-V\frac{\partial^2 a}{\partial T^2}+\varphi_{TT}\right]\left[\langle J\, d\boldsymbol{n}, d\boldsymbol{n}\rangle \langle J \boldsymbol{c}, \boldsymbol{c}\rangle - \langle J\boldsymbol{c}, d\boldsymbol{n}\rangle^2\right]\right. \\
&\quad +(-\varphi_{VV})\left[\left(-V\frac{\partial^2 a}{\partial T^2}+\varphi_{TT}\right)\frac{1}{V}\langle J\, d\boldsymbol{n}, d\boldsymbol{n}\rangle + \left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}-\frac{\boldsymbol{\mu}}{T}, d\boldsymbol{n}\right\rangle^2\right] \\
&\quad +\left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T}+\varphi_{TV}\right]^2 \frac{1}{V}\langle J\, d\boldsymbol{n}, d\boldsymbol{n}\rangle \qquad (5.22)\\
&\quad -2\left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T}+\varphi_{TV}\right]\frac{1}{V}\langle J\boldsymbol{c}, d\boldsymbol{n}\rangle \left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}-\frac{\boldsymbol{\mu}}{T}, d\boldsymbol{n}\right\rangle \\
&\quad \left. +\frac{1}{V}\langle J\boldsymbol{c}, \boldsymbol{c}\rangle \left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}-\frac{\boldsymbol{\mu}}{T}, d\boldsymbol{n}\right\rangle^2 \right\}
\end{aligned}
$$

where D is the denominator,

$$
D=\left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T}+\varphi_{TV}\right]^2 + \left[-V\frac{\partial^2 a}{\partial T^2}+\varphi_{TT}\right]\left[\frac{1}{V}\langle J\boldsymbol{c}, \boldsymbol{c}\rangle - \varphi_{VV}\right],
$$

which is positive, since J is positive-definite, and $\left[-V\frac{\partial^2 a}{\partial T^2}+\varphi_{TT}\right]$ and $(-\varphi_{VV})$ are positive by hypothesis. Now because J is positive-definite, the bilinear form $\langle J\boldsymbol{x}, \boldsymbol{y}\rangle$ is a valid inner product. Thus by the Schwarz inequality,

$$
\langle J\, d\boldsymbol{n}, d\boldsymbol{n}\rangle \langle J\boldsymbol{c}, \boldsymbol{c}\rangle \geqq \langle J\boldsymbol{c}, d\boldsymbol{n}\rangle^2, \qquad (5.23)
$$

so that the first term inside the braces of (5.22) is positive. The second term is clearly positive also. Using (5.23), we see that the sum of the last three terms is greater than or equal to

$$
\begin{aligned}
\frac{1}{V}&\left\{\frac{\left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T}+\varphi_{TV}\right]^2}{\langle J\boldsymbol{c}, \boldsymbol{c}\rangle}\langle J\boldsymbol{c}, d\boldsymbol{n}\rangle^2\right. \\
&\quad -2\left[\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}, \boldsymbol{c}\right\rangle - \frac{\partial a}{\partial T}+\varphi_{TV}\right]\langle J\boldsymbol{c}, d\boldsymbol{n}\rangle \left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}-\frac{\boldsymbol{\mu}}{T}, d\boldsymbol{n}\right\rangle \qquad (5.24)\\
&\quad \left. +\langle J\boldsymbol{c}, \boldsymbol{c}\rangle \left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}-\frac{\boldsymbol{\mu}}{T}, d\boldsymbol{n}\right\rangle^2\right\}.
\end{aligned}
$$

The expression (5.24) may be considered as a two-dimensional quadratic form in the variables $\langle J\boldsymbol{c}, d\boldsymbol{n}\rangle$ and $\left\langle \frac{\partial \boldsymbol{\mu}}{\partial T}-\frac{\boldsymbol{\mu}}{T}, d\boldsymbol{n}\right\rangle$. The diagonal terms of the form are positive, and the discriminant can be seen to be zero. Thus (5.24) is also non-negative, and

$$
d^2 S^* \leqq 0. \qquad (5.25)
$$

This shows that $S^*(\boldsymbol{n})$ is concave over the whole positive orthant. If $\boldsymbol{n}$ is constrained to lie in a given reaction simplex, $S^*(\boldsymbol{n})$ will remain concave, because the simplex is linear. The equality in (5.25) can hold only if that in (5.23) holds. This requires that $d\boldsymbol{n}$ be parallel to $\boldsymbol{c}$. In the reaction simplex, however, this is not possible, since $d\boldsymbol{n}\in\mathscr{R}$, and $\boldsymbol{c}$ always has a non-zero projection in $\mathscr{E}=\mathscr{R}^{\perp}$ for all $\boldsymbol{c}$ in the reaction simplex. Thus

$$d^2 S^* < 0 \tag{5.26}$$

strictly, everywhere in the simplex. Thus, if the system is of type (iv) in Theorem 5.7, the theorem is proven. Using the convention that if $\varphi_T=0$ then $T=$constant, and if $\varphi_V=0$ then $V=$constant, we may show that the theorem applies to all four cases in Theorem 5.7. Thus, suppose $V=$constant ($\varphi_V=0$). Then

$$\frac{\partial\hat{T}}{\partial n_i}=\frac{\left(\frac{\partial\mu_i}{\partial T}-\frac{\mu_i}{T}\right)}{\left[-V\frac{\partial^2 a}{\partial T^2}+\varphi_{TT}\right]}, \tag{5.27}$$

$$\frac{\partial^2 S^*}{\partial n_i\,\partial n_j}=-\frac{1}{TV}\left\{J_{ij}+\frac{V}{\left[-V\frac{\partial^2 a}{\partial T^2}+\varphi_{TT}\right]}\left(\frac{\partial\mu_i}{\partial T}-\frac{\mu_i}{T}\right)\left(\frac{\partial\mu_j}{\partial T}-\frac{\mu_j}{T}\right)\right\}, \tag{5.28}$$

and

$$d^2 S^*=-\frac{1}{TV}\left\{\langle J\,d\boldsymbol{n},d\boldsymbol{n}\rangle+\frac{V}{\left[-V\frac{\partial^2 a}{\partial T^2}-\varphi_{TT}\right]}\left\langle\frac{\partial\boldsymbol{\mu}}{\partial T}-\frac{\boldsymbol{\mu}}{T},d\boldsymbol{n}\right\rangle^2\right\} \tag{5.29}$$

is clearly negative. Similarly, if $T=$constant ($\varphi_T=0$), then

$$\frac{\partial\hat{V}}{\partial n_i}=\frac{(J\boldsymbol{c})_i}{[\langle J\boldsymbol{c},\boldsymbol{c}\rangle-V\varphi_{TT}]}, \tag{5.30}$$

$$\frac{\partial^2 S^*}{\partial n_i\,\partial n_j}=-\frac{1}{TV}\left\{J_{ij}-\frac{(J\boldsymbol{c})_i(J\boldsymbol{c})_j}{\langle J\boldsymbol{c},\boldsymbol{c}\rangle-V\varphi_{TT}}\right\}, \tag{5.31}$$

and

$$\begin{aligned} d^2 S^*=&-\frac{1}{TV[\langle J\boldsymbol{c},\boldsymbol{c}\rangle-V\varphi_{TT}]}\\ &\cdot\{\langle J\boldsymbol{c},\boldsymbol{c}\rangle\langle J\,d\boldsymbol{n},d\boldsymbol{n}\rangle-\langle J\boldsymbol{c},d\boldsymbol{n}\rangle^2-V\varphi_{TT}\langle J\,d\boldsymbol{n},d\boldsymbol{n}\rangle\}\end{aligned} \tag{5.32}$$

which, by 5.23, is again negative.

