KINETICS AND THERMODYNAMICS IN MULTICOMPONENT MIXTURES

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This article reviews the kinetic and thermodynamic behavior of multicomponent mixtures containing a very large number of components. A flurry of activity can be envisaged in recent literature; however, although the needs for lumping in this area have been clearly identified, it is not always easy to catch the links and the relationships among different works. We review various techniques and results showing the logical

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status of the latter and how they can be applied to specific problems. Overall (or global) quantities of interest are identified with reference to industrial problems, and chemical reaction engineering of systems, where one is interested only in the overall kinetics, are presented. Mathematical techniques through which results are obtained can often be cumbersome, and they rely primarily on functional analysis. Such techniques are reviewed in the final section of the article.

I. Introduction

In principle, mixtures containing a very large number of components behave in a way described by the same general laws that regulate the behavior of mixtures containing only a comparatively small number of components. In practice, however, the procedures for the description of the thermodynamic and kinetic behavior of mixtures that are usually adopted for mixtures of a few components rapidly become cumbersome in the extreme as the number of components grows. As a result, alternate procedures have been developed for multicomponent mixtures. Particularly in the field of kinetics, and to a lesser extent in the field of phase equilibria thermodynamics, there has been a flurry of activity in the last several years, which has resulted in a variety of new results. This article attempts to give a reasoned review of the whole area, with particular emphasis on recent developments.

This article is organized as follows. In Section II, we discuss the linear algebra of stoichiometry. Stoichiometry may appear to be a rather trivial subject, but it is in fact far from being so. Thus, it is useful to discuss stoichiometry prior to dealing with the real issues of thermodynamics and kinetics, so that discussion of the latter may be unencumbered by stoichiometric issues. Section III is dedicated to thermodynamics and is divided into three subsections, which deal with phase equilibria, homogeneous chemical equilibria, and heterogeneous chemical equilibria. The first subsection is significantly longer than the other two because of many more recent developments in this area. Section IV is dedicated to kinetics. The first subsection deals with the subject of "lumping": techniques by which a system of order, say, N, can be represented (either exactly or in some well-defined sense of approximation) by a system of order N', with $N' < N$. Again, this subsection, because it deals with a reasonably well-established area, is very concise. The second subsection deals with "overall" kinetics: the kinetic description of some overall quantity of interest (e.g., the total residual sulfur in the hydrodesulfurization of an oil cut) in relation to the underlying true kinetics of individual chemical reactions. Finally, the third subsection is dedicated to the chemical reaction engineering of systems where one is interested only in the overall kinetics.

Section V is dedicated to a few mathematical techniques that are used in the body of the article. We presume the reader has a working knowledge of standard linear algebra, and therefore Section V is restricted to some elementary concepts of functional analysis that are needed.

II. Linear Algebra of Stoichiometry

A. DISCRETE DESCRIPTION

By *discrete description,* we mean a description of multicomponent mixtures where the number of components considered, though possibly very large, is finite. Consider a mixture containing N ($<\infty$) components A_I, $I = 1, 2, \ldots, N$. Given any physical property f of the components (such as concentration and chemical potential), its value for the Ith component is indicated by f_I; the N ordered values of f_I constitute an N-dimensional vector $\mathbf{f}$. The usual scalar product can be defined for vectors $\mathbf{f}$; we introduce the somewhat unusual notation $<\mathbf{f}_1, \mathbf{f}_2>$ for the scalar product, for reasons that soon become apparent (the $<,>$ scalar product is reserved to N-dimensional vectors; we also need vectors of different dimensionality). The notation $<,>$ is also used more generally for sums over the range of the I index.

Although chemistry is usually developed in terms of mole units, we use mass units; in most cases, the choice is a matter of taste, but there are some issues that are best dealt with in mass units. So the fundamental component property is their mass m_I, say, the vector $\mathbf{m}$. Let $\mathbf{I}$ be the N-dimensional vector, all components of which are unity. Then the total mass of our system is $<\mathbf{m}, \mathbf{I}>$, and this is constant in a closed system, even when, due to chemical reactions, the individual masses m_I are not constant.

We now come to stoichiometry. A chemical reaction may be written as

$$\Sigma \sigma_I A_I = 0, \tag{1}$$

where the σ_I's are the mass-based stoichiometric coefficients, taken as positive for the (arbitrarily chosen) products and negative for the reactants; these form a vector $\boldsymbol{\sigma}$.[3] The mass-based stoichiometric coefficients are the ordinary mole-based ones multiplied by the corresponding molecular weights.

The physical meaning of Eq. (1) is as follows. Let q be an arbitrary scalar, and let M_I be the masses of the components in a closed system at some initial condi-

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[3] If one multiplies all the σ_I's by the same nonzero scalar Ω, one is describing of course the same reaction. Equation (1) is invariant under multiplication by Ω. The particular choice $\Omega = -1$ shows that the distinction between reactants and products is arbitrary.

tion (these form a vector **M**). Then the values of **m** at any other time can be expressed as

$$\mathbf{m} = \mathbf{M} + \boldsymbol{\sigma} q; \tag{2}$$

that is, the N-dimensional vector $\mathbf{m} - \mathbf{M}$ is uniquely determined by the scalar q. The latter is called the *extent of the reaction* with respect to **M.**

Now consider the case where there are R independent reactions. We discuss the meaning of *independent* shortly. We use the index J to identify reactions, and sums over the range of the J index, including the scalar product of two R-dimensional vectors, are indicated with $\{,\}$ rather than $<,>$. Each of the reactions is identified by its own set of stoichiometric coefficients, so that we will have an $N \times R$ matrix of stoichiometric coefficients σ_{IJ} [compactly indicated as $\boldsymbol{\sigma}$. In the present interpretation, $\boldsymbol{\sigma}$ in Eq. (2) is an $N \times 1$ matrix]. There are now R extents of reaction, which form an R-dimensional vector **q.** The obvious extension of Eq. (2) is

$$\mathbf{m} = \mathbf{M} + \{\boldsymbol{\sigma},\mathbf{q}\}. \tag{3}$$

The reactions are said to be *independent* if the rank of $\boldsymbol{\sigma}$ is R. This implies that the following equation for the M-dimensional unknown vector $\mathbf{q}^*$ has only the trivial solution $\mathbf{q}^* = \mathbf{0}$:

$$\{\boldsymbol{\sigma},\mathbf{q}^*\} = 0. \tag{4}$$

Equation (4) implies that **q** in Eq. (3) is unique. In fact, suppose there are two **q**'s, $\mathbf{q}_1$ and $\mathbf{q}_2$, resulting in the same $\mathbf{m} - \mathbf{M}$. Equation (3) would imply that $\{\boldsymbol{\sigma},(\mathbf{q}_1 - \mathbf{q}_2)\} = 0$, but this implies that $\mathbf{q}_1 = \mathbf{q}_2$.

Although the given definition of independence of chemical reactions is useful for formal manipulations, it is cumbersome to use when one tries to reduce a set of chemical reactions to an independent one. This is, in fact, achieved very simply by the following procedure. First, write down one of the simplest reactions that comes to mind; say this involves only three components, with nonzero stoichiometric coefficients σ_{11}, σ_{21}, and σ_{31}. These constitute a 3×1 matrix of rank 1 (i.e., of rank equal to the number of reactions written down). Next, write a reaction that involves one and only one new component (component 4 in this example). Because σ_{42} is nonzero, the 4×2 matrix has rank 2, and so on. The procedure is guaranteed to work, and it also shows that R is at most $N - 1$ (the first reaction must include at least two nonzero stoichiometric coefficients).

The procedure just illustrated will be referred to in the following paragraphs as the *constructive* procedure. It would appear at first sight that, if one starts with a 3×1 matrix (as most often will be the case), one always ends up with $R = N - 2$. This, however, is not the case, because, for instance, one could have two entirely disjoint matrices $\boldsymbol{\sigma}_1$ ($N_1 \times R_1$, rank $= R_1$) and $\boldsymbol{\sigma}_2$ ($N_2 \times R_2$, rank $=$

R_2) constituting a global $(N_1 + N_2) \times (R_1 + R_2)$ matrix of rank $R_1 + R_2$. Such entirely disjoint sets of reactions are, however, rather special cases: The difference $N - R$, though certainly not always equal to 2, is invariably a small number.

Substituting the condition of mass conservation in Eq. (3) one obtains

$$<\{\boldsymbol{\sigma},\mathbf{q}\},\mathbf{I}> = \{\mathbf{q},<\boldsymbol{\sigma}^{\mathrm{T}},\mathbf{I}>\} = 0, \tag{5}$$

which must be satisfied for arbitrary **q.** It follows that $<\boldsymbol{\sigma}^{\mathrm{T}},\mathbf{I}> = 0$, that is, that the unit vector **I** lies in the kernel of $\boldsymbol{\sigma}^{\mathrm{T}}$.[4]

Chemistry imposes a stricter constraint than simply conservation of mass: Individual atoms must also be preserved. Let $K = 1, 2, \ldots, P$ be the atomic species present in any one of the components in the system. Let p_{IK} be the grams of atom K per gram of species I; the matrix p_{IK} will be compactly indicated as **p.** Conservation of atoms can be expressed as

$$<\boldsymbol{\sigma}^{\mathrm{T}},\mathbf{p}> = \mathbf{0} \qquad \text{for all J's and all K's.} \tag{6}$$

We use the standard notation for the inner product in the case of P-dimensional vectors, and more generally for sums over the range of K. Let **i** be the P-dimensional vector all components of which are unity. One has $\mathbf{I} = \mathbf{p} \cdot \mathbf{i}$, and hence mass conservation can be written

$$<\boldsymbol{\sigma}^{\mathrm{T}},\mathbf{p} \cdot \mathbf{i}> = \mathbf{i} \cdot < \boldsymbol{\sigma}^{\mathrm{T}},\mathbf{p}> = 0. \tag{7}$$

Equation (6) (permanence of atoms) implies Eq. (7) (conservation of mass), but the converse is not true, because $<\boldsymbol{\sigma}^{\mathrm{T}},\mathbf{p}>$ could simply be orthogonal to **i** for Eq. (7) to be satisfied.

Because the vector **m** is constrained by the mass conservation requirement $<\mathbf{m},\mathbf{I}> = \text{const}$,[5] the space of possible **m** values has $N - 1$ dimensions. If the number of independent chemical reactions, R, is less than $N - 1$, then some vectors **m** are not accessible at some assigned **M;** this, as will be seen, has important consequences in the consideration of heterogeneous chemical equilibria. Now consider the special case where $R = N - 1$, so that indeed all admissible **m**'s are accessible. Because the kernel of $\boldsymbol{\sigma}$ contains only the zero vector, there exists an $M \times N$ matrix **A** such that

$$\mathbf{q} = <\mathbf{A},(\mathbf{m} - \mathbf{M})>. \tag{8}$$

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[4] Should we have chosen to work in the more usual mole units, the vector of molecular weights would have played the role of **I.** This does not imply any substantial difference, since from a formal viewpoint the crucial issue is that N-dimensional vectors with all components being nonnegative lie in the kernel of $\boldsymbol{\sigma}^{\mathrm{T}}$.

[5] Formally, **m** lies on the intersection of the hyperplane $<\mathbf{m},\mathbf{I}> = \text{const}$ with the positive orthant of the N-dimensional components space (Wei, 1962a).

This in turn implies that $\{\mathbf{A}^{\mathrm{T}},\boldsymbol{\sigma}^{\mathrm{T}}\} = \mathbf{1}$, the $N \times N$ unit matrix. Now let $\mathbf{z}$ be *any* N-dimensional vector lying in the kernel of $\boldsymbol{\sigma}^{\mathrm{T}}$. Since $\Omega\mathbf{I}$, with Ω any arbitrary scalar, also lies in that kernel, one can write

$$<\boldsymbol{\sigma}^{\mathrm{T}},(\mathbf{z} - \Omega\mathbf{I})> = \mathbf{0}. \tag{9}$$

It follows that

$$\begin{aligned}\mathbf{0} &= \{\mathbf{A}^{\mathrm{T}},<\boldsymbol{\sigma}^{\mathrm{T}},(\mathbf{z} - \Omega\mathbf{I})>\} = <\{\mathbf{A}^{\mathrm{T}},\boldsymbol{\sigma}^{\mathrm{T}}\}, (\mathbf{z} - \Omega\mathbf{I})> \\ &= \mathbf{z} - \Omega\mathbf{I};\end{aligned} \tag{10}$$

that is, in this case *only* vectors of the type $\Omega\mathbf{I}$ lie in the kernel of $\boldsymbol{\sigma}^{\mathrm{T}}$. This implies that, given P arbitrary scalars Ω_K, $\mathbf{p}$ equals the dyad $\mathbf{I}\boldsymbol{\Omega}$. Say $p_{IK} = \Omega_K$ does not depend on I: It follows that the brute chemical formulas of all species are multiples of each other (the only reactions are isomerization, oligomerizations, or disproportionations). We refer to this special case as a *merization system.* [Note, incidentally, that in a merization system the constructive procedure would need to start with a 2×1 matrix (in mass units, this would of necessity be of the type $1, -1$), which describes a "merization" reaction. Each additional step would also describe a merization reaction. Hence, an alternative, more heuristic proof has been given for the same result.]

Permanence of atoms can also be seen from a different viewpoint. The condition is $<\mathbf{p}^{\mathrm{T}},\mathbf{m}> = <\mathbf{p}^{\mathrm{T}},\mathbf{M}>$. Now $<\mathbf{p}^{\mathrm{T}},\mathbf{M}>$ is a P-dimensional vector $\mathbf{b}$. While the number of components, N, and independent reactions, R, may grow without bounds (and in the next section we illustrate the description where both are allowed to approach infinity), the number of constraints $<\mathbf{p}^{\mathrm{T}},\mathbf{M}>$ is always finite at P. Finally, it is worth pointing out that in a variety of cases one has additional constraints over and above that of permanence of atoms, such as permanence of benzenic rings or other constraints implied by the chemistry of the reactions involved. Apparently, Wei (1962a) was the first one to identify explicitly the possible existence of constraints other than the permanence of atoms; these can always be expressed as permanence of "something," that is, there are quantities that are invariant as the reactions occur.

Given *any* P-dimensional vector $\mathbf{b}$, the N-dimensional vector $\mathbf{p} \cdot \mathbf{b}$ lies in the kernel of $\boldsymbol{\sigma}^{\mathrm{T}}$: $<\boldsymbol{\sigma}^{\mathrm{T}},\mathbf{p} \cdot \mathbf{b}> = <\boldsymbol{\sigma}^{\mathrm{T}},\mathbf{p}> \cdot \mathbf{b} = \mathbf{0}$. This, as will be seen, has important consequences in the theory of equilibrium. It is also important to realize that a description of the stoichiometry in terms of the condition $<\mathbf{p}^{\mathrm{T}},\mathbf{m}> = <\mathbf{p}^{\mathrm{T}},\mathbf{M}>$ is in many senses equivalent to a description in terms of $\boldsymbol{\sigma}$, and in many formal manipulations it may be preferable when the number of species and/or reactions becomes very large, because the dimensions of $<\mathbf{p}^{\mathrm{T}},\mathbf{M}>$ stay at P no matter how complex the mixture may be.

A more generally applicable method based on linear constraints is as follows (we will make use of this method in most of the following sections). The method is due to Krambeck (1970). Let $\mathbf{m}_1$ and $\mathbf{m}_2$ be two compositions that are both accessible from the initial one. The term $\mathbf{m}_1 - \mathbf{m}_2$ can be regarded as a *reaction vector* in the sense that some linear combination of the reactions considered can bring the system from $\mathbf{m}_2$ to $\mathbf{m}_1$. Now consider all N-dimensional vectors $\mathbf{a}_L$, $L = 1, 2, \ldots, C$, such that $<\mathbf{m}, \mathbf{a}_L> = \text{const}$ and such that $<\mathbf{m}_1 - \mathbf{m}_2, \mathbf{a}_L> = 0$. By "all" we mean that the set is complete, in the sense that there are no other vectors to which some possible $\mathbf{m}_1 - \mathbf{m}_2$ is orthogonal. It is easy to convince oneself that $C = N - R$. The total number of constraints C does not coincide with P, as the simple examples in Appendix A show. The value of C is finite even if both N and R approach infinity. The vectors $\mathbf{a}_L$ (which are N-dimensional ones) form the basis of a vector space that is called the *orthogonal complement* of the space of reaction vectors $\mathbf{m}_1 - \mathbf{m}_2$.

Finally, a slightly different formulation of the linear constraints imposed on the reaction pathways, which is deduced directly from the stoichiometric matrix $\boldsymbol{\sigma}$, has been discussed by Slaughter and Doherty (1994). First, one chooses R components (i.e., as many as there are independent reactions), which are called the *reference components* and identified by an R suffix. One obviously has $\mathbf{m}_R = \mathbf{M}_R + \{\boldsymbol{\sigma}_R, \mathbf{q}\}$, where the reduced stoichiometric matrix $\boldsymbol{\sigma}_R$ is $R \times R$, and hence can be invertible. Because Eq. (4) has only a trivial solution, the reference components may indeed be chosen so that $\boldsymbol{\sigma}_R$ is invertible. One thus has

$$\mathbf{m} = \mathbf{M} + <\{\boldsymbol{\sigma}, \boldsymbol{\sigma}_R^{-1}\}^{\mathrm{T}}, (\mathbf{m}_R - \mathbf{M}_R)> \tag{11}$$

which can be rewritten as

$$\mathbf{m} - <\{\boldsymbol{\sigma}, \boldsymbol{\sigma}_R^{-1}\}^{\mathrm{T}}, (\mathbf{m}_R)> = \mathbf{M} - <\{\boldsymbol{\sigma}, \boldsymbol{\sigma}_R^{-1}\}^{\mathrm{T}}, (\mathbf{M}_R)> = \mathbf{m}^{\sim}. \tag{12}$$

It is important to realize that, while $\mathbf{m}^{\sim}$ is, like the vectors $\mathbf{a}_L$, an N-dimensional vector, $N - R$ of its components are zero.

B. CONTINUOUS DESCRIPTION

When the number of components in the mixture becomes very large, a continuous description is in many cases preferable to a discrete one.[6] This is not in any way related to a physically significant difference: In real life, *any* mixture is made up of a finite (if possibly very large) number of components, and hence a continuous description (where the number of components is essentially regarded as infinitely large) is certainly nothing more than a mathematical

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[6] One may choose simply to consider cases, such as discussed in Appendix A, where in a discrete description N approaches infinity; this leads to a countable infinity of components. It turns out that there are very few instances where the distinction between a countable infinity and an R^1 continuum makes any difference.

artifact.[7] The reason for choosing such an artifact is related simply to the fact that the algebra of integrals is easier to work with than that of finite sums. It is also worthwhile to point out that, once the formalism of a continuous description is used to perform actual numerical calculations, the computer code will necessarily transform back integrals to finite sums, so that the distinction, if it has any conceptual meaning at the level of formal manipulations, becomes a very fuzzy one at the level of numerical calculations.[8]

The earliest formulation of a continuous description is probably due to De Donder (1931): His Chapter 3 is titled "Systèmes Renfermant une Infinité de Constituants." It is worthwhile to quote *verbatim* (except for minor differences in notation):

> nous supposerons que la *masse* de chacun de ces constituants est infiniment petite; prise à l'instant t, la masse du constituant d'indice x sera désignée par $dm(x)$, ou x est une variable qui varie d'une manière continue de x_0 à x_1, deux nombres fixes donnés dans chaque système considéré. . . . Cette masse du constituant d'indice x correspond, en réalité, à l'intervalle compris entre x et $x + dx$.

There are a number of conceptual pearls in De Donder's Chapter 3; here we simply want to point out our italics for the word "masse": De Donder, 30 years before anybody else, recognized that, in spite of what permanence of atoms seems to suggest as the simple way of doing things, a description based on mass (which is preserved when chemical reactions occur) is preferable to a description based on moles (which are not preserved).

De Donder's pioneering contribution was acknowledged[9] in what is nowadays commonly regarded as the fundamental work on the continuous description of complex mixtures (Aris and Gavalas, 1966). In hindsight, the continuous description can be seen as nothing more than the extension to an infinite-dimensional

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[7] Aris (1968), who certainly cannot be held responsible for a lack of appreciation of mathematical artifacts, when considering the continuous description of kinetics writes: "At first sight it would seem that there is nothing in chemical kinetics that demands more than a thorough understanding of autonomous systems of nonlinear differential equations, for it could be argued that a continuum of reactions such as we have introduced above is an artificial way of describing a discrete, even if fine-grained, situation. However this might not be so, for from a theoretical point of view one would certainly want to investigate the integro-differential equations that arise in the limit of an infinite number of species, and from a practical standpoint this approach has already proved to be of value."

[8] Except for the fact that the numerical code may choose *pseudo-components* (i.e., ways of discretizing the relevant integrals), which have no direct physical meaning. For instance, if x is taken to be (proportional to) the number of carbon atoms in, say, a mixture of hydrocarbons, the computer code, if cleverly programmed, may well choose to discretize x in such a way that the corresponding number of actual carbon atoms is not an integer (see, e.g., Shibata *et al.*, 1987).

[9] Apparently the Aris and Gavalas paper was written with no knowledge of De Donder's work; the latter is quoted in a footnote with the following wording: "We are indebted to Prof. R. Defay for drawing our attention to this reference. The work reported here had been completed when we learned of De Donder's discussion, but little overlap and no conflict of material is found."

Hilbert space of a finite-dimensional normed vector space discrete description. However, there are a number of cases where the extension to an infinite-dimensional Hilbert space cannot be dealt with in too cavalier a fashion, and these will be discussed as the need arises; at this stage, we simply discuss a few essential points about the mathematical formalism connected with a continuous description.

