# Continuum Theory for Lumping Nonlinear Reactions

A lumping procedure is proposed for continuous reaction mixtures whose components undergo nonlinear reactions. A species-type distribution function is introduced to ensure that the *lumped* continuous mixture is kinetically consistent with the underlying *lumped* discrete mixture. It is shown that, if the mixture contains some virtually unreactive species, the lump after a long time will react at a second-order rate. This is true as long as the underlying unlumped reactions are irreversible $n$th-order with $n < 2$ or reversible first order. When many first-order reversible reactions are lumped together, the apparent behavior of the lump can qualitatively look like that of a reversible reaction. Practical implications of these predictions are discussed. Some published data are reconciled in light of the present theoretical development.

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## Introduction

In catalytic or thermal processing of complex hydrocarbon mixtures (e.g., petroleum feedstocks, coal liquids, and the like), the reaction involves an indefinitely large number of species, the analysis of which is costly or near impossible. As a result, in analyzing the kinetic data one almost always has to lump chemically similar species together and treat the lump as a pseudospecies. For example, in hydrodenitrogenation (HDN) the disappearance rate of total nitrogen is measured, rather than that of the individual nitrogen compounds.

Due to its practical importance, the development of kinetically consistent theories for lumping a large number of reactions has long been the subject of many investigations (Weekman, 1979, and the references therein; Coxson and Bischoff, 1987). A mathematically expedient approach has been to approximate the inherently discrete system by a continuum (DeDonder, 1931; Aris and Gavalas, 1966). Kinetic lumping in this case is done via integration, instead of summation. The advantage is that problems represented by integrals are in many cases more tractable. For a first-order reaction mixture, Aris (1968) has shown that the effect of a continuous concentration-reactivity spectrum is to give a higher reaction order for the disappearance of the lump. In particular, if the spectrum could be represented by an exponential distribution, the overall order would be two. Krambeck (1984) has further shown that if a first-order reaction mixture contains some virtually unconvertible reactants, the lump after a long time would disappear at a second-order rate for any arbitrary concentration-reactivity spectrum. Although these predictions are made for certain special circumstances, it is remarkable to note that second-order kinetics are quite common in petroleum processing (Ho, 1988; Venuto and Habib, 1978).

An important assumption in Aris's (1968) and Krambeck's (1984) treatments is that the individual reactions are first order and irreversible. While this assumption is not particularly restrictive, it is highly desirable to be able to generalize their treatments to nonlinear reaction mixtures because such mixtures do arise in practice (e.g., in HDN; see Ho, 1988). Conceivably, the nonlinear problem is more involved. Indeed, Ho and Aris (1987) have shown that a straightforward extention of prior treatments to nonlinear kinetics results in obvious inconsistencies.

In this study we propose a lumping procedure for continuous reaction mixtures whose components can undergo nonlinear reactions. For ease of discussion, we first describe the difficulties of using conventional procedure for lumping nonlinear kinetics. We then propose a procedure that overcomes these difficulties. The key to the procedure is the introduction of a species-type distribution function which ensures that the *lumped* continuous mixture is kinetically consistent with the underlying *lumped* discrete mixture. To illustrate the use of the procedure, we consider several lumping problems of practical interest. We show that the long-time asymptotic analysis of Krambeck (1984) can be carried over to irreversible $n$th-order reactions with $n < 2$ as well as to reversible first-order reactions. Also, we extend Aris's (1968)

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all-time analysis to reversible reaction mixtures. Specifically, we show that when many reversible first-order reactions are lumped together, the apparent behavior of the lump can look like that of a reversible reaction. Next we discuss practical implications of these theoretical results. Some experimental observations are reconciled in light of the present development. The final section describes a more general treatment of the nonlinear lumping problem, in an attempt to put our procedure in broader perspective with conventional procedure.

## Preliminaries: Lumping in a Discrete Mixture

Consider an isothermal closed system containing a total of $N$ different types of reactants, each of which reacts irreversibly at an $n$th-order rate. To describe this system, we write the following very large set of mass balance equations ($N$ is very large):

$$\frac{dc_i}{dt} = -k_i c_i^n, \qquad i = 1, 2, \ldots, N.$$

$$t = 0, \qquad c_i = c_i(0) \tag{1}$$

where $c_i(t)$ is the concentration of the $i$-type reactant with a rate constant $k_i$. In many practical situations, the reaction order $n$ can be assumed to be constant for all species. In this case, the only kinetic parameter that is species dependent is $k_i$. Hence, we are dealing with a one-parameter system. The treatment of multiparameter systems is discussed in later sections.

Obviously, here the different types of reactants are distinguished by $i$. For a given reactant of type $i$, we are interested in its reactivity $k_i$ and concentration $c_i$. Take HDN as an example. It is often reasonable to assume that commercial feedstocks of comparable boiling range generally have the same nitrogen compound types (e.g., quinolines, benzoquinolines, hydroquinolines). They differ only in the concentrations of the individual compound types. The intrinsic HDN reactivities of various nitrogen compounds can be determined via reaction studies using "synthetic feeds" containing one or more "model" compounds (Ho, 1988).

In principle one can construct a "feed specification diagram" shown in Figure 1 where $i$ is chosen as the basic variable. This choice is reasonable because, experimentally, there is no point to measure $k_i$ or $c_i$ until the reactant types are identified. Note that in Figure 1 we have, without loss of generality, arranged the sequence of $i$ in such a way that $k_i > k_j$ for $i > j$. (We shall discuss the assumption of $k_i \neq k_j$ for $i \neq j$ in the final section.) The most important point we wish to convey here is that the relationship between $k_i$ and $i$ is almost invariably *nonlinear* in practice. Mechanistically, a plot like Figure 1 is quite useful in that one may be able to relate $i$ to a unifying structural parameter (e.g., reasonance energy, basicity, and molecular weight) and thereby establishes a correlation between molecular structure and reactivity.