As a corollary of Theorem 5.13, we have

Theorem 5.14. *A completely holonomic closed system with only thermodynamic equilibrium points has a unique equilibrium point in each reaction simplex, and every trajectory beginning in the simplex approaches this point as a limit (*i.e., *remains eventually in every neighborhood of the point) if*

$$\begin{aligned}\varphi_{TT}&\geqq V\frac{\partial^2 a}{\partial T^2},\\ \varphi_{VV}&\leqq 0.\end{aligned} \tag{5.33}$$

Proof. The equilibrium set is non-empty because the system is holonomic (Theorem 5.8). This point is unique because S^* must be stationary at thermodynamic equilibrium, and because (5.33) implies that S^* is strictly concave over each reaction simplex. Theorem 5.11 then establishes the convergence of trajectories.

6. Polynomial Kinetics and the Law of Mass-Action

Many kinetic rate expressions have the form of polynomials in concentration:

$$f(T,c)=\sum_{\alpha=1}^{Q} h_\alpha(T)\prod_{j=1}^{N} c_j^{q_{j\alpha}}. \tag{6.1}$$

These arise theoretically by supposing the overall chemical change to be comprised of elementary reaction steps, each of which obeys the law of mass action. Consider, for example, the single elementary step

$$\sum_{i=1}^{N} q_{i\alpha}\mathscr{A}_i \rightleftarrows \sum_{i=1}^{N} q_{i\beta}\mathscr{A}_i \tag{6.2}$$

where the $q_{i\alpha}$ are the stoichiometric coefficients and the $\mathscr{A}_i$ are the symbols for the various chemical species. Then the law of mass action gives, for the rate of step (6.2),

$$r_{\alpha\beta}=(\mathbf{q}_\beta-\mathbf{q}_\alpha)\left[k'_{\alpha\beta}(T)\prod_{j=1}^{N} c_j^{q_{j\alpha}}-k'_{\beta\alpha}(T)\prod_{j=1}^{N} c_j^{q_{j\beta}}\right] \tag{6.3}$$

where $\mathbf{q}_\alpha=(q_{1\alpha}, q_{2\alpha}, \dots, q_{N\alpha})\in R^N$. The requirement that (6.2) be a "balanced" equation is that $(\mathbf{q}_\beta-\mathbf{q}_\alpha)\in\mathscr{R}$, which also follows from (6.3). This may also be written

$$\langle \mathbf{q}_\alpha, \mathbf{v}\rangle=\langle \mathbf{q}_\beta, \mathbf{v}\rangle; \quad \text{all } \mathbf{v}\in\mathscr{E}. \tag{6.4}$$

Thus we define an equivalence relation $\sim$ so that $\mathbf{q}_\alpha\sim\mathbf{q}_\beta$ iff (6.4) is satisfied.

In order to express the reaction rate in the coordinates (T, μ), we assume the system to be an ideal gaseous solution:

$$c_i=e^{\frac{-\mu_i^*(T)}{RT}}\, e^{\frac{\mu_i}{RT}}; \tag{6.5}$$

substituting (6.5) into (6.1), we have

$$r(T,\mu)=\sum_{\alpha=1}^{Q} h_\alpha(T)\, e^{\frac{1}{RT}\langle \mathbf{q}_\alpha, \mu\rangle} \tag{6.6}$$

where

$$h_\alpha(T)=h'_\alpha(T)\, e^{\frac{-1}{RT}\langle \mathbf{q}_\alpha, \mu^*(T)\rangle}.$$

Thus we arrive at the following definition.

Definition 6.1. A polynomial rate expression is one of the form (6.6), where each $\mathbf{q}_\alpha$ is a non-negative vector, $\mathbf{q}_\alpha\neq\mathbf{q}_\beta$ if $\alpha\neq\beta$, and $\mathbf{q}_\alpha\neq\mathbf{0}$; all α. The rate expression will be called *valid* if it satisfies Definition 4.8.

In case all the q_α in (6.6) are equivalent by (6.4), it can be seen that

$$r(T, \mu+v)=\varphi(v)\,r(T, \mu); \quad \text{all } \mu\in R^N,\ v\in\mathscr{E}, \tag{6.7}$$

where $\varphi(v)$ is the common value of $e^{\frac{1}{RT}\langle q_\alpha, v\rangle}$ for all α. This turns out to be quite a useful property, and we suggest the following definition.

Definition 6.2. A kinetically homogeneous rate expression, $r(T, \mu)$, is one for which there exists a continuous scalar function φ: $\mathscr{E}\rightarrow(0, \infty)$ such that $r(T, \mu+v)=\varphi(v)\, r(T, \mu)$ for all $\mu\in R^N$ and all $v\in\mathscr{E}$.

From Definition 6.2 it is clear that $\varphi(v+v')=\varphi(v)\,\varphi(v')$, all v, $v'\in\mathscr{E}$. Since φ is also continuous, we may take $\varphi(v)=e^{\langle w, v\rangle}$ for some $w\in\mathscr{E}$. (See [15].) Also, in case the subspace $\mathscr{E}$ contains the constant vector $\mathbf{1}=(1, 1, \dots, 1)$, kinetic homogeneity will imply ordinary homogeneity in c of order b for $f(T, c)$, where $b=\langle q_\alpha, 1\rangle$:

$$f(T, \theta c)=\theta^b f(T, c). \tag{6.8}$$

To see this, simply note that

$$r(T, \mu+v)=f(T, e^{v_1/RT}c_1\, e^{v_2/RT}c_2, \dots, e^{v_N/RT}c_N). \tag{6.9}$$

Rewriting (6.3) in terms of (T, μ), $r_{\alpha\beta}=(q_\beta-q_\alpha)$, we have

$$[k_{\alpha\beta}(T)\,e^{\frac{1}{RT}\langle q_\alpha, \mu\rangle}-k_{\beta\alpha}(T)\,e^{\frac{1}{RT}\langle q_\beta \mu\rangle}] \tag{6.10}$$

where $k_{\alpha\beta}(T)=k'_{\alpha\beta}(T)\,e^{\frac{1}{RT}\langle q_\alpha, \mu^*(T)\rangle}$. The condition of *detailed balance* requires that $r_{\alpha\beta}$ vanish at equilibrium, regardless of what other elementary steps occur in the system. Since $q_\alpha\sim q_\beta$, then at any thermodynamic equilibrium point v, $e^{\langle q_\alpha, v\rangle}=e^{\langle q_\beta, v\rangle}$, by (6.4). Thus detailed balance requires that $k_{\alpha\beta}(T)\equiv k_{\beta\alpha}(T)$.