1. Inner Product and Norm

Let f_1 and f_2 be two properties of the species in the system (there may be concentrations, vapor pressures, etc.). If the number of species is finite, one has two vectors $\mathbf{f}_1$ and $\mathbf{f}_2$ in a finite-dimensional vector space (the number of dimensions being the number of species). The inner product $<\mathbf{f}_1,\mathbf{f}_2>$ is generalized to the inner product $<f_1(y)f_2(y)>$ in the Hilbert space for two infinite-dimensional vectors $f_1(x), f_2(x)$ as follows (y is the label x when intended as a dummy variable; we assume that x has been normalized so as to be dimensionless, see later discussion):

$$<f_1(y)f_2(y)> = \int_{x_0}^{x_1} f_1(y)f_2(y)dy. \tag{13}$$

When the vector $f(y)$ does not contain some delta functions (which is possible), its norm is, trivially, $|f_1(x)| = \sqrt{<f_1(y)f_1(y)>}$.[10]

2. Choice of Label and Normalization

In the discrete description of a mixture of N components, different species are identified by an integer subscript, generally chosen as $1, 2, \ldots, N$. The choice of integer values, and their assignment to individual species, is entirely arbitrary; the only requirement is that the correspondence between indices and species be unequivocal (each index corresponds to only one species, and vice versa). In the continuous description, the *component label* x also has only to satisfy the same requirement. In addition to this, it is generally useful to choose x so that it is dimensionless. For instance, the mass of components with labels between x and $x + dx$ is $m(x)dx$, and unless x is dimensionless $m(x)$ would not have the dimensions of a mass.

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[10] Krambeck (1994b) observes that the scalar product definition should include the number density function $s(x)$, say,

$$<f_1(y)f_2(y)> = \int_{x_2}^{x_1} f_1(y)f_2(y)dy/s(y).$$

This, in addition to other advantages, would guarantee invariance under rescaling of the label x. Equation (13) from this viewpoint, could be regarded as applying to the case where $s(x) = 1$.

Suppose one has started by choosing some label x^*, which, although satisfying the requirement of uniquely identifying components, is not dimensionless.[11] Suppose also that x^* is restricted to some interval x^*_1, x^*_2 other than $0, \infty$. One first renormalizes the label by defining x^{**} as $(x^* - x^*_1)/(x^*_2 - x^*)$, which ranges between 0 and ∞. Furthermore, for any given problem, some externally imposed mass distribution $M(x^{**})$ is generally available. (This may be, for instance, the initial mass distribution in a batch reactor. Sometimes it is preferable to assign an external concentration distribution rather than a mass distribution.) The quantity M is regarded as already normalized with respect to the total mass of the system, so that the zeroth moment of $M(x^{**})$ is unity. The *average* value of x^{**} in the mixture, x_{AVG}, is $<y^{**}M(y^{**})>$. One now defines a dimensionless normalized label x as $x = x^{**}/x_{AVG}$. This, of course, guarantees that the first moment of the $M(x)$ distribution, $<yM(y)>$, is identically unity.

It is also often useful, given some quantity $u(x)$ and some weighting function $h(x)$, to define an *overall*[12] quantity U as the weighted integral of $u(x)$ over the label range $U = <h(y)u(y)>$ and, should $u(x)$ also depend on some other variable τ, $u = u(x, \tau)$, one, of course, has $U(\tau) = <h(y)u(y, \tau)>$. Often we will restrict our attention to the special case where $h(x)$ is identically equal to unity.[13] Finally, for purposes of analysis it is often useful to choose a specific mathematical form for $M(x)$. A powerful form is that of a *gamma distribution,* which contains only one dimensionless parameter, α:

$$M(x) = \phi(\alpha,x) = \alpha^{\alpha}x^{\alpha-1}e^{-\alpha x}/\Gamma(\alpha), \tag{14}$$

which, for any value of α, indeed has the property $<M(y)> = <yM(y)> = 1$. Here, $\phi(\alpha,x)$ is unimodal, but apart from this constraint it is a very powerful distribution: It approaches the single-component distribution $\delta(x - 1)$ when α approaches infinity, the exponential distribution $\exp(-x)$ when $\alpha = 1$, and it is admissible (in the sense that all moments $<y^N\phi(\alpha,y)>$ are finite) for any positive α.

We now move to stoichiometry in infinite-dimensional space. The number of independent chemical reactions can, of course, be infinitely large, and one needs to introduce a *reaction label u* that plays for reactions the same role as the com-

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[11] For instance, if one convinces oneself that the value of some property f (the cases where f is vapor pressure and kinetic constant are discussed later) is all that is needed to characterize components, one could choose f itself as the "initial" label. Of course, f may well be dimensional, and its values may well range in an interval other than $0, \infty$.

[12] The word *lumped* is often used in the literature. However, the word *lumping* has come to mean so many different things that it is perhaps somewhat misleading to use it here. Possibly the first use of the word *overall* in the sense used here is due to Astarita (1989b).

[13] In many real-life problems U is the only quantity accessible to direct measurement and/or the only one of interest. For instance, in a hydrodesulfurization process, $u(x)$ would be the concentration distribution of sulfur-containing species, $h(x)$ the amount of sulfur in species x, and U the total concentration of chemically combined sulfur.

ponent label x plays for components; we use v for the reaction label when it is intended as a dummy variable, and integrals over the range of u will be indicated with curly braces.[14] The mass-based stoichiometric coefficient of component x in reaction u constitutes the stoichiometric distribution $\sigma(x,u)$. The first question to be addressed is this: How does one extend the concept of a set of *independent* reactions? This is answered by requiring that the following equation for the unknown vector $\mathbf{q}^*(u)$ have only the trivial solution $\mathbf{q}^*(u) = 0$:

$$\{\sigma(x,v)\mathbf{q}^*(v)\} = 0; \tag{15}$$

that is, the kernel of $\sigma(x,v)$ contains only the zero vector for all x's.

Now let $m(x)dx$ be the mass of components with label between x and $x + dx$, and let $q(u)$ be the corresponding extent of reaction u with respect to the externally imposed mass distribution $M(x)$. One has, as an obvious extension of Eq. (3),

$$m(x) = M(x) + \{\sigma(x,v)q(v)\} \tag{16}$$

and, if the reactions $\sigma(x,u)$ are independent, two different $q(u)$ cannot result in the same $m(x)$.

Now let $I(x)$ be the function that has values of unity for all x's. The total mass of the system (which does not change as chemical reactions occur) is $<m(y)I(y)>$. It follows that $<\{\sigma(y,v)q(v)\}I(y)> = 0$, and by inverting the order of integration that $\{q(v)<\sigma(y,v)I(y)>\} = 0$. Because the latter must be satisfied for arbitrary $q(u)$, it follows that $<\sigma(y,u)I(y)> = 0$; that is, that the kernel of $\sigma(y,u)$ for all u's contains at least nontrivial vectors of the form $\mathbf{\Omega} I(x)$, with $\mathbf{\Omega}$ any arbitrary scalar. [The kernel of $\sigma(y,u)$ plays a crucial role. Indeed, we will see that at equilibrium points the chemical potential vector is restricted to lie in it.]

Equation (16) shows that, given $q(u)$, one can calculate $m(x) - M(x)$. Two possibilities arise:

1. There are some distributions $m(x) - M(x)$ that are not delivered by *any* $q(u)$.
2. All admissible $m(x) - M(x)$ are delivered by some $q(u)$.

Consider the second possibility first. Since the kernel of $\sigma(x,v)$ contains only the zero vector, two different $q(u)$ cannot deliver the same $m(x)$; it follows that there exists a distribution $A(u,x)$ such that

$$q(u) = <A(u,y)[m(y) - M(y)]>, \tag{17}$$

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[14] Of course, curly braces will also identify an inner product and a norm in the infinite-dimensional Hilbert space of reactions. While the latter is infinite dimensional just the same as the space of components, one should be careful in generalizing results from finite-dimensional vector spaces, as the discussion in the following shows for some simple problems.

which in turn implies that $\{A(v,x)\sigma(x,v)\} = \delta(x)$. Let $\mathbf{z}(x)$ be any vector lying in the kernel of $\sigma(y,u)$. Since vectors $\mathbf{\Omega}I(x)$ are guaranteed to lie in the same kernel, $<\sigma(y,u)[\mathbf{z}(y) - \mathbf{\Omega}I(y)]> = 0$. It follows that

$$\begin{aligned} 0 &= \{A(v,y)<\sigma(y,v)[\mathbf{z}(y) - \mathbf{\Omega}I(y)]>\} \\ &= <\delta(y)[\mathbf{z}(y) - \mathbf{\Omega}I(y)]> \\ &= \mathbf{z}(y) - \mathbf{\Omega}I(y). \end{aligned} \tag{18}$$

Hence in case 2 *only* vectors of type $\mathbf{\Omega}I(x)$ lie in the kernel of $\sigma(y,u)$. Now consider the requirement of permanence of atoms. Let $\mathbf{p}(x)$ be the P-dimensional vector the components of which are the gramatoms of the atoms 1, 2, . . ., P per gram of component x present in species x. Permanence of atoms implies that $<\sigma(y,u)\mathbf{p}(y)> = 0$, that is, that all components of $\mathbf{p}(x)$ lie in the kernel of $\sigma(y,u)$. It follows that, in case 2, the brute chemical formulas of all components are multiples of each other [each component $p_i(x)$ of $\mathbf{p}(x)$ has the form $\mathbf{\Omega}_i I(x)$]. Case 2 is an infinite-dimensional merization system. One may notice that the proof of this result[15] represents the extension to the infinite-dimensional case of the proof given in the previous section for the case of a finite-dimensional space.

Let $\mathbf{i}$ be the P-dimensional vector with all components equal to unity, so that $I(x) = \mathbf{i} \cdot p(x)$. It follows that conservation of mass implies that $\mathbf{i} \cdot <\sigma(y,u)\mathbf{p}(u)> = 0$, a condition which the permanence of atoms $<\sigma(y,u)\mathbf{p}(y)> = 0$ certainly implies. However, the converse is not true, because conservation of mass could be guaranteed by a nonzero $<\sigma(y,u)\mathbf{p}(y)>$ provided it is orthogonal to $\mathbf{i}$. Permanence of atoms implies that $<\mathbf{p}(y)m(y)> = <\mathbf{p}(y)M(y)> = \mathbf{b}$, where $\mathbf{b}$ is a P-dimensional vector. Hence this type of constraint remains a finite-dimensional one even in the continuous description. However, when contrasted with Eq. (16), the constraint $<\mathbf{p}(y)m(y)> = \mathbf{b}$ does not yield $m(y)$ explicitly—there are, in fact, an infinite number of $m(y)$ that satisfy the constraint.

Finally, the orthogonal complement method can be extended to the continuous description. The reaction vectors are $m_1(x) - m_2(x) = \{\sigma(x,v)[q_1(v) - q_2(v)]\}$. The set of basis vectors of the orthogonal complement, $a_L(x)$, $L = 1, 2, \ldots, C$, compactly indicated as $a(x)$, is all those vectors to which all possible reaction vectors are orthogonal:

$$<\mathbf{a}(y)\{\sigma(y,v)[q_1(v) - q_2(v)]\}> = 0, \tag{19}$$

or, exchanging the order of integration,

$$\{[q_1(v) - q_2(v)]<\mathbf{a}(y)\sigma(y,v)>\} = 0. \tag{20}$$

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[15] The result is due to Astarita and Ocone (1989), and it generalizes an earlier result for discrete mixtures due to Astarita (1976). The result is relevant for the discussion of the Wei and Prater (1962) paper and of the ample subsequent literature that refers back to the Wei and Prater paper.

Equation (20) must be satisfied for all possible reaction vectors; hence, $<\mathbf{a}(y)\sigma(y,v)> = 0$. Now, given any C-dimensional vector $\mathbf{B}$, the distribution $\mathbf{a}(x) \cdot \mathbf{B}$ is orthogonal to $\sigma(y,u)$: $<\sigma(y,u)\mathbf{a}(y) \cdot \mathbf{B}> = <\sigma(y,u)\mathbf{a}(y)> \cdot \mathbf{B} = 0$. Since the set $\mathbf{a}(x)$ is complete, *only* distributions expressible as $\mathbf{p}(x) \cdot \mathbf{B}$ are orthogonal to $\sigma(y,u)$. Now suppose that, from some independent argument, one has ascertained that some distribution $s(x)$, otherwise unknown, is orthogonal to $\sigma(y,u)$; we will see that, under appropriate qualifying conditions, the equilibrium distribution of chemical potentials, $\mu(x)$, falls into this category. Then there must exist a C-dimensional vector $\mathbf{B}$ such that $s(x) = \mathbf{a}(x) \cdot \mathbf{B}$. Thus the search for an unknown function $s(x)$ (an infinite-dimensional vector) is reduced to the search for a C-dimensional vector.

C. LUMPING AND OVERALL DESCRIPTIONS

As discussed in an earlier footnote, the word *lumping* has come to mean a number of different things. In this article, we use this word with a very restricted meaning: *Lumping* means the attempt to describe a finite-dimensional system (i.e., one described in a discrete way) of dimensions, say, N, by a lower order system of dimensions N^*: Several groups of components (and/or of other quantities such as reactions) are "lumped" into single *pseudocomponents* (or *pseudoreactions*). The lower order system is to be either an *exact* equivalent of the original system or at least, in some sense to be made precise, an *approximate* equivalent of it.

Lumping of a discrete system into a lower order one is discussed, for the case of kinetics, in Section IV, A. In that section we also show that it is possible to lump a continuous system into a finite-order one. The important point is that, in dealing with discrete systems with large (or countably infinite) numbers of components, or with continuous systems, it is very useful to reduce the dimensionality of the composition description for practical calculations. For example, one could consider a subset of similar compounds, such as stereoisomers, to be a single compound, or "lump," with the properties of the racemic mixture. More generally, we can project the composition vector onto a lower dimensional subspace that is not simply a partitioning of the compounds into subsets. One could also reduce dimensionality by some nonlinear parameterization rather than by linear projection, but we do not consider that case here.

An entirely different meaning is assigned in the following to the word *overall*. When we use that word we mean that one is not interested in the fine-grained structure of the system, but only in some gross overall property—such as the total concentration of all species of a certain type. Problems of "overall" behavior may, in principle, be discussed on the basis of both a continuous and a discrete de-

TABLE I
SUMMARY OF NOTATION

	Components	Reactions	Atoms	Constraints
Index (discrete)	I	J	K	L
Label (continuous)	x	u		
Dummy label	y	v		
Dummy label (in functionals)	z	w		
Total number	N (discrete)	R (discrete)	P	C
Sum on index (integral on label)	$<,>$	$\{,\}$	$\cdot$	Σ
Unit vector	$\mathbf{I}$	$\mathbf{i}$		
Matrix		σ_{IJ}	p_{IK}	

scription, but it turns out that they are often more easy to deal with in the continuous description. This has, unfortunately, led to a nested couple of misunderstandings in the literature. First, the terms *lumping* and *overall* have been used as if they were interchangeable, which they are not. Second, *lumping* has been associated (somewhat loosely) with discrete, and *overall* with continuous. In fact, both types of problems (lumping and overall) can be described with both (discrete and continuous) formalisms, and the choice of the formalism is often largely a matter of taste. When it is not a matter of choice, the decision is dictated by the specific problem being considered.

The idea of overall kinetics could be regarded as just an extreme case of lumping where the projection is onto a one-dimensional subspace, such as the unit vector. In this case the overall lump is just the total mass of the system or of some subset of the compounds. However, overall kinetics (and/or thermodynamics) are in no way exact or approximate lumping procedures, since the "lump" may well behave in a way that is totally different from that of the original system.

Be that as it may, in either case (lumping or overall) the procedure can be followed regardless of whether the system is discrete or continuous. Lumping a continuous system onto a finite dimensional subspace can give good approximations or even be exact in some cases. Our notation is summarized in Table I.

III. Thermodynamics

A. PHASE EQUILIBRIA

We assume the reader is familiar with the theory of phase equilibria in mixtures containing a few components. As the number of components increases, one again reaches a point where a continuous description might be preferable. It is relatively straightforward to extend the classical theory to a continuous description, as seen later. However, a number of somewhat unexpected problems arise both in the solution of actual phase equilibrium problems and in a purely conceptual sense. These problems are discussed in some detail.

1. Convexity

We begin with what is logically the first problem to be analyzed, that is, the question of whether a system of assigned average composition will in fact, at equilibrium, exist as a single phase, or whether phase splitting will in fact occur. This problem is a well-known one for a two-component mixture, which may phase split if there is a spinodal region. In the simple two-component case, the analysis is restricted to the curvature of the Gibbs free energy curve. More generally, the problem is related to the convexity of the free energy hypersurface. The analysis presented here is based on work by Astarita and Ocone (1989).

Consider a system where some mole fraction distribution $X^F(x)$ is assigned, with $<X^F(y)> = 1$. Suppose the system exists in a one-phase condition at some pressure p and temperature T. One can define a (Gibbs) free energy of mixing per mole, G^{MIX}, which is the difference between the actual free energy of the one-phase mixture and what one would calculate by linearly adding the free energies of the pure components, each multiplied by the corresponding mole fraction. In an ideal solution, $G^{MIX} = G^{ID}$, where (some subtlety is involved with the following equation that is discussed in the appendix to this section)

$$G^{ID} = RT<X^F(y) \ln[X^F(y)]> < 0. \tag{21}$$

In a nonideal solution, $G^{MIX} = G^{ID} + G^{EX}$, where the excess free energy of mixing G^{EX} at any given temperature and pressure depends on the composition. Say its value is given by a functional $\mathbf{G}[\ ]$ of $X^F(y)$, which also depends parametrically on p and T:

$$G^{EX} = \mathbf{G}[X^F(z); p, \mathrm{T}] \tag{22}$$

and, correspondingly,

$$G^{MIX} = G^{ID} + G^{EX} = \mathbf{G}^*[X^F(z); p, t]. \tag{23}$$

Now suppose the system in fact exists as N separate phases, with $K = 1, 2, \ldots,$ N the phase index; let α_K be the number of moles of phase K per mole of the system. The α_K's must satisfy the mass balance condition

$$\Sigma\alpha_K = 1. \tag{24}$$

Let $X^K(x)$ be the mole fraction distribution in phase K. The X^K's must satisfy the mass balance condition

$$\Sigma\alpha_K X^K(x) = X^F(x). \tag{25}$$

In the multiphase condition, the total free energy of mixing per mole of system is

$$\Sigma\alpha_K \mathbf{G}^*[X^K(z); p,T]; \tag{26}$$

should the system exist as a single phase, it would be:

$$\mathbf{G}^*[X^{\mathrm{F}}(z); p,T]. \tag{27}$$

It follows that the system will in fact exist as a single phase if, for *any* choice of the scalars α_K and the distributions $X^K(x)$ satisfying Eqs. (24) and (25), one has

$$\mathbf{G}^*[X^F(z); p,T] < \Sigma\alpha_K \mathbf{G}^*[X^K(z); p,T]. \tag{28}$$

When Eq. (28) is satisfied at some given $X^{\mathrm{F}}(x)$, the functional **G***[ ] is said to be *globally convex* at that composition. If **G***[ ] is globally convex at *all* possible compositions, it is said to be *unconditionally convex.* Clearly, if **G***[ ] is unconditionally convex, the system will exist in a one-phase condition at all possible compositions, and the theory of homogeneous chemical equilibria discussed in the next section applies. In particular, if no phase splitting is possible, the functional giving the chemical potentials as depending on composition is invertible: There cannot be two (or more) different compositions corresponding to the same chemical potential distributions, since these would correspond to two (or more) different phases in equilibrium with each other.

If, at some given composition $X^{\mathrm{F}}(x)$, **G***[ ] is not globally convex, then there is at least one combination of more than one phase satisfying the mass balance constraints [Eqs. (24) and (25)] that corresponds to a smaller free energy than the one-phase condition. This means that the one-phase condition is unstable to *large* composition perturbations—there is no requirement that the $X^K(x)$'s of the equilibrium phases should be "close" to $X^{\mathrm{F}}(x)$. Physically, that means that phase splitting may need to occur by *nucleation.* It is therefore of interest to consider infinitesimal stability of the one-phase condition. Again, we consider several phases in amounts satisfying Eq. (24), but we now require all of them to have *almost* the same composition as the average $X^{\mathrm{F}}(x)$. Thus, we write

$$X^K(x) = X^{\mathrm{F}}(x) + \delta X^K(x) \tag{29}$$

with the $\delta X^K(x)$'s satisfying the following mass balance constraint:

$$\Sigma\alpha_{\mathrm{K}}\delta \mathrm{X}^{\mathrm{K}}(\mathrm{x}) = 0. \tag{30}$$

The free energy of mixing per mole of each phase is now that of the feed mixture plus the deviation $<\mu(y)\delta X^K(y)>$, and hence the condition of infinitesimal stability is

$$\Sigma\alpha_{K<}\mu(y)\delta X^K(y)> > 0. \tag{31}$$

The functional **G***[ ] is said to be *locally convex* at $X^{\mathrm{F}}(x)$ if Eq. (31) is satisfied. If **G***[ ] is locally convex everywhere, it is also unconditionally convex. The set of compositions at which **G***[ ] is not locally convex is called the *spinodal set.* (The reader should check that this definition is the obvious extension of the definition of a spinodal region in, say, a two-component mixture.)

It is important to realize that the convexity conditions only refer to the free energy of mixing. The actual free energy of the mixture equals the free energy of mixing plus the linearly additive term $<G^0(y)X^F(y)>$, where $G^0(x)$ is the pure-component free energy of component x. The term does not contribute anything to the properties of convexity, since $<G^0(y)X^F(y)>$ is neither convex nor concave.

Equation (21) shows that G^{ID} is unconditionally convex. It also shows that in the neighborhood of the "corner" compositions $X^F(x) = \delta(x - x^*)$ (i.e., very dilute solutions in a "solvent" x^*), the local convexity of G^{ID} is in fact infinitely large. It follows that in such neighborhoods also **G***[ ] is globally convex—the spinodal region cannot reach the corners (which is another way of saying that solubility can never be exactly zero). Now if a spinodal set exists, where **G***[ ] is locally not convex (and hence also globally not convex), it seems reasonable that a set of compositions should exist that is, in a vague sense, "between" the corners and the spinodal set, which are locally convex but are not globally convex. That set of compositions is called the *metastable set.*

A feed composition in the metastable set is stable to infinitesimal composition disturbances but is unstable to finite ones; hence, for such a composition phase splitting can only occur by nucleation, and not simply by Brownian motion (which, at most, supposedly results in infinitesimal composition disturbances). Hence, a metastable composition may be observed as a one-phase system in the laboratory: Superheated liquids and subcooled vapors are elementary one-component examples. In contrast with this, one-phase spinodal compositions, by virtue of being unstable to infinitesimal perturbations, will never be observed in the laboratory.