Let $C(t)$ be the concentration of the reactant lump at any time $t$, we then have

$$C(t) = \sum_{i=1}^{N} c_i(t) \tag{2}$$

That is, the lump is contributed by Eq. 1 the individual concentrations and Eq. 2 the number of reactant types. While this seems to be a trivial point, its importance will become apparent in our later development of a continuum analog of Eq. 2.

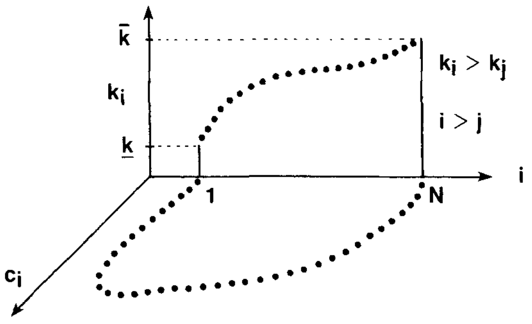

**Figure 1. Feed specification diagram showing that a discrete mixture is characterized by three properties: $i$, $k_i$ and $c_i$.**

It should be emphasized that a real mixture is always discrete. In the next two sections we address the question of how to lump reactions in a continuous mixture while preserving all the properties of the underlying discrete mixture. We first describe the difficulties of conventional lumping procedure.

## Lumping in a Continuous Mixture: Conventional Procedure

When $N$ is sufficiently large, one may treat $k$ as a continuous variable and use it to designate the individual species. For the moment let us suppose that we can approximate Eq. 2 by an integral of the form

$$C(t) \approx \int_{\underline{k}}^{\bar{k}} g(k, t)\, dk \tag{3}$$

in which $\bar{k}$ and $\underline{k}$ are the upper and lower limits of $k$ for the mixture in question, respectively. The integrand $g$ is yet to be determined. An inspection of Eq. 3 indicates that the reactant concentration can be defined only for an interval of $k$; that is, the product $g(k, t)dk$ is the total concentration of species with rate constants between $k$ and $k + dk$. And $g(k, t)$ necessarily needs to be interpreted as a concentration distribution function.

Note that $N$ approaches infinity does not necessarily imply $\bar{k} \to \infty$. But one may reasonably assume the difference between $\underline{k}$ and $\bar{k}$ becomes larger as $N$ increases. For mathematical convenience, it is customary to estimate Eq. 3 by taking $\underline{k} \to 0$ and $\bar{k} \to \infty$ (Aris, 1968; Hutchinson and Luss, 1970). We then have

$$C(t) \approx \int_0^{\infty} g(k, t)\, dk \tag{4}$$

As in the above equation, we shall use the symbol $\approx$ in our subsequent developments as a reminder of the approximate nature of the continuum description. Of course, we must assume that $g(k, t)$ is of such a form that the integral in Eq. 4 exists and is finite. Equation 4 will be referred to as the conventional lumping procedure.

To determine $g$, one needs to impose some compatibility requirements which are based on our basic premise that the continuous mixture must be kinetically consistent with the underlying discrete mixture. In light of Eq. 1, one may be led to write the following conservation equation for the differential lump $g(k, t)dk$ ($= dC$)

$$\frac{d[g(k, t)dk]}{dt} = -k[g(k, t)dk]^n \tag{5}$$

This equation, however, is meaningless except $n = 1$, in which case the terms $dk$ divide out. This is not surprising because $g(k, t)dk$ itself is a lump. The analogous situation in the discrete case is that $(\Sigma c_i)^n = \Sigma c_i^n$ only when $n = 1$.

Alternatively, the foregoing may be discussed in terms of what Ho and Aris (1987) called the "single-component identity" which says that if the mixture has only one component of reactivity $k^*$, then the kinetic behavior of the lump must degenerate to that of a single component of reactivity $k^*$. With Eq. 4 this compatibility requirement is met only when $n = 1$ (Ho and Aris, 1987).

It is tempting to think of circumventing the above difficulty by modifying the reaction constitutive equation (Krambeck, 1988). For example, one may propose a new power law kinetics of the following form

$$\text{rate} = kc(k, 0)^{1-n} c(k, t)^n \tag{6}$$

Equation 5 then becomes

$$\begin{aligned} \frac{d[gdk]}{dt} &= -k[g(k, 0)dk]^{1-n} [g(k, t)dk]^n \\ &= -kg(k, 0)^{1-n} g(k, t)^n dk \end{aligned} \tag{7}$$

As can be seen, the terms $dk$ divide out. However, the drawback here is that the kinetics represented by Eq. 6 is too restrictive. Equation 6 says that the reaction rate at any instant time $t$ depends on the reactant's concentration at that instant as well as at time zero (i.e., a memory effect). It also says that the initial rate ($t \rightarrow 0$) is always first order. This type of kinetics does not appear to be representative of those encountered in practice. A lumping procedure that does not require any changes or modifications to the form of traditional kinetics will be discussed later.

There is yet another difficulty in using the conventional procedure: The kinetic behavior of the lump, in the absence of additional information (more on this in the final section), cannot be uniquely defined by $g(k, 0)$. Two very different feeds may have the same $g(k, 0)$. For example, one feed is made up of a large number of reactant types with rate constants between $k$ and $k + dk$, but each of them has a low concentration. The other feed is made up of a small number of reactant types but each of them has a high concentration. These two lumps will react differently (except in the case of first-order reactions where the extent of reaction is independent of initial concentration). However, Eq. 4 tells us that they are kinetically identical; this difficulty originates from not considering the fact that the number of reactant types per unit range of $k$ can vary along the $k$ axis, Figure 1.