Suppose now that many elementary steps occur between many "reactant sets" $q_1, q_2, \dots, q_Q$. The total rate may then be written

$$r=\sum_{\alpha=1}^{Q}\sum_{\beta\neq\alpha}^{Q}k_{\alpha\beta}(T)(q_\beta-q_\alpha)\,e^{\frac{1}{RT}\langle q_\alpha, \mu\rangle} \tag{6.11}$$

where $k_{\alpha\beta}(T)\equiv 0$ for any pair α, β for which $q_\alpha\sim q_\beta$ does not hold. The expression (6.14) may be written more compactly if we define $k_{\alpha\alpha}(T)$ to be $-\sum\limits_{\substack{\beta\neq\alpha\\ \beta=1}}^{Q}k_{\alpha\beta}(T)$:

$$r=\sum_{\alpha=1}^{Q}\sum_{\beta=1}^{Q}k_{\alpha\beta}(T)\,q_\beta\, e^{\frac{1}{RT}\langle q_\alpha, \mu\rangle}. \tag{6.12}$$

Thus we are led to the definition

Definition 6.3. A reaction rate expression is said to be of mass action type if it is of the form

$$r(T, \mu)=\sum_{\alpha=1}^{Q}\sum_{\beta=1}^{Q}k_{\alpha\beta}(T)\,q_\beta\, e^{\frac{1}{RT}\langle q_\alpha, \mu\rangle} \tag{6.13}$$

and if

(definition of $k_{\alpha\alpha}$) $$\sum_{\beta=1}^{Q} k_{\alpha\beta}(T)\equiv 0; \quad \text{all } T\in\mathscr{T}, \tag{6.14}$$

(mass balance) $$k_{\alpha\beta}(T)\neq 0 \rightarrow \boldsymbol{q}_\alpha \sim \boldsymbol{q}_\beta, \tag{6.15}$$

(detailed balance) $$k_{\alpha\beta}(T)\equiv k_{\beta\alpha}(T); \quad \text{all } T\in\mathscr{T}, \tag{6.16}$$

(non-negative rate constants) $$k_{\alpha\beta}(T)\geqq 0 \quad \text{if} \quad \alpha\neq\beta, \tag{6.17}$$

(positive stoichiometric coefficients) $$q_{i\alpha}\geqq 0; \quad \text{all } i,\alpha. \tag{6.18}$$

Normally, the elements $q_{i\alpha}$ will be integers, but we will not restrict them here. Also useful is

Definition 6.4. A reaction rate expression satisfying all the requirements of Definition 6.3 except equation (6.17) will be called of pseudo mass action type.

We are then led to some theorems:

Theorem 6.5. *Any valid polynomial rate expression may be decomposed into a sum of kinetically homogeneous polynomial rate expressions, so that at any thermodynamic equilibrium point each individual expression is zero and has the property that* $B=\left\|\dfrac{\partial r_i}{\partial \mu_j}\right\|$ *is symmetric.*

Proof. Because of Theorem 4.4, we have

$$\boldsymbol{r}(T,\boldsymbol{v})=\sum_{\alpha=1}^{Q}\boldsymbol{h}_\alpha(T)\, e^{\frac{1}{RT}\langle \boldsymbol{q}_\alpha,\boldsymbol{v}\rangle}=0; \quad \text{all } \boldsymbol{v}\in\mathscr{E}. \tag{6.19}$$

Using the equivalence relation $\sim$, we collect the $\boldsymbol{q}_\alpha$ into equivalence classes $\mathscr{S}_k$, $k=1,\dots,S$. Then

$$\sum_{k=1}^{S} e^{\frac{1}{RT}\langle \boldsymbol{w}^{(k)},\boldsymbol{v}\rangle}\sum_{\alpha\in\mathscr{S}_k}\boldsymbol{h}_\alpha(T)=0; \quad \text{all } \boldsymbol{v}\in\mathscr{E}$$

where $\boldsymbol{w}^k$ is the common projection of the $\boldsymbol{q}_\alpha$ in $\mathscr{S}_k$ onto $\mathscr{E}$. Now the $\boldsymbol{w}^{(k)}$ are all different, since otherwise two classes can be combined. Thus, since the exponentials are independent,

$$\sum_{\alpha\in\mathscr{S}_k}\boldsymbol{h}_\alpha(T)=0, \quad k=1,\dots,S.$$

Since the $\boldsymbol{h}_\alpha(T)$ are non-zero, this implies that there is at least one $\boldsymbol{q}_3$ equivalent to a given $\boldsymbol{q}_\alpha$. Now let

$$\boldsymbol{r}^{(k)}(T,\boldsymbol{\mu})=\sum_{\alpha\in\mathscr{S}_k}\boldsymbol{h}_\alpha(T)\, e^{\frac{1}{RT}\langle \boldsymbol{q}_\alpha,\boldsymbol{\mu}\rangle}.$$

Clearly,

$$\boldsymbol{r}(T,\boldsymbol{\mu})=\sum_{k=1}^{S}\boldsymbol{r}^{(k)}(T,\boldsymbol{\mu}),$$

$$\boldsymbol{r}^{(k)}(T,\boldsymbol{v})\equiv 0; \quad \text{all } \boldsymbol{v}\in\mathscr{E}.$$

The matrix $B(T, \mu)=\left\|\frac{\partial r_i}{\partial \mu_j}\right\|$ can be expressed at equilibrium by

$$B(T, v)=\sum_{k=1}^{S} e^{\frac{1}{RT}\langle w^{(k)}, v\rangle} B^{(k)}(T); \qquad v \in \mathscr{E}$$

where $B^{(k)}(T)=\| \sum_{\alpha \in \mathscr{S}_k} h_{i\alpha}(T)\, q_{j\alpha} \|$.

By axiom A'4, the matrix $B(T, v)$; $v\in\mathscr{E}$, is symmetric. Thus

$$B(T, v)-B^*(T, v)=\sum_{k=1}^{S} e^{\frac{1}{RT}\langle w^{(k)}, v\rangle}\{B^{(k)}(T)-B^{(k)*}(T)\} \equiv 0 .$$

Since the exponentials are independent, this implies that $B^{(k)}(T)=B^{(k)*}(T)$ for each k.

Theorem 6.6. *Any kinetically homogeneous polynomial rate expression whose thermodynamic equilibrium points are regular is of pseudo-mass action type.*

Proof. Let $\boldsymbol{r}(T, \boldsymbol{\mu})=\sum_{\alpha=1}^{Q} \boldsymbol{h}_\alpha(T)\, e^{\frac{1}{RT}\langle \boldsymbol{q}_\alpha, \boldsymbol{\mu}\rangle}$. Then, by regularity, the rank of $B(T, \mathbf{0})$, where

$$B(T, \mathbf{0})=\left\|\left(\frac{\partial r_i}{\partial \mu_j}\right)_{\boldsymbol{\mu}=\mathbf{0}}\right\|=\left\|\sum_{\alpha=1}^{Q} h_{i\alpha}(T)\, q_{j\alpha}\right\|=\|b_{ij}(T)\| ,$$

is the same as the dimension of $\mathscr{R}$. Thus the only left null vectors of $B(T, \mathbf{0})$ are the elements of $\mathscr{R}^{\perp}$. By A4, $B(T, \mathbf{0})$ is symmetric, so the elements of $\mathscr{R}^{\perp}$ are also the only right null vectors of $B(T, \mathbf{0})$. Thus any vector $\boldsymbol{u}$ for which $B(T, \mathbf{0})\boldsymbol{u}=\mathbf{0}$ satisfies

$$\langle \boldsymbol{u}, \boldsymbol{h}_\alpha\rangle=0; \qquad \alpha=1, \ldots, Q$$

since each $\boldsymbol{h}_\alpha \in \mathscr{R}$. This implies that there exists a matrix $s_{\alpha k}$ with the property

$$h_{i\alpha}(T)=\sum_{k=1}^{N} s_{\alpha k}(T)\, b_{ki}(T)=\sum_{k=1}^{N} s_{\alpha k}(T) \sum_{\beta=1}^{Q} h_{k\beta}(T)\, q_{i\beta} .$$