2. *Raoult's Law*

We begin the analysis of phase equilibria (for those cases where phase splitting does in fact occur) with the simplest possible case, that of vapor–liquid equilibrium where both the liquid and the vapor phase are ideal, so that Raoult's law applies (Astarita, 1989; Bowman, 1949; Edminster, 1955). In this case the only parameter that completely characterizes every individual component is its vapor pressure b at the temperature considered; hence, one begins by using b itself as the (dimensional) component label. Let $X^L(b)$ and $X^V(b)$ be the mole fraction distributions in the liquid and vapor phases, respectively, and let p be the total pressure. Obviously, the zeroth moments of both distributions are unity. The continuous form of Raoult's law is:

$$pX^V(b) = bX^L(b). \tag{32}$$

It follows, trivially, that, provided vapor–liquid equilibrium is indeed possible at the assigned values of temperature and pressure, pressure p is the first moment of the liquid-phase mole fraction distribution. It is therefore natural to define the dimensionless label x as b/p, that is, as the ratio of the vapor pressure to the total pressure. This now requires the first moment of $X^L(x)$ to be unity, $<yX^L(y)> = 1$. Raoult's law takes the form

$$X^V(x) = xX^L(x). \tag{33}$$

As simple as these equations are, they result in some unexpected problems. Consider first the case where $X^L(b)$ is assigned. The practical problem becomes the determination of the bubble point at some given temperature. The pressure corresponding to the bubble point is $<bX^L(b)>$—that part is easy. One can now renormalize to $x = b/p$, and use Eq. (33) to calculate the vapor phase composition $X^V(x)$. Notice, however, that $X^V(x)$ will not have the same functional form as $X^L(x)$; while the latter has a first moment equal to unity, $<yX^L(y)> = 1$, the former has (-1)th moment equal to unity, $<X^V(y)/y> = 1$. If, for instance, one uses a gamma distribution, $X^L(x) = \phi(\alpha,x)$, $X^V(x)$ will not be given by a gamma distribution.

Now consider the converse case where $X^V(b)$ is assigned. The practical problem here is the determination of the dew point at some assigned temperature. The dew point pressure is now $p = 1/<X^V(b)/b>$. Renormalizing the label as $x = b/p$, one can use Eq. (33) to calculate $X^L(x)$, but this will not have the same functional form as $X^V(x)$. If one insists that the liquid phase mole fraction distribution should be given by a gamma distribution $\phi(\alpha,x)$, one needs to assign $X^V(x)$ as a modified gamma distribution $\Phi(\alpha,x)$:

$$\Phi(\alpha,x) = x\phi(\alpha,x). \tag{34}$$

Notice that the (-1)th moment of $\Phi(\alpha,x)$ is unity, but its first moment is not. Also, $\Phi(\alpha,x)$ is legitimate for $\alpha > 0$, just as $\phi(\alpha,x)$ and hence $\Phi(\alpha,0) = 0$ whatever the value of α: There cannot be a finite mole fraction of components with vanishingly small vapor pressure in the vapor phase. [In fact, $\phi(\alpha,x)$ as a mole fraction distribution is legitimate only for $\alpha \gtrsim 1$; see Appendix B to this section. The argument above holds *a fortiori*.]

The dew point and bubble point calculations do not present peculiar problems, but the flash calculation does. Let $X^F(x)$ be the mole fraction distribution in the feed to a flash, and let α be the vapor phase fraction in the flashed system. The mass balance is:

$$X^F(x) = \alpha X^V(x) + (1 - \alpha)X^L(x), \tag{35}$$

which is of course a special case of Eq. (25).

If the assigned pressure, p, satisfies $p < 1/<X^F(b)/b>$, the flashed condition will be all vapor; if it satisfies $p > <bX^F(b)>$, it will be all liquid. A nontrivial flash problem arises when $<bX^{\mathrm{F}}(b)> \geq p \geq 1/<X^{\mathrm{F}}(b)/b>$. The borderline cases $<bX^{\mathrm{F}}(b)> = p$ and $1/<X^{\mathrm{F}}(b)/b> = p$ give rise to the bubble point and dew point calculations ($\alpha = 1$ and $\alpha = 0$), respectively. We are not interested in the case of $0 < \alpha < 1$.

One could still, of course, insist that $X^{\mathrm{L}}(x)$ be a gamma distribution $\phi(\alpha,x)$ and, correspondingly, that $X^{\mathrm{V}}(x) = \Phi(\alpha,x)$. However, with any nontrivial value of α, the corresponding $X^{\mathrm{F}}(x)$ could not be either a gamma or a modified gamma distribution, but only a linear combination of those. *It is the mass balance condition in Eq. (24) that causes the problem* (Luks *et al.*, 1990; Sandler and Libby 1991; Shibata *et al.*, 1987).

It is often useful to define a partition coefficient $K(x)$ as follows:

$$K(x) = X^{\mathrm{V}}(x)/X^{\mathrm{L}}(x). \tag{36}$$

In the case where Raoult's law applies, and x has been normalized as b/p, the partition coefficient $K(x)$ is simply x [see Eq. (33): more generally, $K(x)$ depends only on x and is made equal to it by renormalization]. However, as seen later, in general $K(x)$—whatever the dimensionless label x may be—depends on the whole mole fraction distribution in either phase.

3. *Nonideal Liquid Solutions*

If the liquid phase is not an ideal solution, one cannot use b/p as the dimensionless label, since there might very well be more than one component endowed with the same vapor pressure but otherwise behaving differently from the viewpoint of phase equilibrium. Let x be an appropriate dimensionless label (in the sense that no two components with the same x behave differently in any significant way). One may define the *activity coefficient* of component x in the liquid phase, $\tau(x)$, as follows. Let $\mu(x)$ be the chemical potential of component x (which, at equilibrium, is the same in the liquid and vapor phases). Then

$$\mu(x) = RT \ln[X^{\mathrm{L}}(x)\tau(x)]. \tag{37}$$

Now, if the vapor phase is an ideal gas, the equilibrium equation becomes

$$pX^{\mathrm{V}}(x) = b(x)\tau(x)X^{\mathrm{L}}(x) \tag{38}$$

so that $p = <b(y)\tau(y)X^{\mathrm{L}}(y)>$, that is, the equilibrium pressure is *not* (proportional to) the first moment of $X^{\mathrm{L}}(x)$. It is clear that the problems discussed in the previous section become even more severe.

The flash problem is of course still subject to the mass balance condition in Eq. (35). The bubble point pressure ($\alpha = 0$) is $<b(y)\tau(y)X^{\mathrm{F}}(y)>$, and this is relatively easy to calculate because the activity coefficients $\tau(x)$ are those at the feed composition $X^{\mathrm{F}}(x)$ and they are at worst very weak functions of pressure. The situation is different for the dew point pressure ($\alpha = 1$), which is $1/<X^{\mathrm{F}}(y)/\tau(y)b(y)>$.

The activity coefficients are those at the liquid composition, which needs to be calculated from Eq. (38) with $pX^{\mathrm{F}}(x)$ on the left side.

In principle, in addition to the dew point and bubble point cases, there may be another case where the composition of at least one of the two phases is known: the case where $X^{\mathrm{F}}(x)$ is an *azeotropic* composition, so that Eq. (35) is trivially satisfied with $X^{\mathrm{F}}(x) = X^{\mathrm{V}}(x) = X^{\mathrm{L}}(x)$. Equation (38) shows that, at an azeotropic composition, $b(x)\tau(x) = p$ is a constant (it has the same value at all x's). Because $\tau(x)$ depends on the liquid phase mole fraction distribution $X^{\mathrm{L}}(x)$, there may well be one particular composition at which this rather stringent condition is satisfied.

One could still *define* a partition coefficient $K(x)$ as $X^{\mathrm{V}}(x)/X^{\mathrm{L}}(x)$; however, Eq. (38) shows that $K(x)$ depends on the whole liquid phase mole fraction distribution, as does $\tau(x)$. Even more generally, if one relaxes the condition that the vapor phase should be ideal [so that fugacity coefficients would appear on the left side of Eq. (38)] or if one considers any two-phase system (for instance, a liquid–liquid system where nonunity activity coefficients would need to be considered for both phases), $K(x)$ would depend on both distributions. Say its value is delivered by the following functional:

$$K(x) = \mathbf{K}[X^{\mathrm{V}}(z), X^{\mathrm{L}}(z); x, p, T]. \tag{39}$$

This formulation, while of absolutely general validity, is so complicated that approximate methods of solution of phase equilibrium problems have to be developed. A few essential aspects of these approximate methods are discussed in the next subsection.

4. *Approximate Methods*

Cotterman and Prausnitz (1991) have reviewed the approximate methods that have been used in the solution of phase equilibrium problems within the framework of a continuous description (or, often, a semicontinuous one, where a few components are dealt with as discrete ones). These methods are based on relatively trivial extensions of classical methods (which make use of Gibbs free energy equations, equations of state, and the like) to a continuous description.

Two approximation methods are, however, peculiar to the continuous description: the so-called *method of moments,* and the *quadrature method.* Some basic conceptual issues about these two methods are discussed next.

In the method of moments (Cotterman *et al.,* 1985; Luks *et al.,* 1990), as applied for example to a flash calculation, a functional form for $X^{\mathrm{V}}(x)$ and $X^{\mathrm{L}}(x)$ is assumed. This will in general contain one or more parameters. One then writes an appropriate model for the chemical potentials in the two phases, and one calculates the values of the parameters by requiring higher and higher moments of the distributions to match the equilibrium condition (equality of chemical potentials in the two phases).

The problem with this method is that, as discussed in Section III,B,2, the functional form of the distributions in the two phases will be different, and both will in general be different from the functional form for the feed (except in the dew point and bubble point limits, where one of the two distributions, but not the other one, will be of the same functional form and, in fact, equal to the distribution in the feed). Hence in this classical formulation the method of moments produces what has been called the *conservation of mass problem* (Luks *et al.,* 1990): the mass balance equation, Eq. (35), can be satisfied only approximately.

The difficulty illustrated above has been discussed by Sandler and Libby (1991), who propose an alternate procedure for the method of moments as applied to a flash calculation. First, one chooses a functional form for one of the two distributions, with which one to choose being suggested by the particular problem one is trying to address. Next, one uses the mass balance condition, Eq. (35), to calculate the functional form for the mole fraction distribution in the other phase. The method of moments (or other solution procedures) can then be used to determine the parameters from the equilibrium condition. Following this procedure, no mass conservation problem arises.

The quadrature method is based on the following approach (Shibata *et al.,* 1987). Given a mixture with N components, where N is a fairly large number, one may want to describe it as mixture with N' ($<N$) pseudocomponents where N' is some manageably small number, and where one hopes that the description in terms of the pseudocomponents reproduces to within some acceptable degree of approximation the behavior of the real mixture. This is easily recognized as a problem of approximate lumping, and the question that arises is the following one: Given that one has decided what N' might be, how does one choose the pseudocomponents so that the level of approximation of the lumping scheme is as good as can be achieved?

The answer to this question is in fact made easier if one allows N to approach infinity, and therefore one works with a continuous description. One sets up the continuous formulation of the phase equilibrium problem, which will certainly contain (weighted) integrals of the relevant distribution functions. These integrals must be represented by the sum of N' terms, which reduces to a quadrature problem: Given an integral over x that has to be represented by a sum of N' terms, how do we choose the best N' values of x so that a discrete quadrature [say $<f(y)>$ is approximated with $\Sigma W_K f(x_K)$, with W_K the appropriate weighting constants, and the sum being intended for $K = 1, 2, \ldots, N'$] approximates as well as possible the value of the integral?

Formulated in this way, the problem reduces to one originally considered by Gauss (see, e.g., Stroud and Secrest, 1966). Shibata *et al.* (1987) review and extend methods for doing that. The important point is that theorems are available that can be used to determine the best quadrature points and the corresponding weighting constants, while in the case of a discrete description the choice of pseudocomponents is mostly a guessing game. There are, however, two prices to be paid when choosing this approach.

First, pseudocomponents determined by the quadrature method may well be unrealistic ones; for instance, if the label x is (proportional to) the number of carbon atoms, pseudocomponents may well correspond to noninteger x_K values. This may be aesthetically unpleasant, but it does not represent a real problem. More seriously, the appropriate pseudocomponents obviously depend on the composition and, hence, in a repeated calculation such as is required in a distillation tower, pseudocomponents will need to be different at each step. This puts out of tilt the mass balance equations that are coupled to the equilibrium ones, and, even if this problem could be circumvented (as, at least in principle, it can), the procedure would certainly not be applicable to existing software for distillation column calculations.

B. HOMOGENEOUS CHEMICAL EQUILIBRIA

In this section, we discuss the general problem of chemical equilibrium under the assumption that the system considered is guaranteed to exist in a one-phase (homogeneous) condition at all possible compositions. We initially follow the logical approach discussed in Chapter 3 of Astarita (1989a), and we are therefore very concise in the first subsection, referring the reader to that work for details.

1. The Classical Theory

We begin by analyzing the discrete case, where the mass vector at time t, $\mathbf{m}(t)$, is given by Eq. (3), which is rewritten here:

$$\mathbf{m}(t) = \mathbf{M} + \{\sigma, \mathbf{q}(t)\}. \tag{40}$$

This implies that all quantities (such as pressure, and free energy) which are functions of composition (i.e., of $\mathbf{m}$), can in fact be regarded as functions of $\mathbf{q}$. In particular, pressure p depends in principle on volume, temperature, and composition. We can write

$$p = f(V, T, \mathbf{q}). \tag{41}$$

Since the system is homogeneous, the function $f(\ )$ is invertible for volume. (This is not true for systems that may split into two or more phases. For instance, H_2O at 100°C and 1 atm may have, at equilibrium, any volume between that of the liquid and that of steam.) This in turn implies that the state of the system, which in principle is the set V, T, $\mathbf{q}$, may also be taken to be p, T, $\mathbf{q}$. The latter is more generally useful, and the following discussion is based on that choice. Partial derivatives are indicated as δ/δ, with the understanding that the independent variables are indeed p, T, and q.

In particular, the partial derivative of the Gibbs free energy G with respect to the vector of extents of reaction $\mathbf{q}$ is called the affinity, $\boldsymbol{\theta}$:

$$\boldsymbol{\theta} = \delta \mathrm{G}/\delta \mathbf{q}. \tag{42}$$

As the chemical reactions proceed, $\mathbf{q}$ changes in time; its rate of change is called the *rate of reaction* vector $\mathbf{r}$:

$$d\mathbf{q}/dt = \mathbf{r}(p,T,\mathbf{q}). \tag{43}$$

At some assigned values of p and T, the equilibrium extent of reaction, $\mathbf{q}^*$, is such that the corresponding rate of reaction is zero:

$$\mathbf{q}^*(p,T) : \mathbf{r}(p,T,\mathbf{q}^*(p,T)) = 0. \tag{44}$$

If one is able to calculate the value of $\mathbf{q}^*$ for any given values of $\mathbf{p}$ and $\mathbf{T}$, one obviously can calculate the equilibrium composition from Eq. (40). Now the second law of thermodynamics implies that, at constant pressure and temperature, the Gibbs free energy can never increase, which for the case at hand reduces to the following condition:

$$\{\boldsymbol{\Theta},\mathbf{r}\} \leq 0. \tag{45}$$

At equilibrium $\{\boldsymbol{\Theta},\mathbf{r}\} = 0$; hence, it has a maximum there. It follows that its differential is zero at equilibrium, and, since at equilibrium $\mathbf{r} = 0$ by definition, the equilibrium affinity $\boldsymbol{\Theta}^*$ is such that, for any infinitesimal displacement from equilibrium $d\mathbf{q}$ resulting in some infinitesimal reaction rate $d\mathbf{r}$,

$$\{\boldsymbol{\Theta}^*,d\mathbf{r}\} = 0. \tag{46}$$

Given an infinitesimal displacement $d\mathbf{q}$ from equilibrium, one obtains from Eq. (43), with $\mathbf{B} = \delta\mathbf{r}/\delta\mathbf{q}$

$$d\mathbf{r} = \{\mathbf{B},d\mathbf{q}\}. \tag{47}$$

It follows that condition (46) reduces to

$$\{d\mathbf{q},\{\mathbf{B}^{\mathrm{T}},\boldsymbol{\Theta}^*\}\} = 0. \tag{48}$$

Because this has to hold for arbitrary $d\mathbf{q}$, one has

$$\{\mathbf{B}^{\mathrm{T}},\boldsymbol{\Theta}^*\} = 0. \tag{49}$$

Now let $\mathbf{D}$ be the set of vectors lying in the kernel of $\mathbf{B}^{\mathrm{T}}$; Eq. (49) implies that $\boldsymbol{\Theta}^*$ lies in $\mathbf{D}$. Truesdell (1984) calls "weak" an equilibrium point where $\boldsymbol{\Theta}^*$ is nonzero. We will restrict attention to the (likely) case where $\mathbf{D}$ contains only the zero vector, that is, to the case where only strong equilibria exist (for the discrete case, $\mathbf{D}$ contains only the zero vector provided $\det\mathbf{B}$ is nonzero). For that case, the equilibrium condition becomes

$$\boldsymbol{\Theta}^* = 0. \tag{50}$$

It is worthwhile to observe for future reference that, if indeed the equilibrium points are strong ones, det **B** is nonzero, and hence **r**(**q**) is invertible at equilibrium. We will also make the (likely) assumption that the systems considered are, in Coleman and Gurtin's (1967) terminology, strictly *dissipative,* that is, that Eq. (45) is satisfied as an equality only at equilibrium points.

Since $\mathbf{\Theta}$ is a function of **q**, Eq. (50) by itself does not exclude the possibility of the existence of more than one equilibrium value $\mathbf{q}^*$. However, should more than one $\mathbf{q}^*$ exist, the Gibbs free energy hypersurface would necessarily include a spinodal region, and this is impossible for systems that are homogeneous over the whole composition space. Hence, in such systems the equilibrium composition is guaranteed to be unique.

Given the definition of $\boldsymbol{\theta}$ in Eq. (42), the relationship between **m** and **q** in Eq. (40), and the definition of the (mass-based) chemical potential vector $\boldsymbol{\mu} = \delta G/\delta \mathbf{m}$, Eq. (50) reduces to the following (classical) form:

$$<\boldsymbol{\sigma}^{\mathrm{T}},\boldsymbol{\mu}^*> = 0; \tag{51}$$

that is, the vector of equilibrium chemical potentials lies in the kernel of $\boldsymbol{\sigma}^{\mathrm{T}}$. As was discussed in Section II,A, given any P-dimensional vector **b**, the N-dimensional vector $\mathbf{p} \cdot \mathbf{b}$ lies in the kernel of $\boldsymbol{\sigma}^{\mathrm{T}}$; the same argument applies to whatever set of linear constraints is imposed on the system, and that, as also discussed in Section II,A, is likely to be a low-order set. Thus the search for an N-dimensional vector $\boldsymbol{\mu}^*$ reduces to the search for a C-dimensional vector **b**.

The concise analysis just given can be easily generalized to a continuous description. The distribution of affinities, $\theta(u)$, is defined as

$$\theta(u) = \delta G/\delta q(u), \tag{52}$$

while the second law of thermodynamics takes the form

$$\{\theta(v)r(v)\} \leq 0. \tag{53}$$

Both the affinity distribution and the rate of reaction distribution are uniquely determined (at fixed p and T) by the distribution of extents of reactions, and thus one can write

$$\theta(u) = \mathbf{\Theta}[q(w);u], \tag{54}$$

$$r(u) = \mathbf{R}[q(w);u], \tag{55}$$

where both $\mathbf{\Theta}[\,;\,]$ and $\mathbf{R}[\,;\,]$ are functionals of the extent of reaction distribution $q(u)$ that also depend parametrically on the reaction label u.

Now let $\delta q(u)$ be an arbitrary (and in fact infinitesimal) displacement of $q(u)$ from the equilibrium distribution $q^*(u)$; and let $B(v;u)$ be the functional derivative of $\mathbf{R}[\,;\,]$ at $q^*(u)$. The corresponding (infinitesimal) $\delta r(u)$ is given by

$$\delta r(u) = \{B(v;u)\delta q(v)\}, \tag{56}$$

which is evidently the continuous generalization of Eq. (47). The generalization of Eq. (48) is

$$\{\boldsymbol{\theta}[q^*(w);v]\{B(v';v)\delta q(v')\}\} = 0. \tag{57}$$

This has to hold for arbitrary $\delta q(u)$. Hence,

$$\{\boldsymbol{\theta}[q^*(w);v]B(v,u)\} = 0. \tag{58}$$

The argument (and the assumptions) following Eq. (49) can now be duplicated to yield the result that, if the set **D** of functions $s(v)$ to which $B(v,u)$ is orthogonal contains only the zero function (i.e., if attention is restricted to systems for which only strong equilibria are possible), the equilibrium condition is

$$\theta^*(u) = 0 \tag{59}$$

and that, since the kernel of $B(v,u)$ contains only the zero function, the functional $\mathbf{R}[\,;\,]$ can be inverted at $q^*(u)$. This leads to the following generalization of Eq. (51):

$$<\sigma(y,u)\mu^*(y)> = 0. \tag{60}$$

It is important to realize that *any* distribution of chemical potentials satisfying Eq. (51) (in the discrete case) or Eq. (60) corresponds to an equilibrium composition. Of course, given an initial value **M** or $M(y)$, infinitely many of such equilibrium compositions will not satisfy the mass balance condition [Eq. (40) or its equivalent continuous form].