## Lumping in a Continuous Mixture: a More Flexible Procedure

Our objective here is to numerically approximate Eq. 2, a sum over reactant type $i$, by an integral over reactivity $k$. This may be viewed as a problem of coordinate transformation—from an "$i$ coordinate" to a "$k$ coordinate." With this in mind, our first step of course is to consider the relationship between $k_i$ and $i$, which holds the link between the discrete and the continuum descriptions, Figure 2. Note that $c_i(t)$ and $c(k, t)$ in Figure 2 generally have different shapes, although they are in one-one correspondence with each other.

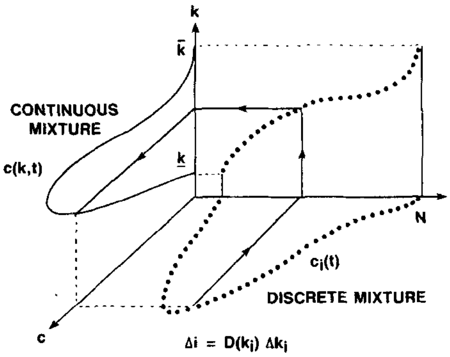

**Figure 2. One-to-one mapping between a discrete and a continuous mixture.**

The $i$'s are equally spaced along the $i$ axis (the reactant type is uniformly distributed along the $i$ axis), but the corresponding $k_i$'s are in general not equally spaced. (The distribution of the reactant type along the $k$ axis needs not be uniform.) The $i$-to-$k$ coordinate transformation therefore involves a change of local scales. To do the transformation, we must know how an incremental change in $i$ is related to the corresponding incremental change in $k_i$. This can be determined from the reciprocal of the local slope $D$ of the $k_i$ vs. $i$ "curve"

$$D(k_i) = \frac{\Delta i}{\Delta k_i} = \frac{(i + 1) - i}{k_{i+1} - k_i} = \frac{1}{\Delta k_i} > 0 \tag{8}$$

Note that in this equation $\Delta i$ = constant = 1.

Mathematically, $D(k_i)$ may be regarded as the Jacobian of the $i$-to-$k$ coordinate transformation. A large value of $D(k_i)$ means that the reaction mixture has lots of different types of reactants with rate constants near $k_i$ (however large or small their concentrations may be). Figure 3 shows an illustrative example of a $k_i$ vs. $i$ relation. The corresponding $D(k_i)$ vs. $i$ and $D(k_i)$ vs. $k_i$ relations are shown in Figures 4 and 5, respectively. In the region where the $k_i$ vs. $i$ "curve" is convex (concave),

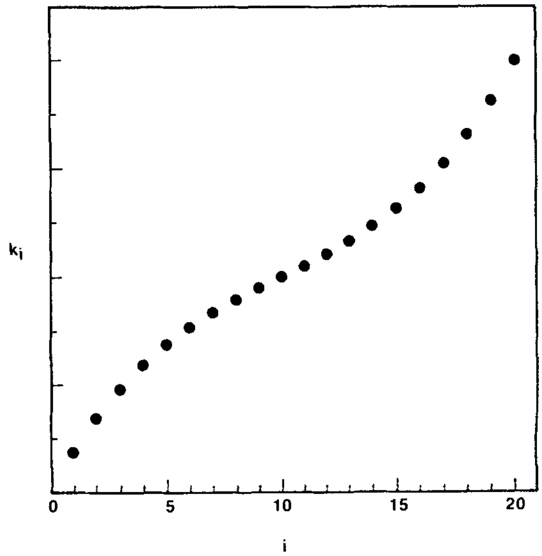

**Figure 3. Hypothetical relation between $k_i$ and $i$, $k_i > k_j$ for $i > j$.**

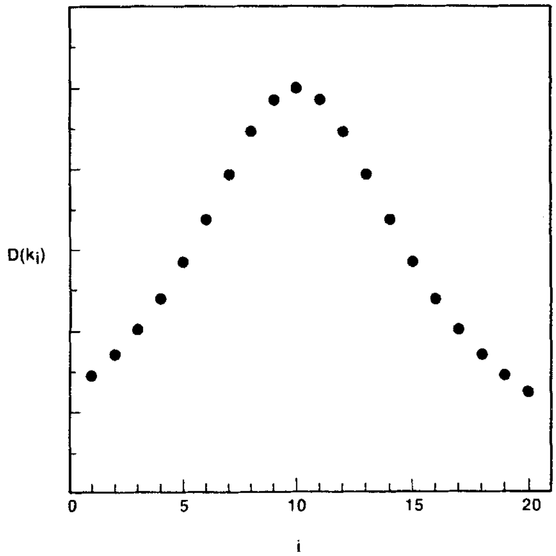

**Figure 4. Dependence of *D*(*k*$_i$) on *i* corresponding to Figure 3.**

$D(k_i)$ will increase (decrease) as $k_i$ increases. While $D(k_i)$ is defined only at the discrete points of $k_i$, it can be treated as a continuous function of $k$ as $N$ approaches infinity. And $D(k)dk$ represents the number of species types with rate constants between $k$ and $k + dk$. The function $D(k)$, therefore, is a species-type distribution function and must satisfy the following compatibility (or normalization) condition

$$\frac{1}{N}\int_0^\infty D(k)\,dk \approx 1 \tag{9}$$

which says that the total number of reactant types is conserved. If the reaction system in question has only one species, $D$ becomes the Dirac delta function. On the other hand, if the system has an indefinitely large number of species, $D$ is a continuous function approximating a series of delta functions, so that Eq. 9 is satisfied.