This may be written

$$\boldsymbol{h}_\alpha(T)=\sum_{\beta=1}^{Q} k_{\alpha\beta}(T)\, \boldsymbol{q}_\beta \tag{6.22}$$

where

$$k_{\alpha\beta}(T)=\sum_{k=1}^{N} s_{\alpha k}(T)\, h_{k\beta}(T) . \tag{6.23}$$

Further,

$$k_{\gamma\alpha}(T)=\sum_{i=1}^{N} s_{\gamma i}(T)\, h_{i\alpha}(T)=\sum_{i=1}^{N} \sum_{k=1}^{N} s_{\gamma i}(T)\, s_{\alpha k}(T)\, b_{ki}(T) .$$

Since $b_{ik}(T)=b_{ki}(T)$,

$$k_{\gamma\alpha}(T)=k_{\alpha\gamma}(T) . \tag{6.24}$$

Since $\boldsymbol{h}_\alpha(T) \in \mathscr{R}$; all α, T,

$$\langle \boldsymbol{v}, \boldsymbol{h}_\alpha(T)\rangle \equiv 0 \equiv \sum_{\beta=1}^{Q} k_{\alpha\beta}(T)\langle \boldsymbol{v}, \boldsymbol{q}_\beta\rangle , \tag{6.25}$$

and, since $\boldsymbol{r}(T, \boldsymbol{\mu})$ is kinetically homogeneous, $\langle \boldsymbol{v}, \boldsymbol{q}_3\rangle = \langle \boldsymbol{v}, \boldsymbol{w}\rangle$; all β. Thus

$$\sum_{\beta=1}^{Q} k_{\alpha\beta}(T) \equiv 0; \quad \text{all } T \in \mathscr{T}. \tag{6.26}$$

Condition (6.15) is automatically satisfied because of kinetic homogeneity.

Theorem 6.7. *A rate expression of mass action type is valid.*

Proof. We have already assumed that $\mathscr{R}^{\perp}$ has a positive element, so it suffices to demonstrate A′3 and A′4.

Rewriting (6.13), we have

$$\boldsymbol{r}(T, \boldsymbol{\mu}) = \sum_{\alpha=1}^{Q} \sum_{\beta>\alpha} k_{\alpha\beta}(T)(\boldsymbol{q}_\beta - \boldsymbol{q}_\alpha)\left(e^{\langle \boldsymbol{q}_\alpha, \boldsymbol{\mu}\rangle} - e^{\langle \boldsymbol{q}_\beta, \boldsymbol{\mu}\rangle}\right), \tag{6.27}$$

$$\langle \boldsymbol{\mu}, \boldsymbol{r}(T, \boldsymbol{\mu})\rangle = \sum_{\alpha=1}^{Q} \sum_{\beta=1}^{Q} k_{\alpha\beta}(T)\left(\langle \boldsymbol{q}_\beta, \boldsymbol{\mu}\rangle - \langle \boldsymbol{q}_\alpha, \boldsymbol{\mu}\rangle\right)\left(e^{\langle \boldsymbol{q}_\alpha, \boldsymbol{\mu}\rangle} - e^{\langle \boldsymbol{q}_\beta, \boldsymbol{\mu}\rangle}\right). \tag{6.28}$$

Since the function e^t is monotone, and since $k_{\alpha\beta}(T) \geqq 0$, each term in the sum will be non-positive. A term will only be zero if either $k_{\alpha\beta}(T) = 0$, $\langle \boldsymbol{q}_\alpha, \boldsymbol{\mu}\rangle$ and $\langle \boldsymbol{q}_\beta, \boldsymbol{\mu}\rangle = -\infty$, or $\langle \boldsymbol{q}_\alpha, \boldsymbol{\mu}\rangle = \langle \boldsymbol{q}_\beta, \boldsymbol{\mu}\rangle$. Thus $\langle \boldsymbol{\mu}, \boldsymbol{r}(T, \boldsymbol{\mu})\rangle = 0$ implies that $\boldsymbol{r}(T, \boldsymbol{\mu}) = \boldsymbol{0}$, and $\langle \boldsymbol{\mu}, \boldsymbol{r}(T, \boldsymbol{\mu})\rangle < 0$ otherwise, so that A3 is established. Also, from (6.27),

$$B(T, \boldsymbol{\mu}) = \left\| \frac{\partial r_i}{\partial \mu_j} \right\| = \left\| \sum_{\alpha=1}^{Q} \sum_{\beta>\alpha} k_{\alpha\beta}(T)(q_{i\beta} - q_{i\alpha})\left(q_{j\alpha} e^{\langle \boldsymbol{q}_\alpha, \boldsymbol{\mu}\rangle} - q_{j\beta} e^{\langle \boldsymbol{q}_\beta, \boldsymbol{\mu}\rangle}\right) \right\|. \tag{6.29}$$

Again, if $\boldsymbol{r}(T, \boldsymbol{\mu}) = \boldsymbol{0}$, each term in (6.27) will vanish (since otherwise (6.28) will not be zero) so that each term in (6.29) will either vanish or be of the form

$$-k_{\alpha\beta}(T)(q_{i\alpha} - q_{i\beta})(q_{j\alpha} - q_{j\beta})\, e^{\langle \boldsymbol{q}, \boldsymbol{\mu}\rangle} \tag{6.30}$$

where $\langle \boldsymbol{q}, \boldsymbol{\mu}\rangle = \langle \boldsymbol{q}_\alpha, \boldsymbol{\mu}\rangle = \langle \boldsymbol{q}_\beta, \boldsymbol{\mu}\rangle$. Since $k_{\alpha\beta}(T)$ is symmetric by (6.19), the matrix resulting from the sum of terms of the form of (6.30) must be symmetric, so that $B(T, \boldsymbol{\mu})$ is symmetric whenever $\boldsymbol{r}(T, \boldsymbol{\mu}) = \boldsymbol{0}$, establishing A4.

Theorem 6.8. *For a rate expression of mass action type, any thermodynamic equilibrium point is also regular.*

Proof. We will show that any thermodynamic equilibrium point of (6.13) is also regular. Thus we calculate from (6.13)

$$B(T, \boldsymbol{\mu}) = \left\| \frac{\partial r_i}{\partial \mu_j} \right\| = \left\| \sum_{\alpha=1}^{Q} \sum_{\beta=1}^{Q} k_{\alpha\beta}\, q_{i\beta}\, q_{j\alpha}\, e^{\langle \boldsymbol{q}_\alpha, \boldsymbol{\mu}\rangle} \right\| \tag{6.31}$$

and consider

$$B(T, \boldsymbol{0}) = \left\| \sum_{\alpha=1}^{Q} \sum_{\beta=1}^{Q} k_{\alpha\beta}\, q_{i\beta}\, q_{j\alpha} \right\|. \tag{6.31$'$}$$

Suppose there is a $\boldsymbol{u} \in \mathscr{R}^N$ such that $B(T, \boldsymbol{0})\, \boldsymbol{u} = \boldsymbol{0}$. Then

$$\sum_{\alpha=1}^{Q} \sum_{\beta=1}^{Q} k_{\alpha\beta}(T)\, \boldsymbol{q}_\beta \langle \boldsymbol{q}_\alpha, \boldsymbol{u}\rangle = \boldsymbol{0}. \tag{6.32}$$

Multiplying by $\boldsymbol{u}$, we have

$$\sum_{\alpha=1}^{Q}\sum_{\beta=1}^{Q} k_{\alpha\beta}(T)\langle \boldsymbol{q}_\beta, \boldsymbol{u}\rangle\langle \boldsymbol{q}_\alpha, \boldsymbol{u}\rangle = \boldsymbol{0}. \tag{6.33}$$