2. *The Orthogonal Complement Method*

In this and the next subsection, we present a concise summary of the recent analysis given by Krambeck (1994a). As was discussed in Section II,A, the orthogonal complement of the reaction space is C dimensional: The vectors $\mathbf{a}_L$ are a basis for the orthogonal complement, and they are such that, given two values $\mathbf{m}_1$ and $\mathbf{m}_2$, which are both stoichiometrically accessible from some initial composition **M** (so that some linear combination of the reactions may in fact bring the system from $\mathbf{m}_1$ to $\mathbf{m}_2$), $<(\mathbf{m}_1 - \mathbf{m}_2),\mathbf{a}_L> = 0$ for all L's, $L = 1, 2, \ldots, C$. This implies that

$$<\mathbf{a}_L,\{\sigma,(\mathbf{q}_1 - \mathbf{q}_2)\}> = 0, \tag{61}$$

which is equivalent to

$$\{(\mathbf{q}_1 - \mathbf{q}_2), <\sigma^{\mathrm{T}},\mathbf{a}_L>\} = 0. \tag{62}$$

Because Eq. (62) has to hold for arbitrary $\mathbf{q}_1 - \mathbf{q}_2$, one obtains

$$<\sigma^{\mathrm{T}},\mathbf{a}_L> = 0; \tag{63}$$

that is, all of the $\mathbf{a}_L$'s lie in the kernel of $\boldsymbol{\sigma}^{\mathrm{T}}$ (and only linear combinations of them lie in it). When this is compared with Eq. (51), one concludes that $\boldsymbol{\mu}^*$ lies in the orthogonal complement, that is, that $\boldsymbol{\mu}^*$ can be expressed as

$$\boldsymbol{\mu}^* = \sum_1^C \alpha_L \mathbf{a}_L. \tag{64}$$

The coefficients α_L play the role of the usual Lagrange multipliers in the determination of the minimum of Gibbs free energy. *Any* set of α_L's determines an equilibrium point (but infinitely many of these are not accessible from the initial composition). The great advantage of the orthogonal complement method is that the number of linear constraints, C, is invariably small, regardless of how large N and R might be.

The method is easily generalized to a continuous description, where the basis vectors of the orthogonal complement are C distributions $a_L(x)$; the analog of Eq. (64) is simply

$$\mu^*(x) = \sum_1^C \alpha_L a_L(x). \tag{65}$$

The strength of the orthogonal complement method, in the case of homogeneous systems, lies also in the following fact. If the system is guaranteed to be homogeneous at all possible compositions, the (constant pressure and temperature) $\boldsymbol{\mu}(\mathbf{m})$ function is invertible: Should there be two different values of $\mathbf{m}$ resulting in the same $\boldsymbol{\mu}$, these would correspond to two different phases. Equations (64) and (65) show that the surface of equilibrium points is a C-dimensional linear subspace in chemical potential space. Finding the equilibrium composition for any given $\mathbf{M}$ simply involves mapping this subspace into composition space, and this is easily achieved if $\boldsymbol{\mu}(\mathbf{m})$ is invertible, as it is for homogeneous systems. Krambeck (1994) discusses examples, in both the discrete and continuous formulation: the general case of ideal gas mixtures and the specific one of olefin oligomerization.

3. *Behavior in a Neighborhood of Equilibrium*

The restriction to strong equilibria implies that $\mathbf{r}(\mathbf{q})$ (or, in the continuous formulation, $\mathbf{R}[\,,])$ is invertible near equilibrium. Now consider the vector $\mathbf{f}$ defined as $d\mathbf{m}/dt$, say,

$$\mathbf{f} = \{\boldsymbol{\sigma}, \mathbf{r}\}. \tag{66}$$

The vector $\mathbf{f}$ depends on $\mathbf{m}$, and, since in a homogeneous system $\boldsymbol{\mu}(\mathbf{m})$ is invertible, one may regard $\mathbf{f}$ as a function of $\boldsymbol{\mu}$:

$$\mathbf{f} = \mathbf{f}(\boldsymbol{\mu}). \tag{67}$$

Let $\mathbf{C}$ be the $N \times N$ matrix $d\mathbf{f}/d\boldsymbol{\mu}$ at equilibrium. Krambeck (1970) has shown that the condition of detailed balancing[16] is equivalent to the requirement that $\mathbf{C}$ be symmetric:[17]

$$\mathbf{C} = \mathbf{C}^{\mathrm{T}}. \tag{68}$$

Since $\boldsymbol{\mu}(\mathbf{m})$ is invertible, $\mathbf{J} = d\boldsymbol{\mu}/d\mathbf{m}$ possesses an inverse $\mathbf{J}^{-1}$ at equilibrium. Let $\mathbf{K}$ be $d\mathbf{f}/d\mathbf{m}$. One has, at all strong equilibrium points,

$$\mathbf{C} = <\mathbf{K},\mathbf{J}^{-1}>. \tag{69}$$

Notice that, if all the mass rates f_I are multiplied by the same (but otherwise arbitrary) function of $\mathbf{m}$, the result still holds; in other words, linearity near equilibrium may be the quasilinearity of a uniform kinetics of the type that is discussed in Section IV,B.

Wei and Prater (1962) analyzed the case of monomolecular reactions, for which in general

$$\mathbf{f} = <\mathbf{K},\mathbf{m}>. \tag{70}$$

It is now useful to define the following modified inner product [,] (where $\mathbf{x}$ and $\mathbf{y}$ are N-dimensional vectors):

$$[\mathbf{x},\mathbf{y}] = <\mathbf{x},<\mathbf{J},\mathbf{y}>>. \tag{71}$$

One can then show that $\mathbf{K}$ is self-adjoint with respect to [,]:

$$[\mathbf{x},<\mathbf{K},\mathbf{y}>] = [<\mathbf{K},\mathbf{x}>,\mathbf{y}]. \tag{72}$$

Thus, $\mathbf{K}$ has a complete set of eigenvectors that is mutually orthogonal with respect to [,], and has real eigenvalues. This is the essential result for the Wei and Prater (1962) analysis of reaction pathways in monomolecular systems. The latter

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[16] The condition of detailed balancing is that each individual reaction should be at equilibrium. Consider, for instance, a system of three isomers, A, B, and C. It is conceivable that A only reacts to form B, B only to form C, and C only to form A. If the three kinetic constants are equal, the equilibrium condition would be that the concentrations of all three isomers are the same. However, this would not satisfy the detailed balancing condition, since the reaction between A and B would not by itself be at equilibrium (equilibrium is only attained through a cycle).

[17] The symmetry of $\mathbf{C}$ is seen to be a special case of the Onsager reciprocal relations. However, it is somewhat misleading to regard the result from that viewpoint: The symmetry is a consequence of the requirement of detailed balancing (and of mass action kinetics), not a blind application of Onsager's relations. In his 1970 paper, Krambeck included the following footnote concerning this point: "While the requirement that the matrix $\mathbf{C}$ be symmetric at equilibrium is strongly suggested by the Onsager–Casimir reciprocal relations for homogeneous systems as presented on page 123–124 of Truesdell (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." The discussion in Truesdell to which Krambeck refers makes it abundantly clear that in the alleged Onsager–Casimir theorems there is nothing to suggest that it is necessarily $\mathbf{C}$ that should be symmetric.

analysis has been strengthened by Krambeck (1984b). Even stronger constraints on reaction pathways, based on the assumption that every individual term $\theta_j r_j$ in Eq. (45) (and not only their sum) is nonpositive, have been established by Shinnar and Feng (1985). In this regard, see also the discussion in Section IV,B,4,b.

While Eq. (70) holds *in general* for monomolecular systems, it holds only in a neighborhood of equilibrium for the general case considered by Krambeck (1994):

$$\delta \mathbf{f} = \langle \mathbf{K}, (\mathbf{m} - \mathbf{m}^*) \rangle. \tag{73}$$

However, in view of Eq. (69), **K** in Eq. (73) is again self-adjoint with respect to [,]. The results are rather easily generalized to the case of continuous mixtures.

C. HETEROGENEOUS CHEMICAL EQUILIBRIA

It is of course well known that in nature heterogeneous chemical equilibria are possible: systems in which chemical reactions may take place, and which at equilibrium will exist in more than one phase. The question that arises is the analysis of the conditions under which heterogeneous chemical equilibria are possible in multicomponent mixtures. In this section, we follow closely the analysis that was recently presented by Astarita and Ocone (1989); earlier work on the subject is due to Caram and Scriven (1976) and Astarita (1976).

In systems where heterogeneous chemical equilibria prevail, both chemical and phase equilibrium conditions must be simultaneously satisfied. In practice, this means that the chemical equilibrium condition—Eq. (51) in the discrete description, and Eq. (60) in the continuous one—must be satisfied in one phase, and the phase equilibrium condition [μ or $\mu(x)$ to be the same in all phases] must be satisfied; this clearly guarantees that the chemical equilibrium condition is automatically satisfied in all phases.

It is in the area of heterogeneous chemical equilibria that a formulation in mass units turns out to be definitely preferable to a mole-based one. This can best be seen by considering a system where only components A and B are present, and a simple reaction such as the following one might take place:

$$\mathrm{A} = 2\mathrm{B}. \tag{74}$$

Let $1 - q$ be the number of moles of A, and consequently $2q$ be the number of moles B, and $1 + q$ the total number of moles. Since q determines the composition of the system, G^{MIX} is a unique and, in principle, known function of q, $G^{\mathrm{MIX}} = w(q)$. In Section III,A, we showed that, in the absence of chemical reactions, statements about the Gibbs free energy are only significant to within a term which is linear in the composition. This is not true when chemical reactions can take place, because, for instance in the case at hand, the pure component Gibbs free energy of component B is given by

$$2G_B{}^0 = G_A{}^0 + G^S, \tag{75}$$

where G^S is the standard free energy of reaction which, in principle, is known.

The Gibbs free energy per unit mole of the mixture, g, can now be calculated as

$$g = (G_A{}^0 + qG^S)/(1 + q) + w(q), \tag{76}$$

and one can try to find a minimum of g by imposing that

$$dg/dq = 0 = dw/dq + (G^S - G_A{}^0)/(1 + q)^2. \tag{77}$$

This, however, does not determine the value of q at which dg/dq is zero, since the value of $G_A{}^0$ is arbitrary. The problem, as can be easily checked, does not arise in the case of an isomerization reaction A = B, for which the equivalent of Eq. (77) is

$$dg/dq = G^S + w(q), \tag{78}$$

which determines the value of q, which minimizes the Gibbs free energy unequivocally. This is because in the case of an isomerization reaction the total number of moles is preserved as the reaction takes place. Since in mass units the total mass is preserved anyhow, in a mass units formulation the problem does not arise, and the location of minima of g in the reaction subspace is unequivocal.

We now move to a general formulation for the discrete case, where $g(\mathbf{q})$ has to be intended as the Gibbs free energy per unit mass that would prevail should the system exist in a one-phase condition. Clearly, given a value of $\mathbf{M}$, $g(\mathbf{q})$ is defined only for those compositions that are stoichiometrically accessible from $\mathbf{M}$, that is, only within the reaction subspace of composition space (i.e., it is not defined in the orthogonal complement). Of course, within the reaction subspace there may well be more than one minimum. In our 1989 work, we have proved the following theorems:

1. The absolute minimum of g in the reaction subspace lies in a homogeneous region of it (i.e., at a point that is unconditionally convex).
2. If there is more than one minimum of g in the reaction subspace, there is a spinodal region in it.
3. All minima that are not the absolute one lie in a metastable region of the reaction subspace (except for the freak case where more than one of such minima corresponds to exactly the same value of g, which is at most a singular point in parameter space).

The three theorems are easily proved by considering two local minima of g, $\mathbf{q}_1$ and $\mathbf{q}_2$, and the linear trajectory connecting them, $\mathbf{q} = \alpha\mathbf{q}_1 + (1 - \alpha)\mathbf{q}_2$.

It follows from these theorems that (again except for the freak cases mentioned), as long as one is restricted to the reaction subspace, heterogeneous chemical equilibria are impossible—the true absolute minimum is homogeneous, and it will eventually be reached at least by nucleation of new phases and mass transfer.

However, one is in general not restricted to the reaction subspace: the system considered may very well split into more than one phase in a direction orthogonal to the reaction subspace, that is, in the orthogonal complement of it. This is impossible in the (exceptional) cases where the system considered is a merization one, in the sense discussed in Section II. In all systems where the orthogonal complement has more than one dimension (i.e., in systems subjected to at least one linear constraint in addition to mass balance), phase splitting in one of the directions of the orthogonal complement is possible, and heterogeneous chemical equilibria may prevail. However, since the dimensionality of the orthogonal complement is likely to be small, the number of phases present at a heterogeneous chemical equilibrium point is also likely to be small.

The analysis discussed given here rather trivially extended to a continuous description, as Astarita and Ocone (1989) have shown.

IV. Kinetics

A. EXACT AND APPROXIMATE LUMPING

As discussed in Section III,C, the concept of "lumping" is related to the idea that it might be possible, in analyzing the kinetic behavior of a multicomponent mixture, to substitute for the real system (which involves a very large, possibly infinitely large number of chemical reactions) a lower order system with a finite number of pseudocomponents which, in some sense to be made precise, behaves either exactly or approximately in the same way as the original system. The concept was originated by the works of Wei and Kuo and of Kuo and Wei in 1969; its fundamental mathematical structure is based on the older works of Wei (1962a) and of Wei and Prater (1962).

Consider first a discrete *monomolecular* system in which every species present can transform to any other one by a first-order reaction. In such a system, the kinetic equation at all possible compositions is given by Eq. (70), which is repeated here:

$$d\mathbf{m}/dt = -\langle \mathbf{K},\mathbf{m} \rangle, \tag{79}$$

where $\mathbf{K}$ is an $N \times N$ matrix of pseudokinetic constants. [In Section III,B, Eq. (70) was written without the minus sign; here we follow as closely as possible the Wei and Kuo terminology.]

The matrix $\mathbf{K}$ must satisfy several constraints, which are best illustrated by considering a simple three-component system. The rate of formation of component 1 from components 2 and 3 is $k_{21}m_2 + k_{31}m_3$, where the k's are true kinetic constants; hence for the off-diagonal elements of **K** one has the constraint

$$K_{IJ} = -k_{IJ} \leq 0 \qquad \text{(off-diagonal).} \tag{80}$$

Conversely, the rate of consumption of component 1 is $(k_{12} + k_{13})m_1$, and hence for the diagonal elements:

$$K_{II} = \Sigma k_{IJ}, \tag{81}$$

where the sum is intended over J different from I. Given Eq. (80), one sees that the entries in each column of **K** sum to zero, so that Eq. (81) can be written as

$$<\mathbf{K}^{\mathrm{T}},\mathbf{I}> = 0. \tag{82}$$

Finally, there must exist at least one stationary point $\mathbf{m}^*$ (corresponding to chemical equilibrium) such that

$$<\mathbf{K},\mathbf{m}^*> = 0. \tag{83}$$

We now wish to substitute for this system a lower order one of $N^{\wedge}(<N)$ pseudocomponents, the masses of which are linear combinations of the masses of the original components. In general, we want to introduce an $N^{\wedge} \times N$ "lumping matrix" **L** such that

$$\mathbf{m}^{\wedge} = <\mathbf{L},\mathbf{m}>. \tag{84}$$

In this section, we indicate with [,] the sum over the $I^{\wedge}$ index, $I^{\wedge} = 1, 2, \ldots, N^{\wedge}$. Since the ^ system is of lower order, there must exist couples of different **m**'s, $\mathbf{m}_1$ and $\mathbf{m}_2$, which result in the same $\mathbf{m}^{\wedge}$, say, $<\mathbf{L},\mathbf{m}_1> = <\mathbf{L},\mathbf{m}_2>$. Such couples will be called **L**-equivalent, and indicated with the notation $\mathbf{m}_1 \approx \mathbf{m}_2$.

Now one may want to impose another constraint, namely, that each of the original N species appears in only one of the $N^{\wedge}$ species; hence, every column of **L** has to be a unit vector of the type 0, 0, . . ., 1, . . ., 0. This is called "proper" lumping. Lumping that is not proper, however, is possible; see Section II,C.

So far, lumping has been defined, but nothing has been said concerning the dynamic behavior of the ^ system. Now we come to the definition of "exact" lumping: A system is said to be exactly "lumpable" by the matrix **L** if there exists an $N^{\wedge} \times N^{\wedge}$ matrix $\mathbf{K}^{\wedge}$, enjoying the same properties as **K** does (i.e., off-diagonal elements of $\mathbf{K}^{\wedge}$ are nonpositive, $[\mathbf{K}^{\wedge\mathrm{T}},\mathbf{I}^{\wedge}] = 0$, and there exists at least an $\mathbf{m}^{\wedge *} = <\mathbf{L},\mathbf{m}^*>$ for which $[\mathbf{K}^{\wedge},\mathbf{m}^{\wedge *}] = 0$), such that

$$d\mathbf{m}^{\wedge}/dt = -[\mathbf{K}^{\wedge},\mathbf{m}^{\wedge}]. \tag{85}$$

A corollary of the definition is that any two **L**-equivalent mass distributions have the same rate in the ^ system; that is, if $\mathbf{m}_1(0) \approx \boldsymbol{m}_2(0)$, then $\mathbf{m}_1(t) \approx \mathbf{m}_2(t)$ at all later times $t > 0$. This property can also be used as a definition of an exactly lumpable system.

Now if Eq. (85) holds, then

$$d\mathbf{m}^{\wedge}/dt = -[\mathbf{K}^{\wedge}, <\mathbf{L},\mathbf{m}>]. \tag{86}$$

On the other side, one also has

$$d\mathbf{m}^{\wedge}/dt = <\mathbf{L}, d\mathbf{m}/dt> = -<\mathbf{L}, <\mathbf{K},\mathbf{m}>>, \tag{87}$$

which implies the fundamental result of Wei and Kuo (1969), namely, that in order to have exact lumping,

$$[\mathbf{K}^{\wedge},\mathbf{L}] = <\mathbf{L},\mathbf{K}>. \tag{88}$$

Many of the Wei and Kuo results are strengthened by the result that Eq. (88) also applies to analytical functions of **K** (in particular, the extension to "uniform systems" discussed in Section III,B follows from this result). Given any matrix-valued analytical function of **K**, **F**(**K**) (where **F** is a square matrix of the same order as its square-matrix argument), one can show that

$$[\mathbf{F}(\mathbf{K}^{\wedge}),\mathbf{L}] = <\mathbf{L},\mathbf{F}(\mathbf{K})>. \tag{89}$$

Wei and Prater (1962) showed that **K** is always diagonizable. It follows that if **x** is any eigenvector of **K**, the corresponding eigenvalue α is real [see the discussion following Eq. (72)], where

$$<\mathbf{K},\mathbf{x}> = \alpha\mathbf{x}. \tag{90}$$

Transforming to the ^ system, one has

$$[\mathbf{K}^{\wedge}, <\mathbf{L},\mathbf{x}>] = <\mathbf{L}, <\mathbf{K},\mathbf{x}>> = \alpha<\mathbf{L},\mathbf{x}>, \tag{91}$$

which can be satisfied only in two cases: either $<\mathbf{L},\mathbf{x}> = 0$, or $<\mathbf{L},\mathbf{x}>$ is an eigenvector of $\mathbf{K}^{\wedge}$ with α being the corresponding eigenvalue.

As already observed by Wei and Kuo (1969), this result really simply means that, as one lumps the system into a lower order one by way of the **L**-transformation, several eigenvectors necessarily "vanish," in the sense that the corresponding eigenvectors in the ^ system are zero. In the transformed system, the $\mathbf{K}^{\wedge}$ matrix can have at most $N^{\wedge}$ nonzero eigenvectors. The original eigenvectors, which do not vanish, preserve the same eigenvalues in the transformed system.

Wei and Kuo (1969) have shown a direct construction of the matrix $\mathbf{K}^{\wedge}$ from the knowledge of the eigenvectors and eigenvalues of **K**. A simpler construction (for proper lumping) was proposed by Coxson and Bischoff (1987b): Let **S** be the diagonal $N^{\wedge} \times N^{\wedge}$ matrix whose elements are the inverses of the number of species in each "lump," that is, in each ^ pseudospecies. Then $\mathbf{K}^{\wedge} = [[<\mathbf{L},\mathbf{K}>,\mathbf{L}^{\mathrm{T}}],\mathbf{S}]$.

The distinction of the original eigenvectors into a set of vanishing ones and a set of eigenvalue preserving ones forms the basis of the Ozawa (1973) analysis of exact lumping.

For further details on the Wei and Kuo analysis of exact lumping, and for alternate mathematical descriptions of the same problem, the reader is referred to the original literature. We move here to a brief discussion of an extension due to Bailey (1972), who considered the case where the original system is a continuous one, so that Eq. (79) is written as

$$dm(x)/dt = -<K(x,y),m(y)>. \tag{92}$$

Now suppose that one still wants to lump the system into a finite, $N^\wedge$-dimensional one. This can be achieved by defining an $N^\wedge$-dimensional set of $L_{I^\wedge}(x)$ distributions, $\mathbf{L}(x)$, such that

$$\mathbf{m}^\wedge = <\mathbf{L}(y),m(y)>. \tag{93}$$

For exact lumping, one now again requires Eq. (85) to hold. Bailey (1972) has shown that the analog of Eq. (88) is, for the case at hand,

$$<\mathbf{L}(y),K(x,y)> = [\mathbf{K}^\wedge,\mathbf{L}(x)]. \tag{94}$$

Another type of extension of the Wei and Kuo results is to bilinear kinetic forms, an extension that was originally discussed by Li (1984), and later analyzed in much more detail by Li and Rabitz (1989, 1991a,b,c). Practical and experimental aspects of the general problem of exact lumping, some of which had already been discussed by Wei and Kuo (1969) and by Kuo and Wei (1969), are excellently reviewed by Weekman (1979).

An important consideration about exact lumping is the following one, which is due to Coxson and Bischoff (1987a). If one considers reactor types other than a batch (or, equivalently, a plug flow) reactor, exact lumping carries over. In other words, the dynamics of the reduced system behave as if they were representative of true intrinsic kinetics. (This, as discussed in Section IV,C, is not true for overall kinetics, which may be regarded as nonexact lumping.) A somewhat similar result was proved by Wei and Kuo (1969) for the case of reactions with diffusion, such as occurs in porous catalysts.

The constraints required for exact lumping are invariably very strict, and it is only natural that works have been published where the concept of "approximate" lumping is introduced. In its simplest possible form, approximate lumping is achieved when Eq. (88) [or its semicontinuous analog, Eq. (94)] holds only in some appropriately defined approximate sense, rather than exactly.

It is in the area of approximate lumping that the distinction between the meaning of *lumping,* as used in this article, and of *overall* kinetics, possibly becomes a fuzzy one. For instance, the analysis of many parallel irreversible first-order reactions, to be briefly discussed in the next section, has been called *lumping* in the literature, though it is not in any sense an exact (Wei–Kuo) lumping, nor an approximate one: One chooses to consider only one lump, as given later by Eq. (97) but the qualitative kinetic behavior of the "lump" in no way resembles that of the original system (except when the latter consists in fact of only one species). The lump does not even follow first-order kinetics, let alone respect the other constraints required of the matrix $\mathbf{K}^{\wedge}$ by the Wei and Kuo definition of an exactly lumpable system.