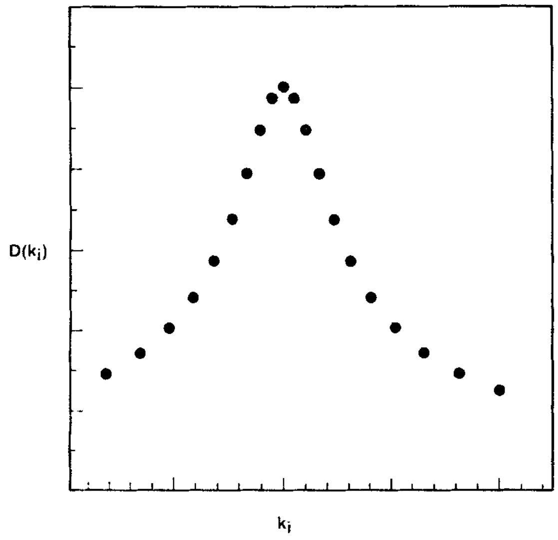

**Figure 5. Dependence of *D*(*k*$_i$) on *k*$_i$ corresponding to Figure 3.**

Corresponding to $D(k)$, there is a continuum of concentration $c(k, t)$ defined "at a point $k$." The properties of the continuous mixture are thus characterized by $k$, $c(k, t)$, and $D(k)$, each of which has a direct counterpart in the discrete case. In other words, all the properties of the underlying discrete mixture are preserved.

Having defined the Jacobian of the transformation, we can write $c_i(t)\Delta i = c(k_i, t)D(k_i)\Delta k_i$ and propose the following weighted integral to approximate the total reactant concentration in the underlying discrete mixture

$$C(t) \approx \int_0^\infty c(k, t)D(k)\,dk \tag{10}$$

As can be seen, the total reactant concentration is contributed by both the "individual" concentrations—and the total number of reactant types (cf. Eq. 2). For a given kinetics, $C(t)$ is uniquely determined by the two feed properties, $c(k, 0)$ and $D(k)$. Suppose that $c(k, 0) = 1$ for all $k$, then $C(0) \approx N$, which is consistent with the underlying discrete mixture.

Numerically, $D(k)$ is a weighting factor considering the fact that the $k_i$'s may not be equally spaced along the $k$ axis. So when Eq. 10 is discretized, the corresponding $i$'s are equally spaced along the $i$ axis, and a sum of equally weighted concentrations is obtained, *viz.*

$$\begin{aligned}\text{Eq. } 10 &\approx \sum_{i=1}^{N} c(k_i, t)\, D(k_i)\Delta k_i \\ &= \sum_{i=1}^{N} c_i(t)\frac{1}{\Delta k_i}\Delta k_i = \sum_{i=1}^{N} c_i(t) = \text{Eq. } 2\end{aligned} \tag{11}$$

That is to say, the kinetic behavior of the lump remains invariant under coordinate transformation ($i$ to $k$ and *vice versa*). We thus establish the requirement of "coordinate invariance."

The single-component identity can be easily established because $D(k)$ takes care of the discreteness of the system. This frees up $c(k, t)$ which needs to satisfy only the system conservation/constitutive equations (in the conventional approach, all the burden falls on $g$), as shown below

$$C(t) \approx \int_0^\infty c(k, t)\,\delta(k - k^*)\,dk = c(k^*, t) \tag{12}$$

$$\begin{aligned}\frac{dc(k^*, t)}{dt} &= -k^*\, c(k^*, t)^n \\ t = 0, \quad c(k^*, t) &= c(k^*, 0)\end{aligned} \tag{13}$$

Equation 13, as it should be, does not contain the $dk$ terms seen in Eq. 5. Since the system conservation/constitutive equations should remain invariant under coordinate change, Eq. 13 is also a statement of "coordinate invariance."

Alternatively, the whole of the foregoing can be put more concisely as follows

$$\begin{aligned}\frac{dC}{dt} &\approx \int_0^\infty D(k)\frac{dc(k, t)}{dt}\,dk \\ &= -\int_0^\infty D(k)\, kc(k, t)^n\,dk \\ &= -\int_0^\infty \delta(k - k^*)\, kc(k, t)^n\,dk \\ &= -k^* c(k^*, t)^n\end{aligned} \tag{14}$$

### *Additional remarks on D*

Basically, the presence of $D(k)$ in Eq. 10 says that the integral (lumping) must be carried out in a manner consistent with the inherent $k - i$ relationship in the underlying discrete mixture. $D(k)$ has a well-defined physical meaning. It depends on the reactant types in the feed, but is independent of the concentration of each reactant type. ($D$ is time-independent.) Take HDN as an example. It two feeds contain two different sets of nitrogen compounds, then these two feeds have different $D$ functions. One has to determine the $D$ function for each feed.

Fortunately, in many practical situations, one often can reasonably assume that a group of similar feedstocks (say virgin gas oils) have the same nitrogen compound types. But the concentration of each compound type varies from feedstock to feedstock. In this case, all the feedstocks in this group have a common $D$ function [but different $c(k, 0)$].

As described early, $D$ can be derived from the $k_i - i$ relation. The latter can in principle be determined *a priori* from reaction studies using model compounds. Experimentally, it is easier to identify reactant types than to quantify reactant concentration. So once $D(k)$ is determined, it may be used to obtain $c(k, 0)$ by inverting Eq. 10. For first-order kinetics, one may follow the eigenfunction method described by Ostrowsky et al. (1981).

The most practical approach is to choose known functions for $D(k)$ and $c(k, 0)$ with adjustable parameters and fit the $C(t)$ data to find the best parameter values. Analytically, one should also try to get as much information as possible without knowing $c(k, 0)$ and $D(k)$ *a priori*; this would invoke some kind of asymptotic analysis.