Now because of (6.14), (6.16), and (6.17), the matrix $K(T) = \| k_{\alpha\beta}(T) \|$ is symmetric and negative semi-definite (see [11]). Thus the sequence $\langle \boldsymbol{q}_\alpha, \boldsymbol{u}\rangle$; $\alpha = 1, \ldots, Q$ must be a null vector of $K(T)$. Therefore

$$\sum_{\beta=1}^{Q} k_{\alpha\beta}(T)\langle \boldsymbol{q}_\beta, \boldsymbol{u}\rangle = 0 \tag{6.34}$$

for all α, so that $\langle \boldsymbol{u}, \boldsymbol{r}(T, \boldsymbol{\mu})\rangle \equiv 0$ for all $\boldsymbol{\mu} \in R^N$. This shows that if $B(T, \boldsymbol{0})\boldsymbol{u} = \boldsymbol{0}$, then $\boldsymbol{u} \in \mathscr{E}$. On the other hand, any element of $\mathscr{E}$ is a left null vector of $B(T, \boldsymbol{0})$, and by symmetry a right null vector of $B(T, \boldsymbol{0})$. Thus $B(T, \boldsymbol{0})$ has rank equal to the dimension of $\mathscr{E}^\perp = \mathscr{R}$, and $(T, \boldsymbol{0})$ is a regular equilibrium point.

The expression $\boldsymbol{r}(T, \boldsymbol{\mu})$ can be decomposed into kinetically homogeneous rate expressions because of Theorem 6.5. Also, because of (6.15), each of these will again be of mass action type. Thus

$$\boldsymbol{r}(T, \boldsymbol{\mu}) = \sum_{k=1}^{S} \boldsymbol{r}^{(k)}(T, \boldsymbol{\mu}) \tag{6.35}$$

where

$$\boldsymbol{r}^{(k)}(T, \boldsymbol{\mu}) = \sum_{\alpha\in\mathscr{S}_k}\sum_{\beta\in\mathscr{S}_k} k_{\alpha\beta}(T)\boldsymbol{q}_\beta e^{\frac{1}{RT}\langle \boldsymbol{q}_\alpha, \boldsymbol{\mu}\rangle}. \tag{6.36}$$

Note that β is only summed over $\mathscr{S}_k$ because $k_{\alpha\beta}(T) = 0$ if $\alpha \in \mathscr{S}_k$ and $\beta \notin \mathscr{S}_k$ by (6.1). Then we may write

$$B(T, \boldsymbol{v}) = \sum_{k=1}^{S} e^{\langle \boldsymbol{w}^{(k)}, \boldsymbol{v}\rangle} B^{(k)}(T, \boldsymbol{0}); \quad \text{all } \boldsymbol{v} \in \mathscr{E} \tag{6.37}$$

where

$$B^{(k)}(T, \boldsymbol{0}) = \| \sum_{\alpha\in\mathscr{S}_k}\sum_{\beta\in\mathscr{S}_k} k_{\alpha\beta}(T) q_{l\beta} q_{j\alpha} \|.$$

Now because each $B^{(k)}(T, \boldsymbol{0})$ is symmetric and negative semi-definite, the null space of $B(T, \boldsymbol{v})$ is just the intersection of the respective null spaces of the $B^{(k)}(T, \boldsymbol{0})$. But this is clearly equal to $\mathscr{E}$, so that $B^{(k)}(T, \boldsymbol{v})$ has rank equal to the dimension of $\mathscr{R}$ for all $\boldsymbol{v} \in \mathscr{E}$; i.e., for all thermodynamic equilibrium points. Thus any thermodynamic equilibrium point of (6.13) is also regular.

Theorem 6.9. *Given any kinetically homogeneous rate expression of mass action type, a matrix $k_{\alpha\beta}(T)$ satisfying equation* (6.13) *may be calculated from equation* (6.23).

Proof. The validity of (6.23) depends on the regularity of the equilibrium point $(T, \boldsymbol{0})$. Since this is a thermodynamic equilibrium point, Theorem 6.8 implies that it is regular.

Theorem 6.9 provides an answer to the following question: given a polynomial rate expression, test it to see if it is of mass action type, and calculate a matrix $k_{\alpha\beta}(T)$ satisfying (6.13). The procedure is first to decompose the rate expression into its kinetically homogeneous parts, and then to use equation (6.23) to calculate $k_{\alpha\beta}(T)$. If this is possible, the rate expression is established to be at least of pseudo-mass action type, and if it turns out that $k_{\alpha\beta}(T)\geqq 0$ if $\alpha\neq\beta$, the job is finished. If the matrix $k_{\alpha\beta}(T)$ satisfying (6.13) were unique, this would be all there is to it. It turns out, however, that there are, in general, many matrices $k_{\alpha\beta}(T)$ satisfying (6.13) for a given rate expression, and that some of these do not satisfy (6.17), even though others do. Thus the fact that the matrix $k_{\alpha\beta}(T)$ calculated from (6.23) contains negative elements with $\alpha\neq\beta$ does not rule out that the rate expression is of mass action type.

It is interesting to note that even though the $k_{\alpha\beta}(T)$ for a given rate expression is not unique, the result calculated from (6.23) is unique. The special property of $k_{\alpha\beta}(T)$ in (6.23) can be seen as follows: The rank of the matrix $h_{i\alpha}$

$$h_{i\alpha}(T)=\sum_{\beta=1}^{Q} k_{\alpha\beta}(T)\,q_{i\beta} \tag{6.38}$$

is equal to the dimension of $\mathscr{R}$. Thus the rank of any $k_{\alpha\beta}$ satisfying (6.27) is equal to or greater than this quantity.

On the other hand, equation (6.23) requires that the rank of our special $k_{\alpha\beta}(T)$ be less than or equal to that of $B(T,\mathbf{0})$ which, in turn, is equal to the dimension of $\mathscr{R}$. Thus the particular $k_{\alpha\beta}(T)$ given by (6.23) is of minimum rank.

Let p be the dimension of $\mathscr{R}$. Then $k_{\alpha\beta}(T)$ will have p independent columns. Since $k_{\alpha\beta}(T)=k_{\beta\alpha}(T)$ and $\sum_{\beta=1}^{Q} k_{\alpha\beta}(T)=0$; all α, the number of independent parameters in $k_{\alpha\beta}(T)$, ρ, is given by

$$\begin{aligned}\rho&=(Q-1)+(Q-2)+\cdots+(Q-\beta)\\&=pQ-\frac{p(p+1)}{2}=\frac{p(2Q-p-1)}{2}.\end{aligned} \tag{6.39}$$

The non-uniqueness of $k_{\alpha\beta}(T)$ arises whenever there exists a matrix $m_{\alpha\beta}$, for which

$$\left.\begin{aligned}&\sum_{\beta=1}^{Q} m_{\alpha\beta}=0; &&\text{all } \alpha,\\ &\sum_{\beta=1}^{Q} m_{\alpha\beta}\,\mathbf{q}_{\beta}=\mathbf{0}; &&\text{all } \alpha\end{aligned}\right. \qquad m_{\alpha\beta}=m_{\beta\alpha};\quad \text{all } \alpha,\beta. \tag{6.40}$$