B. OVERALL KINETICS

In this section, we attack the problem of kinetics in multicomponent mixtures, and we dedicate attention mostly to the case where one is only interested in, or may only be able to determine experimentally, some overall concentration of species of a certain class, such as sulfurated compounds in an oil cut during a hydrodesulfurization process. The presentation is given in terms of a continuous description; special cases of the corresponding discrete description are discussed as the need arises. Instead of working with the masses of individual species, we will work with their mass concentration distribution $c(x)$. In the case of a batch reactor, the distinction is irrelevant, but in the case of a plug flow reactor the concentration-based description is clearly preferable. The discussion is presented in purely kinetic terms for, say, a batch reactor.

It is useful to begin with an extremely simple example. Suppose one has a mixture with only two reactants, A_1 and A_2, both of which react irreversibly with first-order kinetics. A semilog plot of c_I $(I = 1, 2)$ versus time (see Fig. 1) would be linear for both reactants. However, suppose that for some reason one is able to measure only the overall concentration $c_1 + c_2$; this is also plotted in Fig. 1. the curve is nonlinear, and it seems to indicate an overall kinetics of order larger than unit. This shows that the overall behavior of the mixture is qualitatively different

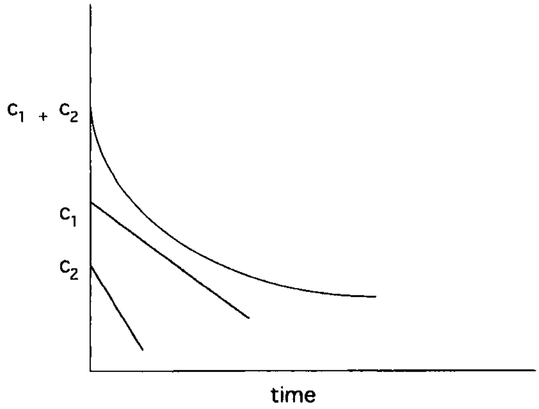

FIG. 1. Time behavior of single reactant and overall concentrations.

from the behavior of individual reactants: Experiments with model compounds (say, with only A_1) do not give information on the overall behavior; conversely, overall experiments (where one measures $c_1 + c_2$) may well mask the actual intrinsic behavior of individual reactants.

We now move to the general case of a continuous description; the pragmatical usefulness of such a type of description in real-life kinetic problems has been discussed by Krambeck (1991a,b). Let $c(x,0)$ be the initial distribution of reactant concentrations in the batch reactor, and let $c(x,t)$ be the concentration distribution at any subsequent (dimensional) time t. We assume that both the label x and the concentration c have already been normalized so that $<c(y,0)> = <yc(y,0)> = 1$. Furthermore, we assume that a (dimensional) frequency factor $k(x)$ can be identified, and that x has been normalized so that $k(x) = k^*x$, where k^* is the average value of $k(x)$ at $t = 0$. One then normalizes the time scale as well by defining the dimensionless time t as k^*t. The "overall" concentration $C(t)$ is defined with a weighting function that is identical to unity, $C(t) = <c(y,t)>$, $C(0) = 1$.

The question that arises is that of the description of the *intrinsic kinetics,* that is, of the constitutive equation for $c_t(x,t)$ in a batch reactor (we indicate partial derivatives with a subscript). Special cases that have been dealt with in the literature are discussed later.

1. Irreversible First-Order Kinetics

This case was analyzed in 1968 by Aris, based on a formalism introduced more generally in an earlier paper (1965a). Essentially the same problem was analyzed again by Bailey in 1972. Because the reactions are irreversible, $c_t(x,t)$ is negative unless $c(x,t)$ is zero. Because the reactions are first order, the only relevant parameter of any species x is the kinetic constant $k(x)$, and this has been reduced by renormalization to k^*x. Hence, the kinetic equation in a batch reactor has the form:

$$-c_t(x,t) = xc(x,t). \tag{95}$$

This integrates (trivially) to

$$c(x,t) = c(x,0) \exp(-xt). \tag{96}$$

The overall concentration $C(t)$ is given by

$$C(t) = <c(y,0) \exp(-yt)>; \tag{97}$$

that is, $C(t)$ is a Laplace transform of $c(y,0)$, with the dimensionless time t playing the rather unusual role of the transform parameter. Notice that $-dC/dt$ (the overall rate of consumption) equals $<yc(y,0) \exp(-yt)>$; that is, it is equal to the first moment of $c(x,t)$.

Now suppose $c(x,0)$ is the gamma distribution $\phi(\alpha,x)$. One can now eliminate $c(x,t)$ between the equations to obtain an *alias* (Aris and Astarita, 1989a), an explicit relationship between $-dC/dt$ and C:

$$-dC/dt = C^{(\alpha+1)/\alpha}. \tag{98}$$

Equation (98) should be discussed in some detail. When α approaches ∞ (which is the case where only reactant $x = 1$ is present in the mixture), it correctly predicts the single-reactant result $dC/dt = -C$. This is worded by saying that the alias satisfies the single-component identity (SCI): When the initial concentration distribution approaches a delta function, one recovers the result for a single component. It is clear that the SCI requirement must be satisfied for *every* kinetic equation, not only the linear one. In fact, one can generalize the requirement to that of the discrete component identity—when the initial concentration distribution approaches the sum of N distinct delta functions, one must recover the corresponding discrete description for N components (Aris, 1991a).

It is also of interest that the apparent overall order of reaction given by Eq. (98) is $(\alpha + 1)/\alpha$; that is, it is always *larger* than the intrinsic order of unity, except when α approaches infinity. When the intrinsic kinetics are linear (first order) the apparent overall order of reaction is larger than the intrinsic one; this, as will be seen, is not necessarily the case when the intrinsic kinetics are nonlinear. Physically, the point is easily understood by considering that, as time goes by, the components with the largest kinetic constants disappear first, and hence that the average kinetic constant of the mixture [which is proportional to the first moment $<yc(y,t)>$] decreases. It follows that, from an overall viewpoint, the overall kinetic constant decreases as the overall concentration decreases; this is typical of reactions of order larger than one.

It is also worthwhile to notice that the overall order of reaction is 2 when $\alpha = 1$, that is, with an exponential distribution. The only value of α for which $\phi(\alpha,0)$ is finite is $\alpha = 1$. This result can be generalized to any initial distribution by simply making use of the limit properties of the Laplace transform: $C(t)$ at large times becomes proportional to $t^{-\Omega}$ if and only if $c(x,0)$ at small x becomes proportional to $x^{\Omega-1}$, $\Omega > 0$. Now if $0 < \Omega < 1$, $c(0,0) = \infty$, and if $\Omega > 1$ $c(0,0) = 0$. It follows that $c(0,0)$ is finite only if $\Omega = 1$, in which case $C(t)$ at large times becomes proportional to $1/t$, which is the behavior typical of sound-order kinetics (Krambeck, 1984b). The question of the large-time asymptotic behavior of the overall kinetics is discussed later in more general terms.

The discrete equivalent of the Aris (1968) result was given by Luss and Hutchinson (1970). The concentration of the Ith component at time t is $c_I(t) = c_I(0) \exp(-k_I t)$, and the overall concentration is $C(t) = <\mathbf{c}(t),\mathbf{I}>$; if the k_I's are arranged in ascending order $C(t)$ is a Dirichlet series of type K_I. Properties of this series relevant to the case at hand are discussed by Aris (1991a). It is easy to convince oneself that the algebra of the discrete description can easily be more cumbersome than that of the continuous one.

2. *Irreversible Nonlinear Kinetics*

When the intrinsic kinetics are nonlinear, some interesting problems arise that are best discussed first with a discrete description. A possible assumption for the kinetics is that they are *independent,* that is, that the rate at which component I disappears depends only on the concentration of component I itself (this assumption is obviously correct in the first-order case). The difficulties associated with the assumption of independence are best illustrated by considering the case of parallel nth order reactions, which has been analyzed by Luss and Hutchinson (1971), who write the kinetic equation for component I as $-dc_I/dt = k_I c_I^n$, $I = 1, 2, \ldots, N$, where c_I is the (dimensional) concentration of component I at time t. The total initial concentration $C(0)$ is $<\mathbf{c}(0),\mathbf{I}>$, and this is certainly finite. Now consider the following special, but perfectly legitimate case. The value of $C(0)$ is fixed, and the initial concentrations of all reactants are equal, so that $c_I(0) = C(0)/N$. Furthermore, all the k_I's are equal to each other, $k_I = k^*$. One now obtains, for the initial rate of decrease of the overall concentration:

$$-dC(0)/dt = k^* C(0)^n N^{1-n}, \tag{99}$$

which implies that, as the number of components N approaches ∞, $-dC(0)/dt$ approaches zero if $n > 1$, and it approaches infinity if $n < 1$. Clearly both conclusions do not make sense; the paradox is harder to prove but appears also for any initial distribution of concentrations and kinetic constants, provided $C(0)$ is finite, as in practice will always be the case. Indeed, Luss and Hutchinson (1971) state explicitly that serious problems arise if one tries a continuous description—one where N approaches ∞. The mathematical difficulties connected with the assumption of independent kinetics in the continuous description have been discussed by Ho and Aris (1987).

Ho *et al.* (1990) have presented an approach to the description of independent kinetics that makes use of the "method of coordinate transformation" (Chou and Ho 1988), and which appears to overcome the paradox discussed in the previous paragraph. An alternate way of disposing of the difficulties associated with independent kinetics is intrinsic in the two-label formalism introduced by Aris (1989, 1991b), which has some more than purely formal basis (Prasad *et al.,* 1986). The method of coordinate transformation can (perhaps in general) be reduced to the double-label formalism (Aris and Astarita, 1989a). Finally, the coordinate transformation approach is related to the concept of a number density function $s(x)$, which is discussed in Section IV,B.5.

Be that as it may, there is a largely heuristic argument in support of the idea that the assumption of independent kinetics is reasonable only for first-order reactions. If the reactions are first order, the probability of a given molecule to undergo the reaction is a constant, so that the number of molecules of any given reactant that reacts per unit time is simply proportional to how many such molecules there are. For *any* nonlinear kinetics, the probability depends on the environment, and in the case of very many reactants each one of which is present in very small concentrations, the environment is essentially made up of molecules of components other than the one under consideration. Hence it would seem unlikely that the rate at which a given reactant disappears depends only on the concentration of that reactant.

Remaining still in the framework of a discrete description, the environment of reactant I at time t is presumably fully described by the vector $\mathbf{c}(t)$. This suggests that the rate of consumption of reactant I at time t can be written as

$$-dc_I/dt = k_I c_I F_I(\mathbf{c}), \tag{100}$$

where k_I is a frequency factor and $F_I(\mathbf{c})$ is a dimensionless measure of the influence of the environment on the probability of molecules I to undergo the reaction. Kinetics of the type of Eq. (100) will be called *cooperative* in the sense that the rate of reaction of component I depends on the whole instantaneous distribution of concentrations $\mathbf{c}(t)$.

Equation (100) is easily generalized to the dimensionless continuous description:

$$-c_t(x,t) = xc(x,t)\mathbf{F}[c(z,t);x], \tag{101}$$

where $\mathbf{F}[\,;\,]$ is a functional of the concentration distribution at time t, which also depends parametrically on the component label x. The value of $\mathbf{F}[\,;\,]$ is identically unity in the case of irreversible first-order kinetics.

In the very general form of Eq. (101), cooperative kinetics are very hard to deal with mathematically. However, a very strong (but also powerful) assumption of "uniformity" was introduced by Astarita and Ocone (1988): The functional $\mathbf{F}[\,;\,]$ does not depend on the component label x, so that the continuous description of uniform cooperative kinetics is

$$-c_t(x,t) = xc(x,t)\mathbf{F}[c(z,t)]. \tag{102}$$

The assumption of uniformity is in fact justified for some realistic kinetic schemes, such as Langmuir isotherm catalyzed reactions, Michaelis–Menten kinetics, and others (Aris, 1989; Cicarelli *et al.,* 1992). The assumption bears a more than superficial analogy with those systems termed *pseudomonomolecular* by Wei and Prater (1962). Mathematically, it is a very powerful assumption: By crossing out the dependence of $\mathbf{F}[\,;\,]$ on x, its value has been reduced from an infinite-dimensional vector (a function of x) to a scalar. This simplification makes Eq. (102) a quasilinear one, and it can be integrated explicitly by introducing a warped time scale $\tau(t)$, $\tau(0) = 0$. The solution, as can be verified by inspection, is

$$c(x,t) = c(x,0)\exp(-\tau(t)), \tag{103}$$

where $\tau(t)$ is delivered by the following first-order differential equation [which can always be solved for $t(\tau)$ by direct quadrature]:

$$d\tau/dt = \mathbf{F}[c(z,0)\exp(-\tau(t))]. \tag{104}$$

Notice that the overall concentration $C(t) = <c(y,t)>$ is again a Laplace transform of the initial distribution $c(x,0)$, with τ playing the role of the transform parameter. The overall rate of reaction $-dC/dt$ is given by

$$-dC/dt = <yc(y,t)>\mathbf{F}[c(z,0)\exp(-\tau(t))]. \tag{105}$$

Stronger results can be obtained by assigning specific forms to the functional $\mathbf{F}[\;]$. Let $Q(t)$ be a weighted overall concentration at time t, $Q(t) = <K(y)c(y,t)>$, where $K(x)$ is an appropriate weighting function. In many realistic cases the functional $\mathbf{F}[\;]$ can be expressed as a function of $Q(t)$, $\mathbf{F}[\;] = F(Q(t))$. It is also necessary to assign a specific form to the weighting function $K(x)$, and the following one has been proposed by Astarita (1989b) for use in conjunction with $\phi(\alpha,x)$ for $c(x,0)$:

$$K(x) = K^*\Gamma(\alpha)(\alpha x)^{\beta}/\Gamma(\alpha + \beta), \tag{106}$$

which is already normalized so that K^* is indeed the average value of $K(x)$ in the initial mixture. The case where $c(x,0) = \phi(\alpha,x)$ and $K(x)$ is given by Eq. (106) has been termed that of the α, β, Γ distribution by Aris (1989). The interesting point is that, for an α, β, Γ distribution, it is always possible to eliminate $c(x,t)$ between the equations so as to obtain an alias, that is, a function $R(\;)$ satisfying $-dC/dt = R(C)$ (Aris and Astarita, 1989a,b):

$$R(C) = F(K^*C^{(\alpha+\beta)/\alpha})C^{(\alpha+1)/\alpha}. \tag{107}$$

It is also possible to solve explicitly the inverse problem. That is, given a function $R(C)$ (which may well have been measured experimentally by working with the complex mixture), one can determine a function $F(\;)$ that will generate it:

$$F(Q) = (Q/K^*)^{-(\alpha+1)/(\alpha+\beta)}R((Q/K^*)^{\alpha/(\alpha+\beta)}). \tag{108}$$

It is interesting to consider the special case of Langmuir isotherm kinetics (Astarita, 1989b) where $F(Q) = 1/(1 + Q)$. One obtains

$$-dC/dt = C^{(\alpha+1)/\alpha}/(1 + K^*C^{(\alpha+\beta)/\alpha}). \tag{109}$$

Let's discuss Eq. (109) in some detail. First of all, it satisfies the SCI requirement, because when α approaches ∞ it yields $-dC/dt = C/(1 + K^*C)$. The intrinsic kinetics are always of nonnegative order, and approach order zero only when the reactant concentration approaches ∞. In contrast with this, Eq. (109) yields an apparent overall order of reaction that may well be negative at high C if $\beta > 1$.

Physically, the reason for this behavior is as follows. When $\beta > 0$, reactants with higher kinetic constant also have higher adsorption constant; if $\beta > 1$, the adsorption constant grows more rapidly than the kinetic constant. The reactants with the larger kinetic constant disappear first, and, while this makes the average kinetic constant a decreasing function of time, it also results in the disappearance of reactants that compete fiercely for active sites, thus making the catalyst more available. When $\beta > 1$, the latter effect is more important than the former one, and the apparent overall order of reaction at large C becomes negative.

3. *An Aside on Reversibility*

Consider again the general formulation of cooperative uniform kinetics embodied in Eq. (102). Suppose that the value of F[ ] must be nonnegative and must be zero only if the argument function $c(z, t)$ is zero. Then Eq. (102) describes irreversible kinetics, since the rate of consumption $-c_t(x, t)$ becomes zero only when $c(x, t) = 0$. However, Eq. (102) can also describe reversible kinetics. Let $c^*(x)$ be the equilibrium concentration distribution that will eventually be attained from the initial distribution $c(x, 0)$, and let $\mathbf{F}[c^*(z)] = 0$, so that the (reversible) equilibrium condition is satisfied at some nonzero $c^*(x)$. Equation (102), however, can only describe a special form of approach to equilibrium. In fact, suppose that $\mathbf{F}[c(z, 0)]$ is positive (or negative). Equation (102) now implies that the concentration of *all* reactants decreases (or increases) until $c(x, t)$ becomes equal to $c^*(x)$. This implies two things:

1. That c*(x) is smaller (or larger) than $c(x, 0)$ for all x's.
2. That equilibrium is approached monotonically; the sign of $c_t(x, t)$ cannot change

Of course, both restrictions 1 and 2 are trivially satisfied in the case of irreversible reactions, but they may not be unrealistic for some category of reversible ones. Restriction 1 could perhaps be relaxed by extending the range of the label x to negative values. The description of reversible cooperative uniform kinetics has not been attempted in the literature.

Krambeck (1994b) has observed that this way of describing reversibility is probably not physically meaningful, because, for instance, detailed balancing would not be satisfied. On the other hand, one could add a nonunity multiplying function to any example of reversible continuous linear kinetics, thus obtaining reversible uniform kinetics.

4. *Reaction Networks*

So far, only degenerate reaction networks have been considered, where reactants of, say, type A, react irreversibly (or, within rather strict specifications, reversibly) to some otherwise unspecified products. In a mixture containing very many reactants, much more structure than that may exist as far as the topology of reaction networks is concerned.

a. Parallel and Sequential Reactions. We begin the discussion by considering two very simple cases: that of sequential reactions where species of type A may react to form species of type B, and the latter may in turn react to form species of type C [say, in a continuous description, $A(x) \rightarrow B(x) \rightarrow C(x)$], and that of parallel reactions $C(x) \leftarrow A(x) \rightarrow B(x)$ where the original reactants of type A may react to form both B-type and C-type products. Furthermore, we begin by considering the simple case where the intrinsic kinetics are linear.

Let $c_A(x,t)$ and $c_B(x,t)$ be the concentration distribution of the initial reactants of type A, and of the desired products of type B. [The concentration distribution of type C components is obtained from an elementary mass balance, $c_C(x,t) = c_A(x,0) - c_A(x,t) - c_B(x,t)$.] Let $C_A(t) = <c_A(y,t)>$ and $C_B(t) = <c_B(y,t)>$ be the corresponding overall concentrations [with, again, $C_C(t) = 1 - C_A(t) - C_B(t)$]. Attention is restricted to the case where $c_A(x,0)$ is the gamma distribution $\phi(\alpha,x)$. For the sequential case (which in the context of a discrete description was discussed in 1974 by Golikeri and Luss), let x be normalized so that it is proportional to the kinetic constant of the first step. For the parallel case (which in the context of a discrete description was discussed in 1975 by Luss and Golikeri), let x be normalized to be proportional to the sum of the kinetic constants for both steps. Then $c_A(x,t)$ and $C_A(t)$ are obviously given by

$$c_A(x,t) = c_A(x,0) \exp(-xt), \tag{110}$$

$$C_A(t) = [1 + t/\alpha]^{-\alpha}, \tag{111}$$

where Eq. (111) is intended in the limiting sense $C_A(t) = -\ln t$ when $\alpha = \infty$ (single component).

For the sequential case (Aris, 1989), let $\sigma(x)$ be the (dimensionless) kinetic constant for the second step. One obtains

$$c_B(x,t) = \phi(\alpha,x)(e^{-xt} - e^{-\sigma(x)t})/(\sigma(x) - 1). \tag{112}$$

This equation can, of course, be integrated over x for any $\sigma(x)$. In the particularly simple case where $\sigma(x) = \sigma$ (a constant), one obtains (Aris, 1989):

$$(\sigma - 1)C_B(t) = (1 + t/\alpha)^{-\alpha} - (1 + \sigma t/\alpha)^{-\alpha} \tag{113}$$

which satisfies the SCI. The term $C_B(t)$ always goes through a maximum at some value of t, and hence a selectivity problem [a value of t for which $C_B(t)$ is maximized] exists both for the single component and for the mixture cases. Of course, the value of t which maximizes the selectivity still depends on α (i.e., the selectivity problem has a different solution in the mixture and in the single reactant cases).