$D(k)$ is also useful for calculating other physical quantities of a continuous mixture. For instance, if the mass of the species with rate constant $k$ is $m(k)$, then the total mass $M$ of the species in the feed is

$$M = \int_0^\infty m(k) D(k)\, dk \tag{15}$$

Finally, let us mention some limiting shapes of $D(k)$. Suppose that there are only two types of reactants in the feed, then $D(k) = \delta(k - k_f) + \delta(k - k_s)$. Equation 10 reduces to that for a discrete mixture having a fast-reacting ($k_f$) and a slow-reacting species ($k_s$). A "two-$k$ model" of this type has frequently been used to describe hydroprocessing kinetics (for example, Gates et al., 1979). Wei and Hung (1980) have compared this model with second-order kinetics. The other limiting form is $D(k) = \overline{D}$ = constant (e.g., a mean value). In this case the $k_i$'s are equally spaced along the $k$ axis.

## Applications of the New Lumping Procedure

We now use Eq. 10 to predict the disappearance rate of the lump at large $t$ as well as at any $t$.

### *Lumped kinetics at large t*

If the feed has a nonzero amount of virtually unconvertible species, we can obtain information on the long-time behavior of the lump without *a priori* knowledge of $c(k, 0)$ and $D(k)$. Two types of reactions are considered here: irreversible $n$th order and reversible first order.

### *Irreversible nth-order reactions*

The concentration of reactant $k$ in this case is

$$c(k, t) = c(k, 0)\, [1 + (n - 1) c(k, 0)^{n-1} kt]^{1/(1-n)} \tag{16}$$

For $n = 1$, the above expression reduces to the usual exponential form. The two cases $n \geq 1$ and $n < 1$, however, will have to be considered separately.

*$n \geq 1$.* Substituting Eq. 16 into Eq. 10, we obtain

$$C(t) \approx \int_0^\infty c(k, 0) D(k) \cdot [1 + (n - 1) c(k, 0)^{n-1} kt]^{1/(1-n)}\, dk \tag{17}$$

For large $t$, the integrand is appreciable only in a thin region near $k = 0$. Suppose that $c(k, 0)$ and $D(k)$ do not vary considerably over this region and that $c(0, 0) D(0) \neq 0$, the integral asymptotically reduces to

$$C(t) \approx c(0, 0) D(0) \cdot \int_0^\infty [1 + (n - 1) c(0, 0)^{n-1} kt]^{1/(1-n)}\, dk \tag{18}$$

For $n < 2$, the above equation can be analytically integrated to give

$$C(t) \approx \frac{1}{t} \left\{ \frac{c(0, 0)^{2-n} D(0)}{2 - n} \right\} \tag{19}$$

Differentiation of Eq. 19 gives

$$\frac{dC}{dt} \approx - \frac{2 - n}{c(0, 0)^{2-n} D(0)} C^2 \tag{20}$$

We thus obtain an asymptotic second-order reaction with a lumped rate constant of $(2 - n)/D(0)\, c(0, 0)^{2-n}$. As can be seen, the behavior of the lump at large $t$ is governed by the amount of the most refractory species, as might be expected intuitively.

To investigate the case $n \geq 2$, one needs to assume the forms of $D(k)$ and $c(k, 0)$ and perform the integration numerically. Without proof, our conjecture is that an overall order higher than two is plausible. Ozaki et al. (1976) have reported an overall order greater than two for hydrodesulfurization (HDS) of residual oils under certain conditions.

*$n < 1$.* Here we need to consider the phenomenon of "reactant exhaustion." At time $t$, all the species with $k > \kappa(t)$ will have completely been consumed, where $\kappa(t)$ is obtained by solving the following equation

$$1 = (1 - n)\, c(\kappa(t), 0)^{n-1} \kappa(t)\, t \tag{21}$$

and $c(k, t)$ at this particular instant $t$ becomes

$$c(k, t) = \begin{cases} c(k, 0)[1 + (n - 1) c(k, 0)^{n-1} kt]^{1/(1-n)} & k \leq \kappa(t) \\ 0 & k > \kappa(t) \end{cases} \tag{22}$$

For large $t$ and $c(0, 0) \neq 0$, $\kappa$ is small and given approximately by

$$\kappa(t) \approx \frac{1}{(1-n)\, c(0,0)^{n-1}\, t} \tag{23}$$

The total concentration of remaining species at large $t$ is then

$$C(t) \approx c(0,0)\, D(0) \int_0^{\kappa(t)} [1 + (n-1) c(0,0)^{n-1} kt]^{1/(1-n)}\, dk = \frac{1}{t}\left\{\frac{c(0,0)^{2-n}\, D(0)}{2-n}\right\} \tag{24}$$

We thus obtain the same asymptotic second-order kinetics as in the $n \geq 1$ case (Eq. 19). Since here $n < 1$, we note that the order of the lumped kinetics exceeds that of the unlumped kinetics by more than one.

The above analyses extend Krambeck's (1984) theoretical proof to continuous reaction mixtures whose components individually react at an $n$th-order rate with $n < 2$. That is, as long as the reaction mixture contains a nonzero amount of virtually unreactive species, the lump will disappear asymptotically in a second-order manner. In the next section we show that this conclusion can also be carried over to reversible first-order reaction mixtures.

### *Reversible first-order reactions*

An example of lumping reversible reactions is the hydrogenation of aromatic compounds in oil refining (Wilson et al., 1985). Consider the following reversible reaction system

$$A_i \underset{\tilde{k}_i}{\overset{k_i}{\rightleftharpoons}} \tilde{A}_i, \quad i = 1, 2, \ldots, N \tag{25}$$

The corresponding mass balance equations are

$$\frac{dc_i(t)}{dt} = -(k_i + \tilde{k}_i)\, c_i(t) + \tilde{k}_i[c_i(0) + \tilde{c}_i(0)]$$
$$t = 0, \quad c_i(t) = c_i(0) \quad \tilde{c}_i(t) = \tilde{c}_i(0) \tag{26}$$

where $c_i(t)$ and $\tilde{c}_i(t)$ are the concentrations of $A_i$ and $\tilde{A}_i$, respectively. The sum of $c_i(t)$ and $\tilde{c}_i(t)$ is a constant independent of time.