If such a matrix is added to $k_{\alpha\beta}(T)$, the vectors $\mathbf{h}_{\alpha}(T)$ in (6.22) will remain unchanged, and properties (6.24) and (6.25) will be unaffected. Matrices (6.40) will exist whenever there are sequences v_{α}; $\alpha=1,\ldots,Q$, for which

$$\sum_{\alpha=1}^{Q} v_{\alpha}\mathbf{q}_{\alpha}=\mathbf{0} \tag{6.41}$$

i.e., when the vectors $\mathbf{q}_{\alpha}$; $\alpha=1,\ldots,Q$ are not independent. Because the $\mathbf{q}_{\alpha}$ are all equivalent,

$$\sum_{\alpha=1}^{Q} v_{\alpha}\langle\mathbf{q}_{\alpha},\mathbf{v}\rangle=\langle\mathbf{q}_{\alpha},\mathbf{v}\rangle\sum_{\alpha=1}^{Q} v_{\alpha}=0;\qquad \mathbf{v}\in\mathscr{E}. \tag{6.42}$$

Thus v_α also must satisfy

$$\sum_{\alpha=1}^{Q} v_\alpha = 0. \tag{6.43}$$

The number of independent $\boldsymbol{q}_\alpha$ is just $p+1$, where p is the dimension of the $\mathscr{R}$ space, since the $\boldsymbol{q}_\alpha$ must span $\mathscr{R}$ by (6.22), and since they all have the same projection in $\mathscr{E}$ by (6.7). Thus the number of independent sequences v_α; $\alpha = 1, \ldots, Q$ is equal to $Q-p-1$. These form a basis in R^Q for vectors in R^Q whose components, v_α; $\alpha = 1, \ldots, Q$, satisfy (6.41). Let us denote the ith such sequence by $v_{i\alpha}$; $\alpha = 1, \ldots, Q$; $i = 1, \ldots, Q-p-1$. Then, by (6.40), there exists a matrix $t_{\alpha i}$ such that

$$m_{\alpha\beta} = \sum_{i=1}^{Q-p-1} t_{\alpha i} v_{i\beta}; \qquad \alpha, \beta = 1, \ldots, Q. \tag{6.44}$$

But, since $m_{\alpha\beta} = m_{\beta\alpha}$, we may assume that there exists a matrix u_{ij} for which

$$t_{\alpha i} = \sum_{j=1}^{Q-p-1} u_{ij} v_{j\alpha}; \qquad i = 1, \ldots, Q-p-1, \ \alpha = 1, \ldots, Q. \tag{6.45}$$

Thus

$$m_{\alpha\beta} = \sum_{i=1}^{Q-p-1} \sum_{j=1}^{Q-p-1} u_{ij} v_{j\alpha} v_{i\beta}; \qquad \alpha, \beta = 1, \ldots, Q. \tag{6.46}$$

Since $m_{\alpha\beta} = m_{\beta\alpha}$, $u_{ij} = u_{ji}$ and

$$m_{\alpha\beta} = \sum_{i=1}^{Q-p-1} \sum_{j=i}^{Q-p-1} u_{ij} [v_{j\alpha} v_{i\beta} + v_{i\alpha} v_{j\beta}], \tag{6.47}$$

so that the matrices $w_{ij} = [v_{j\alpha} v_{i\beta} + v_{i\alpha} v_{j\beta}]$ form a basis for the matrices $m_{\alpha\beta}$. The number of these is thus $\frac{1}{2}(Q-p-1)(Q-p)$. Thus the matrices $k_{\alpha\beta}(T)$ that all have the same rate expression form a hyperplane of dimension $\frac{1}{2}(Q-p-1)(Q-p)$ in a space of dimension $\frac{1}{2}Q(Q-1)$, whose coordinates are the elements of $k_{\alpha\beta}(T)$ above the diagonal. The degree of freedom of this hyperplane is then

$$\frac{1}{2} Q(Q-1) - \frac{1}{2}(Q-p-1)(Q-p) = \frac{p(2Q-p-1)}{2} = \rho, \tag{6.48}$$

which agrees with (6.39). Thus we see that the number of independent parameters required to specify a mass action reaction rate expression at a given temperature is just ρ. The matrices $k_{\alpha\beta}(T)$ corresponding to a given rate expression fill out, at each temperature, a hyperplane of dimension $\frac{1}{2}Q(Q-1) - \rho$. This may be stated as a theorem:

Theorem 6.10. *Of the variables $k_{\alpha\beta}(T)$ appearing in a kinetically homogeneous rate expression of mass action type, only ρ of those are independent, where*

$$\rho = \frac{p(2Q-p-1)}{2}, \tag{6.49}$$

and where p is the dimension of $\mathscr{R}$, and Q is the number of reactant sets. The matrix $k_{\alpha\beta}(T)$ for a given kinetically homogeneous rate expression is unique if and only if $p = Q-1$.

One question that remains unanswered is under what conditions an expression of pseudo-mass action type will satisfy A′3 of Definition 4.8. It is clear from Theorem 6.7 that the positivity of the off-diagonal elements of $k_{\alpha\beta}$ is a sufficient condition, but it clearly is not necessary in cases where the $k_{\alpha\beta}$ are not unique, since the allowable values of $k_{\alpha\beta}$ fill out a hyperplane in $R^{\frac{Q(Q-1)}{2}}$. In general, there must be a set of ρ linear constraints that the $k_{\alpha\beta}$ must satisfy for a given rate expression to be equivalent to one with all positive off-diagonal $k_{\alpha\beta}$. We have not established, however, that this condition is necessary for A′3 to be satisfied. In order to clarify somewhat the nature of these unanswered questions, and also to illustrate the ideas of this section, we now consider a concrete example.

Suppose that our system contains three species, denoted A, B, and C, and suppose that these undergo all bimolecular isomerization reactions: $A+B\rightarrow A+C$, $A+C\rightarrow C+C$, etc. Then the subspace $\mathcal{E}$ contains only scalar multiples of (1, 1, 1). The quantities $q_{i\alpha}$ defined by (6.13) and $v_{i\alpha}$ defined by (6.41) may be written as follows:

Reactant Set	α	$q_{1\alpha}$	$q_{2\alpha}$	$q_{3\alpha}$	$v_{1\alpha}$	$v_{2\alpha}$	$v_{3\alpha}$
$A+A$	1	2	0	0	1	1	0
$A+B$	2	1	1	0	-2	0	0
$A+C$	3	1	0	1	0	-2	0
$B+B$	4	0	2	0	1	0	1
$B+C$	5	0	1	1	0	0	-2
$C+C$	6	0	0	2	0	1	1

It may be noted that all six $\boldsymbol{q}_\alpha$ are equivalent, so that (6.13) will be kinetically homogeneous. Since in this case, $p=2$ and $Q=6$, the matrix $k_{\alpha\beta}$ will not be unique. In fact,

$$\frac{Q(Q-1)}{2}=15$$

while

$$\rho=\frac{p(2Q-p-1)}{2}=9,$$

so that any set of equivalent $k_{\alpha\beta}$ matrices will fill out a six-dimensional hyperplane in the 15-dimensional space. The basis set of matrices $m_{\alpha\beta}$ for generating this hyperplane can be calculated from the $v_{i\alpha}$ according to (6.47). Thus we let

$$m_{\alpha\beta}^{(ij)}=v_{i\alpha}v_{j\beta}+v_{j\alpha}v_{i\beta} \tag{6.50}$$

with the result

$$m_{\alpha\beta}^{(11)}=\begin{pmatrix} 1 & -2 & 0 & 1 & 0 & 0 \\ -2 & 4 & 0 & -2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -2 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$m_{\alpha\beta}^{(22)}=\begin{pmatrix} 1 & 0 & -2 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -2 & 0 & 4 & 0 & 0 & -2 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & -2 & 0 & 0 & 1 \end{pmatrix},$$