The parallel case has been discussed by Astarita and Ocone (1991). Let $\sigma(x)$ be proportional to the kinetic constant of the $A \rightarrow C$ step, with $0 \leq \sigma(x) \leq x$. One obtains

$$c_B(x,t) = \sigma(x)\phi(\alpha,x)(1 - e^{-xt})/x. \tag{114}$$

The case where $\sigma(x)$ is a constant is trivial, but all other cases are not. For instance, suppose that $\sigma = x^2e^{-x}$, and let $(\alpha + 1)/\alpha = m$. One obtains

$$C_B(t) = m^{\alpha+1} - (m/(1 + t/m))^{\alpha+1}. \tag{115}$$

It follows that the overall selectivity $C_B(t)/C_C(t)$ is not constant in time, contrary to what happens in the single-component case. Astarita and Ocone (1991) also discuss the uniform cooperative case of parallel reactions, and the analogous analysis of the sequential case does not present substantial problems.

b. Bimolecular Reactions. Another problem where the reaction network has some topological structure is that of a system of bimolecular reactions, where every reactant may react irreversibly with any other one. In the dimensionless continuous description, this yields (Scaramella *et al.,* 1991):

$$-c_t(x,t) = c(x,t)<b(x,y)c(y,t)>, \tag{116}$$

where $b(x,y)$ is the dimensionless kinetic constant of the reaction between species x and y; $b(x,y)$ is obviously symmetric, $b(x,y) = b(y,x)$, and it has been normalized so that its average value in the initial mixture is unity:

$$<<b(y,y')c(y,0)>c(y',0)> = 1. \tag{117}$$

The cooperative kinetics described by Eq. (116) are not uniform. A reasonable approximation is to assume that, in the discrete description, the kinetic constant $k_{II'} = (k_{II}k_{I'I'})^{1/2}$, which in the continuous description reduces to $b(x,y) = xy$. This reduces Eq. (116) to cooperative uniform kinetics and, if $c(x,0) = \phi(\alpha,x)$ the solution is obtained by standard techniques as

$$-dC/dt = C^{2(\alpha+1)/\alpha}. \tag{118}$$

This equation is a generalization of the Aris (1968) result given in Eq. (98): The apparent overall order is $(\alpha + 1)/\alpha$ times the intrinsic order of 2. Scaramella *et al.* (1991) have also analyzed a perturbation scheme around this basic solution, which, incidentally, lends itself to a solution via reduction to an integral Volterra equation of the same type as discussed in Section IV,C with regard to a plug flow reactor with axial diffusion. Scaramella *et al.* have also shown that if $b(x,y)$ can be expressed as the sum of M products of the type $b(x)B(y) + B(x)b(y)$, which is a fairly general representation for a symmetric function, the solution can be obtained in terms of M warped times, which are solutions of M coupled ordinary linear first-order differential equations of the type of Eq. (104). As far as we know, this and the one given later in Eq. (123) are the only examples in the literature where a nonuniform cooperative kinetic mechanism has been approached via the introduction of a warped time technique.

An alternate approach to bimolecular systems has been developed in a series of papers by Ho and his coworkers (Chou and Ho, 1989; Ho, 1991a,b; Li and Ho, 1991a,b; White *et al.*, 1994). These authors chose a discrete description, but their analysis can easily be couched in a continuous one, so as to emphasize the comparison with the results given earlier. We base our presentation essentially on the White *et al.* paper, which is the last one of the series and includes the results of previous papers as special cases.

The emphasis of the Ho approach is on the *long time* asymptotic behavior of the system; because all the reactions are irreversible, the long time behavior is simply that both $C(t)$ and $c(x,t)$ approach zero. However, Ho and coworkers define the mole fraction distribution $X(x,t) = c(x,t)/C(t)$, and this is restricted by the obvious requirement that $<X(y,t)> = 1$, so that X necessarily stays finite at least over some range of the label x (as we will see, that range may well reduce to a point, i.e., to a single component).

Beginning with the general kinetic equation, Eq. (116), integration over the label range yields

$$-dC/dt = <c(y,t)<b(y,y')c(y',t)>. \tag{119}$$

Substituting the definition of $X(x,t)$ and rearranging yields

$$-dC/dt = \Omega(t)C^2, \tag{120}$$

where

$$\Omega(t) = <X(y,t)<b(y,y')X(y',t)>>. \tag{121}$$

Should $\Omega(t)$ approach some nonzero limiting value $\Omega(\infty)$, as it can under appropriate conditions, the overall apparent order of reaction would approach 2—contrary to Eq. (118) [which holds if $b(x,y) = xy$]. This apparent contradiction is clarified later. One can now differentiate the definition of $X(x,t)$ and rearrange to obtain

$$-X_t(x,t) = CX(x,t)(<b(x,y)X(y,t)> - \Omega(t)). \tag{122}$$

It is useful to define a warped time $\tau(t)$ as

$$\tau(t) = \int_0^t C(t')dt'. \tag{123}$$

Because $C(t)$ is positive, $\tau(t)$ approaches ∞ when t does so, and is monotonous. With this, one obtains the following autonomous integrodifferential equation:

$$\begin{aligned} -X_t(x,t) &= X(x,t)(<b(x,y)X(y,t)> \\ &\quad -\Omega(t)) = \mathbf{G}[X(z,t)], \end{aligned} \tag{124}$$

where **G**[ ] is a known functional.

It is now of interest to ask oneself whether there are one or more mole fraction distributions $X^\wedge(x)$ that are stationary points, in the sense that $\mathbf{G}[X^\wedge(z)] = 0$. First consider the case where the stationary point corresponds to the survival of only one component, say, $X^\wedge(x) = \delta(x - x^*)$. Correspondingly, $\Omega = b(x^*,x^*)$, and $<b(x,y)X^\wedge(y)> = b(x^*,x^*)$: Any such point is a stationary one. (Of course, infinitely many of such points will not in fact be reached unless one starts from them.) Now consider the special case where the kinetics are uniform, $b(x,y) = xy$. One obtains

$$\mathbf{G}[X(z)] = -X(x)[x<yX(y)> - <yX(y)>^2] \tag{125}$$

so that, since $<yX(y)>$ is always positive, at any stationary point $<yX^\wedge(y)> = x$ for all x's for which $X(x)$ is nonzero. This is clearly possible only if $X^\wedge(x) = \delta(x - x^*)$. Clearly, the surviving component is the most refractory one, $x = 0$, and that component does not react. The result is related to the strong degeneracy of the xy form for $b(x,y)$: If regarded as a continuous linear operator, xy transforms *any* function $X(x)$ into $<yX(y)>x$; we say xy has rank one. More general forms for $b(x,y)$ furnish a nontrivial geometry of possible reaction pathways $X(x,\tau)$, with nontrivial stationary points that may be stable or unstable; if more than one stable stationary point is possible, which one is reached depends on the initial distribution $X(x,0)$. White *et al.* (1994) also show that such stationary points are not approached in a spiraling way—in some vague sense, a principle of microscopic reversibility holds. Once a nontrivial stable stationary point has been reached, Ω stays at some constant value $\Omega(\infty)$, and the overall order of reaction becomes 2 again. [The degeneracy of the xy form for $b(x,y)$ can be seen also from a different viewpoint: $\Omega(\infty)$ can be zero if and only if $b(x,x)$ is zero for some x (the proof is easy). When $b(x,y) = xy$, the condition is satisfied: $b(0,0) = 0$. When $\Omega(\infty) = 0$, the overall order never becomes 2, and this is the case for uniform kinetics.]

c. Cracking. Cracking reactions have a moderately complex topology: Components with any given molecular weight within the admissible class can be formed by cracking of (almost) all higher molecular weight components, and they may in turn crack to (almost) all components of lower molecular weight. The qualification "almost" is related to the fact that there may be a lowest molecular weight formed by the cracking reactions within the class considered. For instance, in the enzymatic hydrolysis of cellulosic materials, where the end product is glucose (the "monomer"), only the dimer and higher oligomers are formed by the action of certain enzymes, while other enzymes catalyze the cracking of the dimer (see, e.g., Cicarelli *et al.,* 1992, and the literature quoted therein).

In cracking reactions, it is natural to choose as the starting label the number of monomers in the oligomer considered. Next, one may renormalize the label as the initial one divided by its average value in the initial mixture: This produces an x that, whatever the initial concentration distribution may be, makes the first moment of the initial distribution equal to unity (the zeroth moment already being unity by a trivial normalization of concentrations). A continuous description is preferable if the initial average number of monomers per oligomer is large as compared to unity. This choice of labeling, of course, makes it impossible to normalize labels so as to be proportional to the kinetic constant(s) of the cracking reactions which any given oligomer may undergo. However, it is reasonable to make the following assumptions:

1. The overall cracking kinetic constant (or, in the case of nonlinear kinetics, the overall frequency factor) is the same for all oligomers.
2. The probability of any given bond within an assigned oligomer being cleaved is the same for all cleavable bonds.
3. The kinetics are either linear or of the cooperative uniform kind described by Eq. (102).

With these assumptions, the kinetic equation becomes:

$$c_t(x,t) = [\int_{x+\epsilon}^{\infty} 2c(y,t)dy/y - c(x,t)]\mathbf{F}[c(z,t)], \qquad (126)$$

where ϵ is the minimum value of x for which the kinetics are in the class considered (in the simplest case where only the monomer does not belong to the class considered, ϵ is the inverse of the average initial value of monomers in the oligomers in the mixture). The following analysis has physical significance only if $\epsilon << 1$. Components with $x \leq \epsilon$ will be called *end products;* in the simplest case referred to earlier, the only end product is the monomer.

In Eq. (126) the first term within the square brackets represents the rate of formation of species x from higher molecular weight ones; the second term represents its rate of cracking to lower molecular weight products. With $\epsilon = 0$ and $\mathbf{F}[\ ]$ identical to unity (first-order intrinsic kinetics), Eq. (126) reduces to the form given by Aris and Gavalas (1966) in the part dealing with thermal cracking of their pioneering work on the continuous description of mixtures.

Again, it is useful to define a warped time $\tau(t)$, $\tau(0) = 0$, which is delivered by the following differential equation:

$$d\tau/dt = \mathbf{F}[c(z,t] \qquad (127)$$

so that Eq. (126) reduces to

$$c_\tau(x,\tau) = [\int_{x+\epsilon}^{\infty} 2c(y,\tau)dy/y - c(x,\tau)]. \tag{128}$$

An important point about Eq. (128) is that it shows that, in the warped time scale τ, the behavior is entirely independent of the form of the functional **F**[ ]; the latter influences only the relationship between the warped time τ and the actual time t. The case of first-order intrinsic kinetics (Aris and Gavalas, 1966) is recovered by simply setting $\tau = t$.

Cicarelli *et al.* (1992) have developed the solution of Eq. (128) by a perturbation expansion, with ϵ the perturbation parameter. They consider the special case of Langmuir isotherm kinetics, where $\mathbf{F}[\ ] = 1/(1 + \langle K(y)c(y,t)\rangle)$. At the zero-order level, $C = \exp(\tau)$. This result simply reflects the fact that, in the distorted time scale τ where the kinetics are linear, two species are formed from one at every reaction step, and hence the total concentration grows exponentially. This, however, does not include the fact that end products are being formed, and thus disappear from the spectrum of concentrations (at the zero-order level, $\epsilon = 0$ and no end products are formed). The critical warped time τ_C at which the zero-order approximation breaks down is estimated as $-\ln \epsilon$; that is, it is well in excess of unity. Even for linear kinetics, there is an induction time significantly longer than the inverse of the kinetic constant during which very few end products are formed (this is even more true for nonlinear kinetics of the type considered). The solution can be obtained formally at all levels of perturbation; the first-order level is of particular relevance because it yields (to within order ϵ) the total amount of end products formed up to the critical time.

d. Polymerization. Polymerization reactions (which are, in a vague sense, the inverse of cracking ones), are of course a typical example of kinetics in a multicomponent mixture, with the different components being the molecules of different molecular weight. Because the latter may in principle reach infinity (as indeed it does in the case of cross-linked polymers), a continuous description where the label is the (appropriately normalized) molecular weight suggests itself naturally.

The literature on the kinetics of polymerization is so ample that it is hopeless to review it here; two recent works of general interest are by Dotson *et al.* (1993) and by Gupta and Kumar (1987). Here we limit our discussion to only two very recent works in the area where a continuous description has been used (Aris, 1993; McCoy, 1993).

McCoy (1993) has considered polymerization reactions that are reversible (i.e., oligomers may depolymerize), and may be either random or proportioned fissions. If the bimolecular kinetic constant and the molar concentration based equilibrium constant K^* are the same for all steps, and if the cracking reactions only break an x-mer into two equal $(x/2)$-mers, it is rather easy to write down the continuous equations describing the kinetics, which, after the appropriate normalizations, take up the following form (Aris, 1993):

$$\begin{aligned} c_t(x,t) &= \int_0^x c(y,t)c(x-y,t)dy \\ &\quad - c(x,t)<c(y,t)> + K^*[4c(2x,t) - c(x,t)], \end{aligned} \tag{129}$$

where the first term on the right represents formation from lower molecular weight components of the x-mer, the second term represents its rate of polymerization to higher molecular weight components, the third term $4K^*c(2x,t)$ represents the rate of formation by cracking of the $(2x)$-mer, and the last term represents cracking. Equation (129) is easy to write down, but it is not at all easy to do anything with it (Aris, 1994). McCoy (1993) chooses to work with the moments of the distribution, and this leads to some moderately strong results.[18] Aris (1993) has limited attention to the case where the reactions are irreversible ($K^* = 0$) and where the mathematics are more tractable: If $c(x,0) = \phi(\alpha,x)$, a formal expression for $c(x,t)$ can be obtained. (It is rather nasty looking, but we encounter no problems when calculating it numerically.) As Aris states, "The final state is of course nothing of everything, though a little more of some things than of others. . . . another possible steady state is $c(x,t) = \delta(x)$, which is everything of nothing. But this is unstable—or, at any rate, nugatory."

e. Conclusions on Reaction Networks. The preceding discussion shows that a few simple cases where the topology of the reaction network is nontrivial can be analyzed, and formal solutions are (within bounds) possible. It also shows that as soon as some structure is assigned to the topology, the mathematics become quite complex, and therefore one concludes that there is little hope of dealing with complex topologies other than numerically. Robust numerical codes capable of dealing with such problems have still to be developed. A possibility that comes to mind is that of *lumping the reaction network;* that is, to substitute for the actual network a simpler one that, in some sense to be made precise, is either exactly or approximately equivalent to the original one. Some tentative steps in that direction have been taken (Allen, 1991; Frenklach, 1985; Froment, 1987; Vynckler and Froment, 1991), and perhaps a rigorous mathematical structure within which such problems should be couched can be found in a series of extremely interesting papers by Feinberg (1980, 1987, 1988, 1989, 1991a,b). A very concise review of some of the contents of these papers is given in Appendix C; further discussion of the Feinberg approach is given in the next section.

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[18] Krambeck (1994b) has observed that the McCoy reversible polymerization kinetics are rather artificial, and that they do not satisfy detailed balance.

5. The Number Density Function

It is useful to introduce the concept of a number density function $s(x)$ by beginning with an important point that emerges from a very recent paper by Ho and White (1994). It may be taken for granted that a continuous description of chemical kinetics is only an approximation: Real mixtures are invariably discrete. Now the approximation is certainly going to be appropriate provided the number of components in the mixture is very large. However, as time progresses, the more reactive components tend to disappear from the mixture, which essentially contains a progressively smaller number of reactants. At very long times, only the most refractory components survive, and these may well be small enough in number that the continuous approximation breaks down. Ho and White have presented a detailed mathematical analysis of this point for the special case of hydrodesulfurization, which at long times is adequately described by intrinsic first-order kinetics. They define a *spacing,* δ, along the label axis x, which essentially measures the (average) thickness of a bar of the hystogram, which is being approximated by a distribution function in the continuous description, and they show that the underlying discreteness of the real mixture becomes significant (in the sense that the continuous approximation breaks down) at dimensionless times t where $t\delta$ exceeds unity. It follows, perhaps in enough generality, that if one is interested in the very long time kinetic behavior of the system, a discrete description based on the (few) very refractory components is preferable to a continuous one.

The Ho and White (1994) analysis is based on the idea of a constant spacing δ; $1/\delta$ then represents the (very large) number of individual components that are in reality present in the mixture over a unit segment of the label axis. In a strict interpretation of the continuous description, $\delta = 0$ (this is, essentially, De Donder's 1931 approach); but of course reality is a different matter. One can define a number density function $s(x)$ such that the number of individual compounds in any interval $[x_1,x_2]$ is

$$\int_{x_1}^{x_2} s(x)dx. \tag{130}$$

One way to interpret $s(x)$ is as a stochastic frequency of occurrence of compounds along the x line. This ameliorates the concern that the integral in Eq. (130) may well not be an integer. It also gives us the courage to apply the concept of a continuous description even when the number of compounds is not all that large, often with excellent results.

Sometimes it is useful to redefine $c(x)$ to $c'(x)$, where

$$c'(x) = c(x)/s(x), \qquad \text{where } c(x) \text{ is continuous;} \tag{131}$$

$$c'(x) = c_I, \qquad \text{where } c(x) = c_I\delta(x - x_I). \tag{132}$$

This has the advantage of being invariant under any distortion of the x scale, and it makes life easier when the mixture contains, in addition to the distributed components, a small number of discrete components, and it is particularly useful in some thermodynamic analysis, where a *semicontinuous* description is often used. It is also useful to note that, since $c'(x)$ is invariant with respect to rescaling the label x, the conceptual problem discussed in Appendix B is alleviated if one uses the logarithm of $c'(x)$.

6. *Conclusion*

The discussion in this section illustrates the wealth of results available for the analysis of the overall kinetic behavior of complex mixtures. The variety of available analytical results should not, however, mask the fact that there is a large area where very little has been done, that is, the area of nonlinear kinetics which are not of the cooperative uniform type. Powerful as the assumption of uniformity has turned out to be, remember that it is a strong assumption; in Aris's (1988) words, "your assumption of uniformity . . . also takes a bit of swallowing. That you can get results, and such striking ones, makes the medicine go down." We might not always have Mary Poppins around to help us out, and, at this stage, when we don't we really don't know what to do. See Appendix C.

C. OVERALL REACTION ENGINEERING

In this section, we still restrict ourselves to the consideration of systems where only the overall behavior is of interest, but we extend the analysis to actual chemical reactors. Indeed, the discussion in the previous section was limited to the overall *kinetics* of multicomponent mixtures; seen from the viewpoint of chemical reaction engineering, the discussion was in essence limited to the behavior in isothermal batch reactors, or, equivalently, in isothermal plug flow reactors. In this section, we present a discussion of reactors other than these two equivalent basic ones. The fundamental problem in this area is concisely discussed next for a very simple example.

Suppose one has performed experiments with the mixture under consideration in a batch reactor, and one has obtained experimentally the overall kinetics—the $R(\,)$ function such that $dC/dt = -R(C)$. For instance, one could obtain $R(C) = C^2$ if the intrinsic kinetics are in fact first order and the initial concentration distribution is $\phi(1,x) = \exp(-x)$. If one were to regard $R(C)$ as a *true* (rather than an apparent) kinetic law, one would conclude that in a CSTR with dimensionless residence time T the exit overall concentration is delivered by the (positive) solution of $TC^2 + C = 1$. The correct value is in fact $C = \langle \exp(-y)/(1 + Ty) \rangle$, and the difference is not a minor one. (To see that easily, consider the long time asymptote, $T >> 1$. The positive solution of $TC^2 + C = 1$ yields $C = T^{-1/2}$, while the actual behavior is $C = \ln T/T$.)[19] What this implies is that, once an apparent overall kinetic function $R(C)$ has been determined experimentally, one needs to perform the following steps.

First, one needs to deconvolute $R(C)$ into some appropriate intrinsic kinetic law. What form the latter might take be suggested by experiments performed with single components.

Next, one needs to use the intrinsic kinetics as the basis for the analysis of a reactor other than a batch or plug flow reactor.

In this section, we restrict our analysis to the second step of this procedure. The nomenclature we use is as follows: $c_F(x)$ is the concentration distribution in the feed to any given reactor, normalized so that $<c_F(y)> = <yc_F(y)> = 1$, and $c_E(x)$ is the corresponding distribution in the product stream. Let $C = <C_E(y)>$ is the overall residue. Finally, let T be the dimensionless residence time in the reactor, that is, the actual residence time times the average value of the frequency factor in the feed mixture.

1. The CSTR

The simplest reactor which is not a batch or a plug flow one is obviously the CSTR. The mass balance for component x is, if the kinetics are of the cooperative uniform type (Astarita and Nigam, 1989),

$$c_F(x) - c_E(x) = Txc_E(x)\mathbf{F}[c_E(z)]. \qquad (133)$$

A warped time technique is again useful. Let the warped dimensionless residence time W be defined as

$$W = T\mathbf{F}[c_F(z)/(1 + Wz)]. \qquad (134)$$

The solution of Eq. (133) is, as can be checked by substitution,

$$c_E(x) = c_F(x)/(1 + Wx), \qquad (135)$$

$$C = <c_F(y)/(1 + Wy)>. \qquad (136)$$

The whole problem has thus been reduced to the solution of Eq. (134), which is a functional equation for the single scalar W. It is, however, a nasty functional equation, not so much for the possible nonlinearity of the functional $\mathbf{F}[\ ]$ itself, but because the argument function is nonlinear in the unknown W. The warped time technique is again useful, but, contrary to what happens in the single-component case, the solution for the CSTR is more difficult than the one for the plug flow reactor or batch reactor.

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[19] This should be contrasted with the result discussed in the second paragraph after Eq. (101): Overall kinetics are far from being exact lumping, and they do not carry over to different reactor types.

a. First-Order Intrinsic Kinetics. For first-order intrinsic kinetics, the solution of Eq. (134) is trivial, since **F**[ ] = 1 and $W = T$, so that the problem reduces to the evaluation of the integral on the right side of Eq. (136), which can of course always be obtained numerically with simple codes that are guaranteed to converge. Also, notice that, when $c_F(x) = \delta(x - 1)$ (the single-component case), Eq. (136) yields $C = 1/(1 + T)$, which is known to be the correct result. Now, more generally, suppose that $c_F(x) = \phi(\alpha,x)$. The integral on the right side of Eq. (136) can be expressed formally in terms of known functions if α is an integer (Astarita and Nigam, 1989). More generally, an expansion is possible for both low and high values of W. Remembering that W is known for first-order kinetics, one obtains

$$W << 1, \qquad C/(1 - C) = 1/W, \tag{137}$$

$$W >> 1, \qquad \begin{cases} C/(1 - C) = \alpha/(\alpha - 1)W, & \alpha > 1. \\ C/(1 - C) = \ln W/W, & \alpha = 1 \end{cases} \tag{138}$$

For a single component ($\alpha = \infty$), one has for all W's $C/(1 - C) = 1/W$ or, equivalently, $C = 1/(1 + W)$, which is known to be the correct result.

Aris (1991a) has analyzed the case of M CSTRs in series, each one endowed with the same residence time T/M. This is one of the homotopies spanning the range between a PFR and a CSTR: When $M = 1$, one has a CSTR, and when M approaches ∞ one has a PFR. The result is

$$C = <\phi(\alpha,y)/(1 + Ty/M)^M>, \tag{139}$$

where the right side is $(\alpha M/T)^\alpha$ times the Tricomi form (Abramowitz and Stegun, 1965; Tricomi, 1954) of the confluent hypergeometric function of α, $1 + \alpha - M$, $\alpha M/T$. It is easy to convince oneself that, when M approaches ∞, one indeed recovers the result of a PFR, and, quite obviously, one recovers Eq. (136) when $M = 1$.

b. Cooperative Uniform Kinetics. When the intrinsic kinetics are of the cooperative uniform type, the equations given earlier in terms of W still hold, but the solution is not completed until Eq. (134) has been solved for w. Astarita and Nigam (1989) have presented a general technique for solving that is based on the use of easily constructed robust numerical codes for the appropriate subproblems, and a graphical technique for the final solution. The case of M CSTRs in series has not been considered in the literature; the problem is not a trivial one, because even if the residence time in each reactor is T/M, the value of W is not the same in all reactors, and Eq. (134) would need to be solved for every reactor in the chain.