Unlike the power law kinetics discussed early, here we are dealing with a two-parameter system: Both $k_i$ and the equilibrium constant $K_i (K_i = k_i/\tilde{k}_i)$ may vary (*nonlinearly*) from species to species. Without loss of generality, we arrange the sequence of $k_i$ in such a way that $k_i > k_j$ for $i > j$. Once this is done, the sequence of $K_i$ is specified. In other words, $K_i$ bears a fixed relation with $i$, and $K_i$ may not be greater than $K_j$ for $i > j$.

The solution of Eq. 26 is

$$c_i(t) = \frac{1}{1 + K_i}[c_i(0) + \tilde{c}_i(0)] + \frac{K_i c_i(0) - \tilde{c}_i(0)}{1 + K_i} e^{-k_i(1+1/K_i)t} \tag{27}$$

To approximate the above discrete system by a continuum, we again choose $k$ as the continuous, species-designating variable. The function $D(k)$ is defined in the same way as before (Eq. 8). The $k_i$ vs. $i$ and $K_i$ vs. $i$ relations allow us to determine $K_i$ as a function of $k_i$. The lumping integral, Eq. 10, for this case can be written as

$$C(t) \approx \int_0^\infty \frac{D(k)}{1 + K(k)}[c(k,0) + \tilde{c}(k,0)]\, dk + \int_0^\infty \frac{K(k)\, c(k,0) - \tilde{c}(k,0)}{1 + K(k)} D(k) e^{-k[1+1/K(k)]t}\, dk \tag{28}$$

in which the function $K(k)$ must be such of a form to assure the integrability of Eq. 28.

To treat the problem analytically, we consider the simple case $K(k) = K =$ constant. (i.e., species with similar $K$ are lumped together.) Equation 28 is then simplified to

$$C(t) \approx \frac{1}{1 + K}[C(0) + \tilde{C}(0)] + \frac{1}{1 + K}\int_0^\infty [Kc(k,0) - \tilde{c}(k,0)]\, e^{-k(1+1/K)t} D(k)\, dk \tag{29}$$

The asymptotic behavior of $C(t)$ for large $t$ can be found in the same vein as before; that is, the exponential term in the above integral is significant only when the product $k(1 + 1/K)t$ is small, which corresponds to a thin region of small $k$. Hence, for large $t$, we have

$$C(t) \approx \frac{1}{1 + K}[C(0) + \tilde{C}(0)] + \frac{1}{t}\frac{K^2}{(1+K)^2}\left[c(0,0) - \frac{\tilde{c}(0,0)}{K}\right] D(0) = C^* + \frac{\lambda}{t} \tag{30}$$

where

$$C^* \equiv \frac{1}{1 + K}[C(0) + \tilde{C}(0)]$$
$$\lambda \equiv \frac{K^2}{(1+K)^2}\left[c(0,0) - \frac{\tilde{c}(0,0)}{K}\right] D(0) \tag{31}$$

from which it readily follows that

$$C(t) \rightarrow C^* \text{ as } t \rightarrow \infty \tag{32}$$

and that

$$\frac{dC}{dt} \approx -\frac{1}{\lambda}(C - C^*)^2 \tag{33}$$

As can be seen, the lump will disappear at a second-order rate to an apparent "equilibrium concentration" $C^*$. The driving force for the reaction is the extent of the deviations from "equilibrium," $C - C^*$. In this sense we may say that the apparent behavior of the lump looks like that of a reversible reaction. The "equilibrium" constant for the lumped system is the same as that for the unlumped system by virtue of the assumption $K(k) = K$. With $K \rightarrow \infty$, Eq. 30 reduces to Eq. 19 by setting $n = 1$ in Eq. 19.

### *Lumped kinetics at all t: reversible first-order reactions*

The investigation has so far been restricted to the limiting case of large $t$ and $c(0,0)D(0) \neq 0$. But to determine the behavior of the lump at all $t$ and to accommodate the case $c(0,0)D(0) = 0$, we need to know *a priori* the shapes of $c(k, 0)$ and $D(k)$. Consider the reversible first-order reaction system discussed earlier. We suppose that no $\hat{A}$'s are present at $t = 0$ (i.e., $\tilde{c}(k, 0) = 0$) and that $K(k) = K =$ constant. In light of Aris's development (1968), we let $c(k, 0)$ and $D(k)$ be described by the following functions which are capable of representing a wide variety of shapes.

$$\begin{aligned} c(k,0) &= p\, k^{\alpha}\, e^{-\beta k} \\ D(k) &= q\, k^{\eta} e^{-\zeta k} \end{aligned} \tag{34}$$

where $p$ and $q$ are normalization constants, and $-1 < \alpha < \infty$ and $-1 < \eta < \infty$. Then at any time $t$, Eq. 10 gives

$$C(t) \approx \frac{C(0)}{1 + K} + \frac{C(0)}{1 + \dfrac{1}{K}} \left[ 1 + \left( 1 + \frac{1}{K} \right) \frac{t}{\beta + \zeta} \right]^{-(\alpha+\eta+1)} \tag{35}$$

in which $C(0)$ is given by

$$C(0) = pq \frac{(\alpha + \eta)!}{(\beta + \zeta)^{\alpha+\eta+1}} \tag{36}$$

Equation 35 implies that

$$\frac{dC}{dt} \approx -\mu\, [pq\, \Gamma(\mu)]^{-1/\mu} \left( 1 + \frac{1}{K} \right)^{\gamma} \left[ C - \frac{C(0)}{1 + K} \right]^{\gamma} \tag{37}$$

where

$$\mu \equiv \alpha + \eta + 1, \quad \gamma \equiv \frac{\alpha + \eta + 2}{\alpha + \eta + 1} \tag{38}$$