$$m_{\alpha\beta}^{(33)}=\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & -2 & 1 \\ 0 & 0 & 0 & -2 & 4 & -2 \\ 0 & 0 & 0 & 1 & -2 & 1 \end{pmatrix},$$

$$m_{\alpha\beta}^{(12)}=\begin{pmatrix} 2 & -2 & -2 & 1 & 0 & 1 \\ -2 & 0 & 4 & 0 & 0 & -2 \\ -2 & 4 & 0 & -2 & 0 & 0 \\ 1 & 0 & -2 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -2 & 0 & 1 & 0 & 0 \end{pmatrix}, \tag{6.51}$$

$$m_{\alpha\beta}^{(13)}=\begin{pmatrix} 0 & 0 & 0 & 1 & -2 & 1 \\ 0 & 0 & 0 & -2 & 4 & -2 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -2 & 0 & 2 & -2 & 1 \\ -2 & 4 & 0 & -2 & 0 & 0 \\ 1 & -2 & 0 & 1 & 0 & 0 \end{pmatrix},$$

$$m_{\alpha\beta}^{(23)}=\begin{pmatrix} 0 & 0 & 0 & 1 & -2 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2 & 4 & -2 \\ 1 & 0 & -2 & 0 & 0 & 1 \\ -2 & 0 & 4 & 0 & 0 & -2 \\ 1 & 0 & -2 & 1 & -2 & -2 \end{pmatrix},$$

It can be verified easily that the addition of any arbitrary linear combination of the above six matrices to a given $k_{\alpha\beta}$ will not change the value of the reaction rate expression calculated from (6.13), nor will it affect properties (6.14), (6.15), (6.16), or (6.18) (note that $q_\alpha \sim q_\beta$ for all α, β in this case; *i.e.*, the expression (6.13) is kinetically homogeneous). We may readily introduce negative values of $k_{\alpha\beta}$, however, so that (6.17) may be violated without altering the final rate expression, (6.13). In fact, we may introduce zeros into the $k_{\alpha\beta}$ matrix in at least six places in the upper triangle. This has been done in the two examples following:

$$\begin{array}{ccc}
k_{11}+k_{12}+\tfrac{1}{2}(-k_{24}+k_{26}-k_{34}+k_{36}) & 0 & k_{13}-k_{12}+k_{24}-k_{26}+k_{34}-k_{36} \\
0 & k_{22}+k_{12}+k_{24}-k_{26} & k_{23}+k_{12}-k_{24}+k_{26} \\
k_{13}-k_{12}+k_{24}-k_{26}+k_{34}-k_{36} & k_{23}+k_{12}-k_{24}+k_{26} & k_{33}+k_{12}-k_{24}+k_{26}-2k_{34}+2k_{36} \\
k_{14}+\tfrac{1}{2}(k_{24}+k_{34}) & 0 & 0 \\
k_{15}+k_{12}-k_{24}-k_{34} & k_{25}-k_{12}+k_{24}+k_{26} & k_{35}-k_{12}+k_{24}-k_{26}+2k_{34} \\
k_{16}+\tfrac{1}{2}(k_{26}+k_{36}) & 0 & 0
\end{array}$$

$$\begin{array}{ccc}
k_{14}+\tfrac{1}{2}(k_{24}+k_{34}) & k_{15}+k_{12}-k_{24}-k_{34} & k_{16}+\tfrac{1}{2}(k_{26}+k_{36}) \\
0 & k_{25}-k_{12}+k_{24}+k_{26} & 0 \\
0 & k_{35}-k_{12}+k_{24}-k_{26}+2k_{34} & 0 \\
k_{44}+\tfrac{1}{2}(k_{24}+k_{26}-k_{34}+k_{56}) & k_{45}-k_{26}+k_{34}-k_{56} & k_{46}+\tfrac{1}{2}(k_{26}+k_{56}) \\
k_{45}-k_{26}+k_{34}-k_{56} & k_{55}+k_{12}-k_{24}+k_{26}-2k_{34}+2k_{56} & 0 \\
k_{46}+\tfrac{1}{2}(k_{26}+k_{56}) & 0 & k_{66}+\tfrac{1}{2}(k_{36}+k_{56})
\end{array} \tag{6.52}$$

$$\begin{array}{ccc}
k_{11}-k_{14}-k_{16}+\tfrac{1}{2}(k_{25}+k_{35}) & k_{12}+2k_{14}-\tfrac{1}{2}(k_{25}+k_{35}) & k_{13}+2k_{16}-\tfrac{1}{2}(k_{25}+k_{35}) \\
k_{12}+2k_{14}-\tfrac{1}{2}(k_{25}+k_{35}) & k_{22}-4k_{14}+k_{23}+k_{25}+k_{35} & 0 \\
k_{13}+2k_{16}-\tfrac{1}{2}(k_{25}+k_{35}) & 0 & k_{33}-4k_{16}+k_{23}+k_{25}+k_{35} \\
0 & k_{24}+2k_{14}-\tfrac{1}{2}(k_{23}+k_{35}) & k_{34}+\tfrac{1}{2}(k_{23}+k_{35}) \\
k_{15}+\tfrac{1}{2}(k_{25}+k_{35}) & 0 & 0 \\
0 & k_{26}+\tfrac{1}{2}(k_{23}+k_{25}) & k_{36}+2k_{16}-\tfrac{1}{2}(k_{25}+k_{25})
\end{array}$$

$$\begin{array}{ccc}
0 & k_{15}+\tfrac{1}{2}(k_{25}+k_{35}) & 0 \\
k_{24}+2k_{14}-\tfrac{1}{2}(k_{23}+k_{35}) & 0 & k_{26}+\tfrac{1}{2}(k_{23}+k_{25}) \\
k_{34}+\tfrac{1}{2}(k_{23}+k_{35}) & 0 & k_{36}+2k_{16}-\tfrac{1}{2}(k_{23}+k_{25}) \\
k_{44}-k_{14}-k_{46}+\tfrac{1}{2}(k_{23}+k_{35}) & k_{45}+2k_{46}-\tfrac{1}{2}(k_{23}+k_{35}) & 0 \\
k_{45}+2k_{46}-\tfrac{1}{2}(k_{23}+k_{35}) & k_{55}-4k_{46}+k_{23}+k_{25}+k_{35} & k_{56}+2k_{46}-\tfrac{1}{2}(k_{23}+k_{25}) \\
0 & k_{56}+2k_{46}-\tfrac{1}{2}(k_{23}+k_{25}) & k_{66}-k_{16}-k_{46}+\tfrac{1}{2}(k_{23}+k_{25},
\end{array} \tag{6.53}$$

In both (6.52) and (6.53), it is clearly shown that the transformed $k_{\alpha\beta}$ may have negative off-diagonal components, even though the original matrix had only positive off-diagonals. In this particular example, it is a simple matter to test whether a given $k_{\alpha\beta}$ matrix is equivalent to one with non-negative off-diagonal components. Thus we may verify that the following nine linear combinations of elements are invariant over a given hyperplane (*i.e.*, under arbitrary additions of the basis matrices (6.51)):

$$z_1=k_{12}+k_{15}+2k_{14},$$
$$z_2=k_{24}+k_{34}+2k_{14},$$
$$z_3=k_{13}+k_{15}+2k_{16},$$

$$\begin{aligned} z_4&=k_{36}+k_{26}+2k_{16}, \\ z_5&=k_{34}+k_{45}+2k_{46}, \\ z_6&=k_{56}+k_{26}+2k_{46}, \\ z_7&=k_{25}+k_{35}+2k_{15}, \\ z_8&=k_{23}+k_{35}+2k_{34}, \\ z_9&=k_{23}+k_{25}+2k_{26}. \end{aligned} \tag{6.54}$$