Astarita and Nigam (1989) have calculated the $C(T)$ curves for CSTRs for a few specific nonlinear kinetic functions. Their results clearly show that the difference between the value of T needed to achieve an assigned conversion in a CSTR and a PFR is, in the case of mixtures, very significantly larger than in the case of a single component with parameters having the average value of the feed mixture. The effect is particularly striking in the case of bimolecular reactions.

2. *Maximum Segregation Reactors*

We now move to the consideration of reactors with an assigned residence time distribution (RTD) $f(t)$, where t is the dimensionless residence time (i.e., the dimensional one times the average frequency factor in the feed). In this section, we indicate with curly braces integrals over t ranging from 0 to ∞. Then $\{f(t)\} = 1$ and $T = \{tf(t)\}$. We also make use of the complementary cumulative RTD, $F(t)$, which is defined as

$$F(t) = \int_t^{\infty} f(t')dt'; \qquad F(0) = 1. \tag{140}$$

Now consider a maximum segregation reactor (Danckwerts, 1958; Zwietering, 1959). Let $C = p(t)$ be the overall concentration in a batch reactor at time t. (This can be calculated for linear and for cooperative uniform kinetics.) Then the product overall concentration in a maximum segregation reactor is easily calculated as (Aris, 1989)

$$C = \{f(t)p(t)\}. \tag{141}$$

Because $p(t) = <c(y,t)>$, the right side of Eq. (141) is a double integral over both x and t, and this can be reconducted to a double-label formalism if the second label is regarded as distributing over residence times (Aris, 1989). Of course, one expects Eq. (141) to hold for *any* degree of micromixing if the intrinsic kinetics are first order, but this remains to be demonstrated.

3. *Maximum Mixedness Reactors*

In the case of a maximum mixedness reactor, one works best with the life expectancy b. The life expectancy distribution in the feed stream, $f(b)$, is exactly the same as the residence time distribution in the product stream, $f(t)$. One can generalize the Zwietering (1959) equation for a maximum mixedness reactor to the case of continuous mixtures (Astarita and Ocone, 1990) to obtain the following functional differential equation for $c(x,b)$:

$$\begin{aligned} c_b(x,b) = {} & xc(x,b)\mathbf{F}[c(z,b)] + f(b)[c(x,b) \\ & - c_F(x)]/F(b), \end{aligned} \tag{142}$$

where the quantity $f(b)/F(b)$ is the intensity function discussed by Shinnar (1993), that is, the residence time distributions of those elements that are still in the reactor.

Solving Eq. (142) poses some difficulties even for the case of a single component; indeed, recent literature on the subject deals with this (Astarita, 1990; Astarita and Ocone, 1993; Cicarelli and Astarita, 1992; Glasser *et al.*, 1987; Glasser and Jackson, 1984; Guida *et al.*, 1994a; Jackson and Glasser, 1986). The solution procedure usually recommended in the literature (see, e.g., Froment and Bischoff, 1990) is in fact applicable only if the limit of the intensity function $f(b)/F(b)$ for b approaching ∞ exists—which may well not be the case, as the counterexample of a plug flow reactor with recycle shows. In spite of these difficulties, Eq. (142) can be solved in general, if only formally.

The warping procedure is again useful. In this case we apply it to the life expectancy b by defining a warped life expectancy β, which is delivered by the following differential equation:

$$d\beta/db = \mathbf{F}[c(z,b)]; \qquad \beta(0) = 0. \tag{143}$$

Since the value of $\mathbf{F}[\;]$ is nonnegative, $\beta(b)$ is invertible, $b = b(\beta)$, and one may define a warped life expectancy distribution:

$$q(\beta) = f(b(\beta))db/d\beta. \tag{144}$$

With this, a formal solution for $c(x,b)$ can be obtained:

$$c(x,b) = \frac{c_F(x)e^{x\beta(b)}}{F(b)} \int_\beta^\infty q(b')e^{-xb'}db'. \tag{145}$$

In the case of first-order kinetics, $\mathbf{F}[\;] = 1$, $\beta = b$, $q(\;) = f(\;)$, and Eq. (145) reduces to

$$c(x,b) = \frac{c_F(x)}{F(b)} \int_b^\infty f(b')e^{-xb'}db'. \tag{146}$$

The exit stream corresponds to $b = 0$, and hence one obtains

$$c_E(x) = c_F(x)\{f(b)e^{-xb}\}, \tag{147}$$

$$\begin{aligned} C &= \langle c_F(y)\{f(b)e^{-yb}\}\rangle \\ &= \{f(b)\langle c_F(y)e^{-yb}\rangle\} = \{f(b)p(b)\}; \end{aligned} \tag{148}$$

that is, as expected, the result is the same as for a maximum segregation reactor.

Going back to the nonlinear case governed by Eq. (145), the distribution in the product stream and the residual are

$$c_E(x) = c_F(x)\{q(b)e^{-xb}\}, \tag{149}$$

$$C = \{q(b)\langle c_F(y)e^{-yb}\rangle\}; \tag{150}$$

that is, the product stream has the same composition one would have in a maximum segregation reactor should the intrinsic kinetics be linear and the RTD be

$q(t)$: All nonlinearities have been buried in the function $q(\,)$. The result is deceivingly simple, because the function $q(b)$ is delivered by the solution of a formidable nonlinear functional differential equation.

Astarita and Ocone (1988) have analyzed a few special cases, and they have shown that for some kinetic schemes the maximum mixedness reactor at large total residence times may give a better overall conversion than the maximum segregation one with the same RTD, even for intrinsic kinetics that would never yield this result for a single component. This shows that the overall behavior of mixtures responds differently than single reactants to changes in the degree of micromixing.

4. *Nonisothermal Reactors*

So far, temperature has never entered the kinetic or reaction engineering equations, since we have essentially restricted our attention to isothermal systems. Of course, real reactors are seldom, if ever, isothermal. The problem of nonisothermality in multicomponent mixtures was considered in 1966 by Aris and Gavalas, and a discussion based on a discrete description was presented in 1972 by Golikeri and Luss, but after that nothing new seems to have appeared in the literature until the 1991 paper by Aris, who considered the rather special case of an adiabatic batch reactor. Aris (1991a) has identified the fundamental problem for nonisothermal reactors: Individual species cannot be simply identified with the frequency factor (or, in the nonisothermal terminology, the preexponential factor); one also needs to assign the activation energy. Hence, a two-label formalism is forced on the problem, with, say, x being proportional to the preexponential factor and x' to the activation energy.

This makes things complicated enough that even in the case of first-order kinetics there is more mathematical structure than one may wish for, and only that case has been considered in the literature. The following discussion is based on a paper by Cicarelli and Aris (1994), which provides a preliminary approach to the problem of a continuous mixture reacting with intrinsic first-order kinetics in a nonisothermal CSTR. As has been known since the pioneering work of Van Heerden (1958), this problem is far from being trivial even for a single reactant; in the case of mixtures, one has to deal with two distributions, one over x and one over x', which are justified on physical grounds, for example, for problems of coal gasification (Anthony and Howard, 1976; Pitt, 1962) and of heterogeneous catalysis (Brundege and Parravano, 1963).

Again making use of the powerful gamma distribution $\phi(\,)$, one could in general consider the case where the feed stream concentration distribution is given by

$$c_F(x,x') = \phi(\alpha,x)\phi(\alpha',x'). \tag{151}$$

However, Cicarelli and Aris (1994) limit attention to the case where only one of the variables is distributed (i.e., to the cases where either α or α' is ∞), so that, after the appropriate normalizations, we obtain

$$c_F(x,x') = \phi(\alpha,x)\delta(x' - 1), \quad \text{distributed over the frequency factors, DFF,} \tag{152}$$

$$c_F(x,x') = \phi(\alpha',x')\delta(x - 1), \quad \text{distributed over the activation energies, DAE.} \tag{153}$$

The mathematics involved are somewhat cumbersome, and numerical techniques are needed. The conclusions reached are the following ones:

1. *DAE case.* Even at $\alpha' = 20$, the steady-state multiplicity curves (Regenass and Aris, 1965) are not very close to those of a single component ($\alpha' = \infty$). The region of multiplicity seems to increase as α' increases, that is, in parameter space the single component case is the most likely to result in multiplicity.
2. *DFF case.* The curves are less sensitive to the value of α than they are to the value of α' in the DAE case; the qualitative behavior is, however, the same.
3. An infinity of multiple steady states (which in principle could exist in a mixture containing infinitely many reactants) is in fact attainable only for degenerate cases. For the DAE case the probability of getting an infinity of multiple steady states increases when α' decreases, but at the same time the region where they may occur shrinks until in the limit it becomes a single point in parameter space.

5. *Multiplicity of Steady States*

Multiple steady states as discussed in the previous subsection are related to the nonisothermicity of the CSTR. However, even in the isothermal case, a CSTR is known to be able to exhibit multiple steady states, periodic orbits, and chaotic behavior for sufficiently complex reaction network structures (see, e.g., Gray and Scott, 1990). When the number of reactions is very large, the problem becomes a formidable one. In a series of papers (Feinberg 1987, 1988, and the literature quoted therein), Feinberg and his coworkers have developed a procedure for CSTRs that can be applied to systems with arbitrarily large numbers of reactants and reactions. The procedure is based on the deficiency concept discussed in Appendix C.

First, one constructs an "augmented" reaction network by adding reactions of the type $0 \rightarrow A$, which represent addition of A to the CSTR via the feed stream, and reactions of the type $A \rightarrow 0$ representing removal of A in the product stream. Next, the deficiency of the augmented network is calculated (with "0" a complex which, by definition, is compatible with A). If the deficiency is zero, the strong deficiency zero theorem (Feinberg, 1987) applies: Provided the kinetics are of the mass action type, no matter what (positive) values the kinetic constants may have, the CSTR cannot exhibit multiple steady states, unstable steady states, or periodic orbits. The result is, in a sense, very strong because the governing differential equations may well constitute a gigantic nonlinear system. In another sense the result is not so strong, because "augmented" networks for CSTRs are almost never of deficiency zero, unless all the "true" chemical reactions are first-order ones.

If the deficiency of the augmented network is one, the results are less strong, but still very important. (It is important to realize that CSTRs where heterogeneous catalysis reactions occur, so that many species are not present in the product stream, often turn out to have deficiency one.) For a subclass of such systems, multiple steady states are impossible, but a single unstable steady state and a periodic orbit are possible. Outside of this subclass, the theory becomes delicate, and one has to make calculations based on an algorithm for the analysis of the topology of the reaction network. The algorithm, however, is now available on diskette (Feinberg, 1994).

It turns out that if a substantial fraction of the reactions involve adsorbed species on a catalyst (these are compounds that do not exit the reactor with the product stream), the deficiency is likely to be zero or one (but see the discussion in Appendix C). For homogeneous CSTRs, where all components are carried out by the product stream, it is easy to have high deficiencies, and the deficiency-oriented Feinberg method offers little advantage.

However, recent work by Schlosser and Feinberg (1994), which is specifically tailored for the analysis of homogeneous CSTRs, takes a completely different approach, where the possibly high deficiency of the augmented reaction network is no problem at all. The Schlosser–Feinberg method is based on the construction of a diagram called the species-complex-linkage (SCL) graph. The method is restricted to homogeneous CSTRs (where all species are present in the product stream), and in this sense it is less powerful than the deficiency-based theory. On the other side, for homogeneous CSTRs the method works for any value of the deficiency of the augmented network (if it works at all): It can tell whether multiple steady states are possible.

The Schlosser and Feinberg approach is based on the analysis of the geometrical topology of the true (not augmented) reaction network; all individual reactions are assumed to be governed by mass action kinetics. (This is a strong, if realistic, assumption: for instance, it implies that the reaction 2A = 2B is not the same thing as the reaction A = B.) The 1994 paper does not contain formal (or even informal) proofs. It gives elementary examples and counterexamples for almost all of the stated results, and the best we could do here is to essentially reword their presentation; hence we simply refer the reader back to that paper; proofs of the theorems can be found in Schlosser's thesis (1988). Their results are of three types:

1. For certain reaction networks (which can easily be identified from an analysis of the geometry) multiple steady states are impossible. For a comple-

mentary class multiple steady states (for *some* values of the residence time and the kinetic constants) are not excluded, but they are by no means guaranteed to be possible.
2. For those cases where only one stable steady state is possible, sustained oscillations cannot be excluded (the single steady state may be unstable). For a restricted class of reaction networks, stability (or lack thereof) of the single steady state can be demonstrated.
3. For some specific geometries of the reaction network, the possibility of multiple steady states for some appropriate set of values of the parameters is guaranteed.

An alternate approach to the analysis of the network geometry from the viewpoint of multiplicity and stability is due to Beretta and his coworkers (1979, 1981); the latter approach is based on knot theory. The Schlosser–Feinberg theory reproduces some of the Beretta-type theory results concerning stability from a somewhat different viewpoint.

There are many (otherwise unremarkable) instances of reaction networks where the Schlosser and Feinberg method gives no answer. Multiple steady states are not excluded but are not guaranteed to be possible either. In actual fact, multiplicity of steady states in isothermal homogeneous CSTRs has seldom been observed. This suggests, as Schlosser and Feinberg conclude, "the existence of as yet unknown theorems which, like theorem 4.1, deny the capacity for multiple steady states but which have an even wider range."

6. Homotopies between the CSTR and the PFR

Aris (1991a), in addition to the case of M CSTRs in series, has also analyzed two other homotopies: the plug flow reactor with recycle ratio R, and a PFR with axial diffusivity and Peclet number P, but only for first-order intrinsic kinetics. The values $M = 1(\infty)$, $R = \infty(0)$, and $P = 0(\infty)$ yield the CSTR (PFR). The M CSTRs in series were discussed earlier in Section IV,C,1. The solutions are expressed in terms of the Lerch function for the PFR with recycle, and in terms of the Niemand function for the PFR with dispersion. The latter case is the only one that has been attacked for the case of nonlinear intrinsic kinetics, as discussed below in Section IV,C,7,b. Guida *et al.* (1994a) have recently discussed a different homotopy, which is in some sense a basically different one; no work has been done on multicomponent mixture systems in such a homotopy.

7. Interference with Diffusion

The discussion in Section IV,B, as well as many of the arguments just given, show how powerful the procedure of warping the time scale is. Unfortunately, the procedure cannot be extended to problems where diffusion interferes with the reaction, since in the latter case there are two time scales (the reaction time and the diffusion time), and one may warp but not the other. There are two other ways of looking at the same problem. First, the warping procedure is used to linearize the kinetic equation; the procedure does not carry over to second-order differential equations such as those that arise when diffusion is taken into account (Aris and Astarita, 1989a,b). Second, as long as the governing equations are, for their differential part, first-order ones, the problems are hyperbolic and the method of characteristics can be used (Guida, 1994); when diffusion is included, the equations become parabolic and the technique does not work anymore. In the context of a discrete description, the problem had been identified in 1971 by Luss and Hutchinson.

a. Porous Catalysts. The (apparently—but there are subtleties involved) simplest problem where diffusion plays a role is the classical problem of the effectiveness factor in a porous catalyst. This problem was analyzed by Golikeri and Luss (1971), who restricted their attention to independent kinetics, which were shown to be a rather special and possibly unrealistic case in Section IV,B. A discrete description was considered as early as 1962 by Wei (1962a,b); this is restricted to systems of first-order reactions, and the analysis is couched in terms of a lumping scheme. The same approach has also been discussed by several authors, and a recent analysis is included in the paper by Li and Rabitz (1991c). The continuous description for the case of cooperative kinetics was analyzed by Ocone and Astarita (1993), and the following discussion is based on that paper.

Because a warped time technique does not carry over to second-order differential equations such as the ones arising when diffusion plays a role, the assumption of uniformity simplifies the mathematics involved only marginally. Let Eq. (102) be assumed as correctly describing the kinetics, with the parameter t being the dimensionless distance into the flat slab catalyst (complications arising for more realistic geometries of the catalyst pellet are easily dealt with). Furthermore, assume that the diffusivity of all reactants is the same (again, this assumption is easily relaxed), and let Φ be the overall Thiele modulus; that is, its square equals the average frequency factor in the external concentration distribution $c_F(x)$ times the square of the catalyst half-width and divided by the diffusivity. The differential equation and boundary conditions of the problem are

$$c_{tt}(x,t) = \mathrm{q}\ \Phi^2 x c(x,t) \mathbf{F}[c(z,t)], \tag{154}$$

$$c(x,0) = c_F(x), \tag{155}$$

$$c_t(x,1) = 0. \tag{156}$$

The case of intrinsic first-order kinetics, **F**[ ] = 1, is easily solved. Let $h(x)$ be the effectiveness factor for reactant x; one simply obtains the obvious extension of the single reactant result:

$$h(x) = tgh(\Phi\sqrt{x})/\Phi\sqrt{x}. \tag{157}$$

The overall effectiveness factor H [which is *not* equal to $<h(y)>$] is given by

$$H = <c_F(y)\sqrt{y}tgh(\Phi\sqrt{y})>/\Phi, \tag{158}$$

which is not equal to the single-component effectiveness factor. For small values of Φ, one obtains

$$H = 1 - \Phi^2<y^2c_F(y)>/3 + 0(\Phi^4), \tag{159}$$

which shows that one recovers the single-component result $H = 1$ only within $O(\Phi^2)$, since in general $<y^2c_F(y)>$ will be different from unity except in the single-reactant limit where $c_F(x) = \delta(x - 1)$. This can easily be seen if $c_F(x) = \phi(\alpha,x)$, where one gets $H\Phi = \Gamma(\alpha + 1/2)/\Gamma(\alpha)\sqrt{\alpha}$, which reduces to $H\Phi = 1$ only when α approaches ∞.

The case of cooperative uniform kinetics cannot be approached by warping the axial position t. A perturbation expansion is, however, useful for small values of Φ. The perturbation is a regular one, and deviations form the zero-order result $H = 1$ can be obtained. It turns out that if the apparent overall order of reaction (Astarita, 1989) at the distribution $c_F(x)$ is negative (which it may well be even if the intrinsic order is positive), the first-order correction for H is positive. That is, at a moderately small Thiele modulus the overall effectiveness factor is larger than unity. The perturbation expansion in the other limit of small values of $1/\Phi$ is a singular one (the perturbation parameter multiplies the highest order derivative). The outer solution is trivial but useless: c is simply zero at all levels of perturbation, reflecting the physical fact that at large Thiele moduli most of the catalyst is not reached by the reacting mixture. The inner (boundary layer) solution reproduces the entire problem, in the form that would apply to an infinitely deep catalyst. While this tells us that $H\Phi$ is going to approach some constant value, the procedure does not yield that value. A formal solution has been provided by Ocone and Astarita (1993), but it requires the solution of a highly nonlinear integrodifferential equation, and it is therefore of little practical use.

A different approach to the estimation of the overall effectiveness factor in porous catalysts was recently presented by Ho *et al.* (1994). These authors analyze the case of parallel bimolecular reactions, a case that is in general not one of uniform kinetics. Rather than trying to solve the coupled set of differential equations, Ho *et al.* chose to search directly for upper and lower bounds to the overall effectiveness factor, which are found by reducing the problem to that of finding the effectiveness factor for a single second-order reaction. The bounds can be estimated if information is available on the average and the spread of the individual Thiele moduli.

b. Flow Reactor with Axial Diffusion. For this problem, in addition to diffusion and reaction (which are present also in the porous catalyst problem), there is also convection; this, somewhat surprisingly, makes the analysis easier (Guida *et al.*, 1994b). Let P be the ratio of the diffusivity (again assumed to be the same for all reactants) to the product of velocity and reactor length, and let t again be the dimensionless distance from the inlet. The differential equations and boundary conditions are, if Eq. (140) is used for the kinetics:

$$Pc_{tt}(x,t) = c_t(x,t) + xc(x,t)\mathbf{F}[c(z,t)], \tag{160}$$

$$c_{\mathrm{F}}(x) = c(x,0) - Pc_t(x,0), \tag{161}$$

$$c_t(x,1) = 0. \tag{162}$$

This is a rather nasty problem to solve numerically, because boundary conditions over the whole range of x are assigned at $t = 0$ and $t = 1$. A perturbation expansion around $1/P = 0$ yields, as expected, the CSTR at the zero-order level; at all higher orders, one has a nested series of second-order linear nonhomogeneous differential equations that can be solved analytically if the lower order solution is available. The whole problem thus reduces to the solution of Eq. (133), which has been discussed before. This is, of course, the high-diffusivity limit that corresponds to a small Thiele modulus in the porous catalyst problem.

The limit $P = 0$ is again singular, but the perturbation expansion can be carried out usefully. The outer solution yields, at the zero-order level, the PFR, for which the solution is available. At every higher order level, one obtains a linear nonhomogeneous first-order integrodifferential equation, which can be reduced to a complete Volterra integral equation; numerical techniques that are guaranteed to converge can easily be set up for the solution. The inner (boundary layer) solution, which is a minor correction near the reactor exit, is an easy problem, since within the boundary layer convection and diffusion balance each other and the nonlinear kinetic term disappears from the equations.

8. *Conclusion*

Astarita (1991) presented a number of problems in chemical reaction engineering from the overall viewpoint in a continuous description, and this was discussed again in 1992 by Astarita and Ocone. Some moderate progress has been made since then in the solution of this kind of problem, but much still needs to be done. In particular, published analyses make use of old, traditional concepts of chemical reaction engineering, such as the RTD, micromixing versus macromixing, and so on; this is not the most modern approach in chemical reaction engineering (see, e.g., the ample literature on the significance of the RTD concept: Evangelista *et al.*, 1969; Glasser *et al.*, 1973; Hildebrand *et al.*, 1990; Leib *et al.*, 1988; Naor and Shinnar, 1963; Shinnar et al. 1972, Shinnar and Rumschintzki, 1989; Silverstein and Shinnar, 1975, 1982; Weinstein and Adler, 1967), but the science of chemical reaction engineering of complex mixtures is still in its infancy, and therefore it is not surprising that so far it has been developed on the basis of rather old concepts of reactor analysis.