Again, we see that there exists an apparent "equilibrium" concentration, $C(0)/(1 + K)$. When either $\alpha$ or $\eta$ is very large, the overall order will be near unity. When $\alpha = \eta = 0$ or $\alpha + \eta = 0$, the overall order will be two. Equation 37 also indicates that the overall order becomes greater than two when $\alpha < 0$ and $\eta < 0$. This corresponds to a feed in which the concentration of "unconvertibles" is so large that the whole feed is virtually unconvertible. While theoretically insightful, this situation is not of much practical interest from the standpoint of catalyst development: if a catalyst does nothing to the feed, it deserves no further attention. As $K$ approaches infinity, Eq. 37 reduces to that for irreversible reactions, a problem treated by Aris (1968).

This example illustrates that the presence of $D(k)$ does not introduce additional analytical difficulties.

The results of the last two sections suggest that in practical situations where the ultimate conversion level is the major concern, one may want to lump together species with similar equilibrium constants.

## Practical Implications

Here we expand the discussions of Ho and Aris (1987) on possible implications of the above theoretical predictions for catalyst evaluation and process research work.

In catalyst exploratory studies, one normally screens a wide variety of experimental catalysts with a standard feed. A catalyst that does not activate certain refractory fraction of the feed might well be evaluated by second-order kinetics after a long time. But if the performance of the catalyst is improved (for instance, by the incorporation of a more effective promoter) so that there is no longer a refractory component, then an overall order less than two would have to be used in evaluating the improved catalyst. In process research work, one generally evaluates different feeds on a selected catalyst over a wide range of conditions. The overall reaction order is expected to increase when switching from an "easy" feed to a "hard" feed. The extent of this increase could be viewed as an index of feed refractoriness. Another expected situation is that the overall order will increase with decreasing reaction severity.

Summarizing, the overall reaction order may be viewed as reflecting the following: (1) whether or not the catalyst is active enough to attack the "unconvertibles" or (2) Whether or not the conditions are severe enough to activate the "unconvertibles." Thus, reaction order in general is expected to be a function of feedstock composition and reaction conditions.

Let us now cite some experimental observations that seem to be relevant to the above supposition. The kinetics of catalytic cracking of gas oils are often reported to be second order (Venuto and Habib, 1978; Weekman, 1979). One could rationalize this by the presence of denuded aromatics which are virtually uncrackable (Gates et al., 1979). Sonnemans (1982) reported that the overall HDS order increased from 1.5 to 2 when switching from a blend of light coker gas oil and virgin gas oil to a light catalytic cracked oil (LCCO). The LCCO feed probably contains some highly aromatic sulfur compounds. Beuther and Schmid (1964) observed that HDS of petroleum resids followed second-order kinetics. Sonnemans (1982) reported an order of two for HDN of LCCO and an order of unity for HDN of virgin gas oils. Heck and Stein (1977) found that HDN and hydrodeoxygenation of coal liquids were best described by second-order kinetics. Some of the nitrogen and oxygen compounds in coal liquids are presumably very aromatic and therefore very refractory (Ho, 1988). Finally, Ozaki et al. (1976) observed that the overall HDS order increased with decreasing temperature.

## More General Treatment

We now wish to generalize our lumping procedure to a slightly more complex situation, with the purpose of putting our procedure in broader perspective with the conventional procedure. Let us consider the following multiparameter reaction system

$$\frac{dc_i}{dt} = -k_i r(c_i, \boldsymbol{u}_i) \tag{39}$$

in which $\boldsymbol{u}_i$ is a vector whose components are system kinetic parameters other than $k_i$. Here one is faced with the problem of what to choose as the continuous variable for labelling the reactants. Suppose that a convenient label $x$ can be found, which is a positive real number. Then each of the system kinetic parameters becomes a function of $x$. In the discrete case $x$ takes on discrete values $(x_1 \ldots, x_i \ldots, x_N)$, each of which corresponds to a reactant type. Without loss of generality, we let $x_i > x_j$ for $i > j$.

The total reactant concentration in the discrete mixture is

$$C(t) = \int \left[\sum_{i=1}^{N} c_i(t, x)\,\delta(x - x_i)\right] dx$$
$$= \sum_{i=1}^{N} c_i(t, x_i) \tag{40}$$

Suppose further that we want to approximate the above partial sum by an integral of the form

$$C(t) \approx \int g(x, t)\, dx \tag{41}$$

We next need to determine the function $g(x, t)$. Equations 40 and 41 suggest that $g$ is linearly related to $c$. For the moment let us propose that

$$g(x, t) = vc(x, t) \tag{42}$$

where $v$ is a constant. In light of Eq. 39, the equation for $g$ to satisfy is then

$$\frac{dg(x, t)}{dt} = -vk(x)\,r\left(\frac{1}{v}\, g(x, t), x\right) \tag{43}$$

However, in order for Eq. 41 to approximate Eq. 40, the sequence of numbers, $x_1, \ldots, x_i \ldots, x_N$, must be equally spaced, as shown below.

$$C(t) \approx \int g(x, t)\, dx \approx \sum_i vc(x_i, t)\Delta x$$
$$= v\Delta x \sum_i c(x_i, t) \tag{44}$$

And the constant $v$ is chosen to cancel out $\Delta x$. If the $x_i$'s are not equally spaced, there is no way of making Eq. 41 a close approximation to Eq. 40 unless one allows $v$ to become a function of $x$.