It also may be verified that these are independent combinations. Thus a given $k_{\alpha\beta}$ will be equivalent to one with non-negative off-diagonal components if and only if z_1 through z_9 of (6.54) are non-negative. While this condition is clearly sufficient for A′3 to be satisfied, it is not obvious that it is also necessary. We also note that knowledge of z_1 through z_9 is sufficient to determine the entire rate expression. Substituting the given $q_{i\alpha}$ in (6.13), we have

$$\begin{aligned} r_A= & -(k_{12}+k_{13}+2k_{15}+2k_{14}+2k_{16})X_A^2+(k_{12}-k_{24}-k_{25}-k_{26})X_A X_B \\ & +(k_{13}-k_{34}-k_{35}-k_{36})X_A X_C+(k_{24}+k_{34}+2k_{14})X_B^2 \\ & +(k_{25}+k_{35}+2k_{15})X_B X_C+(k_{36}+k_{26}+2k_{16})X_C^2, \\ r_B= & (k_{12}+k_{15}+2k_{14})X_A^2+(k_{24}-k_{12}-k_{23}-k_{26})X_A X_B \\ & +(k_{23}+k_{35}+2k_{34})X_A X_C-(k_{24}+k_{45}+2k_{14}+2k_{34}+2k_{46})X_B^2 \\ & +(k_{45}-k_{56}-k_{35}-k_{15})X_B X_C+(k_{56}+k_{26}+2k_{46})X_C^2, \\ r_C= & (k_{13}+k_{15}+2k_{16})X_A^2+(k_{23}+k_{25}+2k_{26})X_A X_B \\ & +(-k_{13}-k_{23}-k_{34}+k_{36})X_A X_C+(k_{34}+k_{45}+2k_{46})X_B^2 \\ & +(k_{56}-k_{45}-k_{25}-k_{15})X_B X_C-(k_{36}+k_{56}+2k_{16}+2k_{26}+2k_{46})X_C^2 \end{aligned} \tag{6.55}$$

where $x_i=e^{\mu_i/RT}$.

Alternatively, this may be expressed in terms of the z_i of (6.54):

$$\begin{aligned} r_A= & -(z_1+z_3)x_A^2+(z_1-z_2-\tfrac{1}{2}z_7+\tfrac{1}{2}z_8-\tfrac{1}{2}z_9)X_A X_B \\ & +(z_3-z_4-\tfrac{1}{2}z_7-\tfrac{1}{2}z_8+\tfrac{1}{2}z_9)X_A X_C+z_2 x_B^2-z_7 x_B x_C+z_4 x_C^2, \\ r_B= & z_1 x_A^2+(-z_1+z_2+\tfrac{1}{2}z_7-\tfrac{1}{2}z_8-\tfrac{1}{2}z_9)X_A X_B+z_8 x_A x_C-(z_2+z_5)X_B^2, \\ & +(z_5-z_6-\tfrac{1}{2}z_7-\tfrac{1}{2}z_8+\tfrac{1}{2}z_9)X_B X_C+z_6 x_C^2, \\ r_C= & z_3 x_A^2+z_9 x_A x_B+(-z_3+z_4+\tfrac{1}{2}z_7-\tfrac{1}{2}z_8-\tfrac{1}{2}z_9)X_A X_C+z_5 x_B^2 \\ & +(-z_5+z_6-\tfrac{1}{2}z_7+\tfrac{1}{2}z_8-\tfrac{1}{2}z_9)X_B X_C-(z_4+z_6)X_C^2. \end{aligned} \tag{6.56}$$

We now show how the above kinetically homogeneous expression may be decomposed into elementary steps. First, the 3 × 3 matrix $B(T, \mathbf{0})$ is calculated:

$$\begin{aligned} b_{11}&=-(z_1+z_2+z_3+z_4+z_7), \\ b_{12}&=b_{21}=z_1+z_2+\tfrac{1}{2}(z_7+z_8-z_9), \\ b_{13}&=b_{31}=z_3+z_4+\tfrac{1}{2}(z_7-z_8+z_9), \\ b_{22}&=-(z_1+z_2+z_5+z_6+z_8), \\ b_{23}&=b_{32}=z_5+z_6+\tfrac{1}{2}(-z_7+z_8+z_9), \\ b_{33}&=-(z_3+z_4+z_5+z_6+z_9). \end{aligned} \tag{6.57}$$

Then the matrix $s_{\alpha i}$, satisfying

$$h_{i\alpha}=\sum_{k=1}^{N} S_{\alpha k}\, b_{ki}, \tag{6.58}$$

must be found. This can be written

$$\boldsymbol{h}_\alpha = B\boldsymbol{s}_\alpha . \tag{6.59}$$

If we denote the "natural inverse" of B by B^{-1} (see [13]), then

$$\boldsymbol{s}_\alpha = B^{-1}\boldsymbol{h}_\alpha . \tag{6.60}$$

Then, by (6.23),

$$k_{\alpha\beta}=\langle \boldsymbol{h}_\alpha, \boldsymbol{s}_\beta\rangle = \langle \boldsymbol{h}_\alpha, B^{-1}\boldsymbol{h}_\beta\rangle . \tag{6.61}$$

The natural inverse of B is given by

$$B^{-1}=\frac{1}{9(b_{12}b_{13}+b_{12}b_{23}+b_{13}b_{23})} \cdot \begin{pmatrix} -(b_{12}+4b_{23}+b_{13}) & -b_{12}+2b_{23}+2b_{13} & 2b_{12}+2b_{23}-b_{13} \\ -b_{12}+2b_{23}+2b_{13} & -(b_{12}+b_{23}+4b_{13}) & 2b_{12}-b_{23}+2b_{13} \\ 2b_{12}+2b_{23}-b_{13} & 2b_{12}-b_{23}+2b_{13} & -(4b_{12}+b_{23}+b_{13}) \end{pmatrix} \tag{6.62}$$

and, from (6.56), the $\boldsymbol{h}_\alpha$ are given by

α	$h_{1\alpha}$	$h_{2\alpha}$	$h_{3\alpha}$
1	$-(z_1+z_3)$	z_1	z_3
2	$(z_1-z_2-\frac{1}{2}z_7+\frac{1}{2}z_8-\frac{1}{2}z_9)$	$(-z_1+z_2+\frac{1}{2}z_7-\frac{1}{2}z_8-\frac{1}{2}z_9)$	z_9
3	$(z_3-z_4-\frac{1}{2}z_7-\frac{1}{2}z_8+\frac{1}{2}z_9)$	z_8	$(-z_3+z_4+\frac{1}{2}z_7-\frac{1}{2}z_8-\frac{1}{2}z_9)$
4	z_2	$-(z_2+z_5)$	z_5
5	z_7	$(z_5-z_6-\frac{1}{2}z_7-\frac{1}{2}z_8+\frac{1}{2}z_9)$	$(-z_5+z_6-\frac{1}{2}z_7+\frac{1}{2}z_8-\frac{1}{2}z_9)$
6	z_4	z_6	$-(z_4+z_6)$

(6.63)

Substitution of (6.57) into (6.62), and then, substitution of (6.62) and (6.63) into (6.61), yields the $k_{\alpha\beta}$ matrix of minimum rank (which, in this case, is equal to two).

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