APPENDIX A: ORTHOGONAL COMPLEMENT

Consider the three-component system formed by the three xylene isomers. This is clearly a merization system, and all values of **m** are stoichiometrically accessible from any initial **M**. There is only one vector (to within multiplication by an arbitrary scalar) to which all reactor vectors $\mathbf{m}_1 - \mathbf{m}_2$ are orthogonal, and that is $\mathbf{a}_1 = \mathbf{I}$; hence, in this case $C = 1$.

A slightly more complex case is that of a mixture of olefins that can only undergo reaction with ethylene:

$$C_{xH}2x + C_2H_4 = C_{x+2}H_{2x+4}, \qquad x = 0, 1, \ldots . \tag{163}$$

Again, **I** is a vector to which all reaction vectors $\mathbf{m}_1 - \mathbf{m}_2$ are orthogonal. However, in this case the total mass of odd-valued x-olefins is also constant, and hence one has also a second basis vector in the orthogonal complement:

$$\mathbf{a}_2 = \{0, 1/3, 0, 1/5, \ldots\}. \tag{164}$$

Notice that x has no upper bound: $C = 2$ even when the number of different olefins in the system approaches infinity. Also notice that the balance of hydrogen does not yield any new linear constraint, in addition to the carbon balance. Finally, note that even if only one disproportionation reaction is allowed, leading from an odd- to an even-numbered olefin, $C = 1$ and the system is a merization one.

APPENDIX B

Consider the discrete equivalent of Eq. (21) so that $G^{ID}/RT = \Sigma X_I \ln X_I < 0$. First of all, it is interesting to determine what is the logical status of this equation (which, in most textbooks on thermodynamics, is derived either from an argument in statistical mechanics, or from consideration of the so-called Van't Hoff box with ideal gases and semipermeable membranes involved in the derivation). Let g^{MIX} be the total dimensionless free energy of mixing, $g^{\mathrm{MIX}} = n_{\mathrm{T}}G^{\mathrm{MIX}}/RT$, where n_{T} is the total number of moles, and let μ_I be the dimensionless chemical potential of component I. We have, to within an irrelevant linear term,

$$g^{\mathrm{MIX}} = \Sigma n_I \mu_I. \tag{165}$$

We want to write as simple a form as possible for the dependence of the chemical potentials on composition, and we want to define as "ideal" a mixture that satisfies this condition (hence the superscript ID). We impose the following requirement: The chemical potential of some component J depends only on the mole fraction of J itself, $\mu_J = f(X_J)$, with the function $f(\ )$ being the same for all components. This is clearly the simplest possible form. We obtain

$$g^{\mathrm{ID}} = \Sigma n_I f(X_I). \tag{166}$$

Now the Gibbs–Duhem equation must be satisfied (recall that the Gibbs–Duhem equation is a simple consequence of the fact that the function, or functional, that delivers the free energy is homogeneous to the first degree; see Section V). For arbitrary δn_I resulting in some $\delta\mu_I$, one must have

$$\Sigma n_I \delta\mu_I = 0. \tag{167}$$

If the δn_I are of the form $x_I \delta n_{\mathrm{T}}$, the Gibbs–Duhem equation would be trivially satisfied since $\delta\mu_I = 0$ for all I's. Now suppose the δn_I sum to some nonzero δn_{T}. One can define new δn_I's as the original ones minus $x_I \delta n_{\mathrm{T}}$, and these would result in the same $\delta\mu_I$'s, but their sum would be zero. It follows that one only needs to make sure that the Gibbs–Duhem equation is satisfied for all sets of δn_I that satisfy $\Sigma \delta n_I = 0$. If Eq. (166) is to hold, one has

$$\delta\mu_I = f'(X_I)\delta n_I / n_{\mathrm{T}}. \tag{168}$$

When this is substituted into Eq. (167), one obtains:

$$\Sigma X_I f'(X_I)\delta n_I = 0. \tag{169}$$

Equation (169) must hold for arbitrary δn_I satisfying $\Sigma \delta n_I = 0$, and clearly the only possibility is that $f'(X_I) = 1/X_I$, that is, $f(X_I) = \ln X_I$. The logarithmic form is the only one that satisfies the stated conditions, and hence the discrete equivalent of Eq. (21) simply follows from the definitions. Clearly, the argument can be generalized to a continuous description [one only needs to apply the Gibbs–Duhem equation in its continuous formulation to a $\delta n(x)$ satisfying $<\delta n(y)> = 0$], and hence Eq. (21) is identified as simply the *definition* of a continuous ideal mixture.

However, going back to the discrete description, consider the special case where all the mole fractions are equal to each other, $X_I = 1/N$; this composition maximizes the absolute value of $\mathrm{G}^{\mathrm{ID}}/RT$. One obtains $\mathrm{G}^{\mathrm{ID}}/RT = \ln(1/N)$, and one seems to have a problem with N approaches infinity: $\mathrm{G^{ID}}/RT$ approaches $-\infty$, if only logarithmically.[20]

The continuous generalization of the case $X_I = 1/N$ would seem to be one where $X^{\mathrm{F}}(x)$ is constant, and this seems to create a problem, as discussed later. Now consider the case where $X^{\mathrm{F}}(x)$ equals the gamma distribution $\phi(\alpha,x)$. One calculates

$$\begin{aligned}\mathrm{G^{ID}}/RT &= \ln[\alpha^{\alpha}/\Gamma(\alpha)]\\ &+ (\alpha - 1)<\phi(\alpha,y) \ln y> - \alpha.\end{aligned} \tag{170}$$

When $\alpha = 1$ (an exponential distribution) one gets $\mathrm{G^{ID}}/RT = -1$. When $\alpha > 1$, $<\phi(\alpha,y) \ln y>$ is guaranteed to converge and there is no problem. However, when $0 < \alpha < 1$, $<\phi(\alpha,y) \ln y>$ does not converge. This implies that a mole fraction distribution, if representable as a gamma function, is only legitimate for $\alpha \geq 1$. More generally, any mole fraction distribution is subject to the condition that $\mathrm{G^{ID}}/RT$ as given by Eq. (21) is finite.

The conceptual point is as follows. The discrete case $X_I = 1/N$ requires the mole fractions of all components to be equal to each other. That does *not,* however, correspond to a constant $X^{\mathrm{F}}(x)$ in the continuous description, because $X^{\mathrm{F}}(x)dx$ is the mole fraction of species between x and $x + dx$, and one would need to require $X^{\mathrm{F}}(x)dx$ to be constant. But this can only be done if one has chosen a specific scaling for the label x: Any label x^* that is given by a monotonous function $x^*(x) = x^*$ would be legitimate, and of course $X^{\mathrm{F}}(x)dx$ could be taken as constant for only one such scale. In other words, in a continuous description one has chosen some label x. The form of the mole fraction distribution must then satisfy certain constraints such as the one discussed earlier for the gamma distribution. The problem is related to the more general problem of the correct generalization to a continuous description of nonlinear formulas.

Indeed, consider the following (largely heuristic) argument. The generalization discussed earlier of the definition of an ideal mixture to the continuous description makes use of the implicit idea that $<n(y)>$ is finite. This seems so trivial that it does not need any discussion, but there is a subtlety involved, which is reminiscent of the so-called "thermodynamic limit" in classical statistical mechanics. Consider a box of volume V at some given temperature and pressure, such that it contains exactly 1 mol of an ideal gas (the problem discussed arises already with ideal gases); that is, it contains $\mathbf{N}$ molecules, where $\mathbf{N}$ is Avogadro's number. If we wish the mole fractions of all components to be the same, the largest number of components that can be squeezed into the box is $\mathbf{N}$ (there is just

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[20] The problem arises also if the mole fractions are not all equal to each other. Let a_I be defined as NX_I. One obtains $\mathrm{G^{ID}}/RT = \Sigma a_I \ln a_I + \ln(1/N)$, where the first term is always finite and in fact small, because $\Sigma a_I = N$. The offending term $\ln(1/N)$ cancels in all phase equilibria calculations.

one molecule of every component). In other words, the number of components in any given system cannot exceed the number of molecules in it. This in turn implies that the number of components may really approach infinity only if the total mass of the system also approaches infinity and, hence, that, at least in principle, one cannot take $<n(y)>$ to be finite. The continuous description can only be seen as an approximation to a discrete description—if based on a number of components, which may be as large as Avogadro's number (which is very large indeed).

APPENDIX C: THE FEINBERG APPROACH TO NETWORK TOPOLOGY

Feinberg bases his approach on the concept of *complex,* which is originally due (in its explicit form) to Horn and Jackson (1972), and which can be traced back in a more implicit form to the work of Krambeck (1970). Complexes are groupings of components that can appear in any given reaction; for instance, in the (molar-based described) reaction

$$A_1 = A_2 + A_3, \tag{171}$$

A_1 and $A_2 + A_3$ are complexes. Let N' be the total number of complexes in any given reaction network.

Next, Feinberg introduces the concept of *linkage class.* A linkage class is a group of complexes that can be formed from one another. Say, for example, in the classical xylene isomers example discussed in Appendix A, there is only one linkage class, since all three components (and complexes) can be formed from every other one. Let N'' be the number of linkage classes. Of course, all complexes within any given linkage class have to be "compatible": They all have to have the same number of atoms of each type. However, some compatible complexes may not belong to some linkage class, as later examples show. (In the part of the theory dedicated to the analysis of CSTRs, Feinberg introduces some *imaginary* complexes, which can be regarded as compatible only in a very formal sense; see Section IV,C,6. This does not concern us here.)

Finally, Feinberg considers the rank of the stoichiometric matrix, R. He then defines a "deficiency" of the reaction network, δ, as $\delta = N' - N'' - R$. In his series of papers, Feinberg obtains a number of strong results for systems of deficiency 0 and deficiency 1; these are not discussed here, and only very concisely in the next section. For the whole strength of the theory the reader is referred to the original Feinberg papers.

Feinberg also keeps track of how the "arrows" connecting any two complexes in a linkage class are oriented; for instance, the case of the three xylene isomers could be regarded as $A \rightarrow B \rightarrow C \rightarrow A$, or as $A \leftrightarrow B \leftrightarrow C \leftrightarrow A$, or any other intermediate case. Again, at this stage we do not need to be concerned with that part of the topology of the reaction network. The reason why, at this stage, we need not worry about the orientation of arrows within a given network is that the deficiency of a network is insensitive to the details of the arrow structure within the linkage classes: The precise nature of the arrows affects the deficiency only to the extent that the arrows determine the linkage classes (Feinberg, 1987, Section 2).

The deficiency of a reaction network depends very strongly on the topology one assigns to it, as the following two examples show. First, consider the system discussed in Appendix B, [see Eq. (165)]. Let N be the largest carbon number taken into consideration. Clearly one can write $N - 3$ reactions of the type of Eq. (165), and each one is a linkage class, so that $N'' = N - 3$. [The equals sign in Eq. (165) can still be interpreted as singly or doubly oriented.] Notice that many compatible complexes do not belong to their possible linkage class: All complexes with more than two compounds, and all complexes consisting of a pair where one of the members is not ethylene, do not belong to any linkage class, in spite of the fact that many such complexes are compatible with all linkage classes except the low-order ones. All of the reactions written down are independent, and hence $R = N - 3$. For each reaction, the quantities written on the right and on the left are complexes, and there are no other complexes (since olefins have been assumed to be able to react only with ethylene). It follows that $N' = 2(n - 3)$; for this system, the deficiency is zero, and the strong results developed by Feinberg for such systems apply (see Section IV,C,6).

However, consider the case where one allows for any two olefins to react with each other, say, with I and J, the carbon numbers of generic olefins:

$$A_I + A_J = A_{I+J}. \tag{172}$$

For $N = 4$, R is obviously 1; for $N = 5$, $R = 2$; and for $N = 6$, $R = 4$, because the reaction $2A_3 = A_6$ cannot be written as a linear combination of reactions of the type of Eq. (165). However, after that adding a new olefin only increases the number of independent reactions by one, so for $N > 5$ one has $R = N - 2$. For every component A_I, $I > 3$, there is one linkage class: all pairs which, as a complex, have the same carbon number (this still leaves out a large number of compatible complexes, because compatible triplets, etc., are excluded). However, the number of complexes and the deficiency now grow very rapidly with N, since they are delivered by a modified Fibonacci series:

N	4	5	6	7	8	9	10	11	12
R	1	2	4	5	6	7	8	9	10
N'	2	4	7	10	14	18	23	28	34
δ	0	0	0	1	3	5	8	11	15

One may ask why any compatible complexes should be excluded from any given linkage class. First of all, the Feinberg theory results are strong if the kinetics are of the mass action type, and hence all reactions that are written down are supposed to be elementary steps in the real chemical mechanism. Realistic elementary steps probably never include more than two molecules, and hence one tends to exclude complexes formed by more than a pair of compounds. Other exclusions may be suggested by our understanding of the chemistry involved; for instance, there may be situations where for some reason or another we come to the conclusion that olefins react to a significant extent only with ethylene.

The same kind of problem (rapid growth of N' and δ with growing N) arises with cracking and with polymerization reactions (of which olefin oligomerization is an example). For instance, in the case of cracking, if one assumes that only the end product (e.g., methane in the cracking of hydrocarbons) is cracked away at each reaction step, the deficiency is zero. [Notice that this assumption is exactly the opposite of assumption 2 just before Eq. (126), i.e., that all bonds are equally cleavable. Here one assumes that only the terminal bonds can be cleaved.] If, on the other side, one assumes the topology to be that considered in Section IV,B,4,c, the deficiency grows very rapidly with N. Notice that, in the first case, there would be no induction time, contrary to the result in Section IV,B,4,c.

However, polymerization and cracking may be the freak cases. Consider, for instance, hydrodesulfurization of an oil cut. Let RS represent any one of the N sulfurated compounds in the mixture; all the reactions are of the following type:

$$RS + H_2 = R + H_2S. \tag{173}$$

These are all independent, so $R = N$; each one represents a linkage class, so $N'' = N$; and each one yields two complexes, so $N' = 2N$, and $\delta = 0$. The deficiency tends to become very large in systems where most of the components have brute chemical formulas that are multiples of each other, which give rise to strongly interconnected networks (very many compatible complexes exist, even if complexes with more than two members are excluded); it stays at 0 or 1 in most systems of the hydrodesulfurization type, where parallel reactions with (almost) no interconnection take place.

APPENDIX D: MATHEMATICAL CONCEPTS

Consider a physical property (such as the total Gibbs free energy G) of a continuous mixture, the value of which depends on the composition of the mixture. Because the latter is a function of, say, the mole distribution $n(x)$, one has a mapping from a function to (in this case) a scalar quantity G, which is expressed by saying that G is given by a *functional* of $n(x)$. [One could equally well consider the mass distribution function $m(x)$, and consequently one would have partial mass properties rather than partial molar ones.] We use z for the label x when intended as a dummy variable inside a functional, and we identify functionals by writing them in the boldface type corresponding to the value, and their arguments within square brackets, say for the case at hand:

$$G = \mathbf{G}[n(z)]. \tag{174}$$

One now needs to extend the concept of a derivative from ordinary functions to functionals. This is done by writing, with $s(z)$ being a displacement function,

$$\mathbf{G}[n(z) + s(z)] = \mathbf{G}[n(z)] + \delta\mathbf{G}[n(z)|s(z)] + \mathbf{R}, \tag{175}$$

where $\delta\mathbf{G}[\ ]$ (called the Frechet differential of $\mathbf{G}[\ ]$) is a functional of both $n(z)$ and $s(z)$ which has the property of being linear in $s(z)$.

The *residual* **R** has the property:

$$\lim_{||s(x)|| = 0} \mathbf{R}/||s(x)|| = 0 \tag{176}$$

and $||s(x)||$ is the "norm" of $s(x)$.

The definition of the norm $||s(x)||$ [which is a nonnegative scalar assigned to any $s(x)$, which should satisfy the usual requirements for a norm, such as the triangular inequality and the fact that $||s(x)|| = 0$ only if $s(x)$ is identically zero] is a delicate question. First of all, in order to give an unequivocal meaning to Eq. (176), one does not need, in fact, to assign a norm, but only a topology. One need only know when the norm becomes vanishingly small, without knowing what the norm is when it is finite. In other words, assigning a norm establishes a "metric" in the space of functions [finite distances between $n(x)$ and $n(x) + s(x)$ are measured by the norm], but different metrics could yield the same topology. However, in practice the easiest way to assign a topology is to assign a metric.

The most common norm is the so-called Euclidean one:

$$||s(x)|| = <s^2(y)>. \tag{177}$$

A Euclidean norm declares two functions that differ only on a countable infinity of isolated points as being "close." This is not too much of a difficulty for the problems we consider, but there is another difficulty. If we want to consider distributions that include one or more discrete components (a semicontinuous distribution), $s(x)$ may well contain some delta functions. This implies, first, that all integrals have to be interpreted as a Stjieltjies ones; but even so one has a problem with the right-hand side of Eq. (177), because the delta function is not Stjieltjies square-integrable. One could be a bit cavalier here and say that we agree that $\delta^2(x) = \delta(x)$, but it is perhaps preferable to keep continuous and discrete components separate. Let, for instance, the mole distribution be $n_1, n_2, \ldots, n_N, n(x)$ in a mixture with N discrete components and a distributed spectrum. One can now define the scalar product as the ordinary one over the discrete components, plus the continuous one over the distribution, and therefore avoid the problem with delta functions.

Because $\delta\mathbf{G}$ is linear in its second argument, it must be expressible as a weighted integral of $s(z)$; the weighting function, however, may still depend on the particular "point" $n(z)$ in Hilbert space where the Frechet differential is evaluated. Hence, the weighting function is given by a functional $\mathbf{G}'[\,;]$ of $n(z)$, which depends parametrically on x; $\mathbf{G}'[\,;]$ is called the functional derivative of $\mathbf{G}[\,]$. One has

$$\delta\mathbf{G}[n(z)|s(z)] = <\mathbf{G}'[n(z);y]s(y)>. \tag{178}$$

This formalism can now be applied, as an example, to our specific physical example where G is the Gibbs free energy and $n(x)$ is the mole distribution. The usual statement in thermodynamics that G is an extensive property can be formalized by requiring the functional $\mathbf{G}[\,]$ to be homogeneous of the first degree. Say for any positive scalar Ω one has

$$\mathbf{G}[\Omega n(z)] = \Omega\mathbf{G}[n(z)]. \tag{179}$$

Subtracting $\mathbf{G}[n(z)]$ from both sides of Eq. (179), taking the limit as Ω approaches unity, and using the definitions given earlier, one obtains

$$\mathrm{G} = <\mathbf{G}'[n(z);y]n(y)>. \tag{180}$$

This leads to the obvious identification of the chemical potential distribution $\mu(x)$:

$$\mu(x) = \mathbf{G}'[n(z);x] \tag{181}$$

so that one obtains the obvious extension of the classical result $\mathrm{G} = <\boldsymbol{\mu},\mathbf{n}>$:

$$\mathrm{G} = <\mu(y)n(y)>. \tag{182}$$

Now consider any infinitesimal variation $\delta n(x)$ from some base distribution $n(x)$. Using the definitions of the functional derivative of $\mathbf{G}[\,]$ and of the chemical potential distribution $\mu(x)$, one would calculate the corresponding infinitesimal variation of G, δG, as $<\mu(y)\delta n(y)>$; differentiating Eq. (181) one would calculate $\delta\mathrm{G} = <\mu(y)\delta n(y)> + <n(y)\delta\mu(y)>$. It follows that

$$<n(y)\delta\mu>(y)> = 0, \tag{183}$$

which is the obvious continuous description equivalent of the Gibbs–Duhem equation.

Now consider again Eq. (182) and the requirement that the right-hand side of it be homogeneous of the first degree. It follows trivially that the functional giving $\mu(x)$, Eq. (181), is homogeneous of degree zero. Say for any positive scalar Ω,

$$\mathbf{G}'[\Omega n(z);x] = \mathbf{G}'[n(z);x]. \tag{184}$$

If we now choose Ω as $1/\langle n(y)\rangle$ (i.e., as the inverse of the total number of moles), so that $\Omega n(x)$ equals the mole fraction distribution $X(x)$, one obtains

$$\mathbf{G}'[X(z);x] = \mathbf{G}'[n(z);x]; \tag{185}$$

that is, the chemical potential distribution depends only on the mole fraction distribution and not on the total number of moles. It follows that any variation $\delta n(x)$ which results in the same mole fraction distribution [i.e., any $\delta n(x)$ expressible as $n(x)\delta\langle n(y)\rangle/\langle n(y)\rangle$] results in a zero variation of $\mu(x)$. It follows that the Gibbs–Duhem equation, Eq. (183), is trivially satisfied for such variations, and hence that one only needs to ascertain, when writing down constitutive equations, that Eq. (183) is satisfied for those $\delta n(x)$ that satisfy $\langle \delta n(y)\rangle = 0$. [It is useful to note that this argument applies provided $\langle n(y)\rangle$ is finite—see Appendix B.]

The functional derivative (and the chemical potential distribution) are examples of a *function* that depends on another one. Consider the case of the chemical potential distribution:

$$\mu(x) = \boldsymbol{\mu}[n(z);x]. \tag{186}$$

If the argument function [$n(z)$ in Eq. (186)] and the value function [$\mu(x)$ in Eq. (186)] are defined over the *same* variable [as is the case in Eq. (186); z is the dummy variable form of x], it is legitimate to ask oneself whether a functional such as $\mathbf{G}'[\,;\,]$ is *invertible* at some $n(x)$. Whether the definition is over the same variable is easily kept track of in one-phase kinetics and thermodynamics: We use x, y, z for the component labels, and u, v, w for the reaction labels. The usual theory of equilibrium in Section III,A is based on the assumption that the functional $\mathbf{r}[q(w);u]$ is invertible at $\mathbf{q}^*(v)$. Also, in homogeneous systems where the isothermal free energy hypersurface is strictly convex, $\boldsymbol{\mu}[n(z);x]$ is invertible at every $n(x)$, and hence $n(x)$ is expressible as $\mathbf{n}[\mu(z);x]$.

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