It thus becomes apparent that there is a need to introduce an $x$-dependent function $D$ with the following property

$$D(x_i) = 1/\Delta x_i \tag{45}$$

and that $g$ needs to be decomposed into the product of $c(x, t)$ and $D(x)$, i.e.

$$g(x, t) = D(x)c(x, t) \tag{46}$$

It can be seen from Eq. 45 that $D$ is determined by relating a sequence of unequally spaced numbers $(\Delta x_i)$ to another sequence of equally spaced numbers $(i)$. This is precisely the key to lumping continuous reactions discussed in the preceding sections. A special case is when all the $x_i$'s are equally spaced. Then $D(x)$ becomes a constant. But the functions $k(x)$ and $\mathbf{u}(x)$ will have to be determined, which again involves the exercise of relating a sequence of unequally spaced numbers ($\mathbf{u}_i$ and $k_i$) to a sequence of equally spaced numbers $(x_i)$.

With Eqs. 45 and 46, one can readily show that Eq. 41 approximates Eq. 40 to any degree of accuracy as long as $N$ is sufficiently large.

If one adopts Eq. 41 as the preferred lumping procedure, one then needs to determine $g$ by solving the following equation

$$\frac{dg(x, t)}{dt} = -D(x)\,k(x)\,r\left(\frac{g(x, t)}{D(x)}, x\right) \tag{47}$$

This equation is very different from Eq. 39. In order to solve it, one has to determine $D$ beforehand.

The alternative procedure consists of the following equations

$$\frac{dc(x, t)}{dt} = -k(x)r(c(x, t), x) \tag{48}$$

$$C(t) \approx \int c(x, t)D(x)\, dx \tag{49}$$

Equation 48 has a direct discrete analog, Eq. 39. And Eq. 49, an integral weighted with a reactant-type distribution function, reduces to a sum of individual concentrations in the discrete case. This procedure seems to be physically clear and is more convenient to use.

In the case of linear kinetics, the $D(x)$ terms will cancel out in Eq. 47, thus obviating the need of finding $D$. Even in this case, the discreteness of the system also indicates the need to decompose $g$ into the product of $c(x, t)$ and $D(x)$. Let $r(c) = c$, Eq. 47 has the same form as Eq. 39, i.e.,

$$\frac{dg(x, t)}{dt} = -k(x)g(x, t) \tag{50}$$

Equation 41 becomes

$$C(t) \approx \int g(x, 0)e^{-k(x)t}\, dx \tag{51}$$

In order to establish the single-component identity, $g(x, 0)$ must be made equal to $g(x, 0) = c(x, 0)D(x) = c(x, 0)\delta(x - x^*)$.

Finally, a few remarks may be in order on the assumption that $x_i \neq x_j$ for $i \neq j$. Suppose that in a mixture, there are $J$ species $(J > 1)$ having exactly the same $x$ values called $\bar{x}$. Each of these $J$ species reacts according to the following equation

$$-\frac{dc_j(t)}{dt} = k(\bar{x})\,r(c_j(t), \bar{x}), \qquad j = 1, 2, \ldots J \tag{52}$$

For linear kinetics we can simply add up $c_j(t)$ and treat the sum as the concentration of a single species of index $\bar{x}$, *viz.*

$$c(\bar{x}, t) = \sum_{j=1}^{J} c_j(t) \tag{53}$$

and $c(\bar{x}, t)$ satisfies the same equation as Eq. 52. For nonlinear kinetics, one may handle the situation by "separating out" these $J$ species; i.e., the concentration of the lump is written as

$$C(t) \approx \int c(x, t)\,D(x)\, dx + \sum_{j=1}^{J} c_j(t) \tag{54}$$

where $D(x)$ is determined in the absence of these $J$ species.

Alternatively, one can abandon $x$ as the label and use a different label. For instance, in the case of reversible reactions, one may use the equilibrium constants as the label if some species have the same forward rate constants.

## Conclusions

We have proposed a kinetic lumping procedure for continuous reaction mixtures whose constituent reactants can undergo nonlinear reactions. The key to the procedure is the introduction of a reactant-type distribution function which ties the continuous mixture to the underlying discrete mixture. Mathematically, the reactant-type distribution function may be viewed as the Jacobian of the transformation from a discrete coordinate to a continuum coordinate. Several examples of practical interest have been worked out to illustrate the use of the procedure. We justify theoretically that the high-order kinetics frequently observed in the processing of complex hydrocarbon mixtures could be interpreted as arising from the presence of some very refractory species.

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## Notation

$C(t)$ = total concentration of reactants at time $t$
$C(0)$ = total concentration of reactant in the feed
$C^*$ = equilibrium concentration, Eq. 31
$c_i(t)$ = concentration of reactant of type $i$ in the discrete mixture
$c(k, t)$ = concentration of reactant with reactivity $k$ in the continuous mixture
$c(k, 0)$ = concentration of reactant with reactivity $k$ in the feed
$D(k)dk$ = number of species types with rate constants in $(k, k + dk)$
$D(k)$ = reactant-type distribution function, Eq. 10
$D(x)$ = reactant-type distribution function, Eq. 46
$\bar{D}$ = mean value of $D(k)$
$g$ = concentration distribution function
$gdk$ = total concentration of species with rate constants in $(k, k + dk)$
$i, j$ = symbols designating reactants of types $i$ and $j$
$J$ = total number of species with identical $x$ values
$K_i$ = equilibrium constant, defined as $K_i = k_i/\tilde{k}_i$
$k_j$ = rate constant for reactant of type $i$
$\tilde{k}_i$ = rate constant for backward reaction
$k$ = rate constant used as a continuous variable
$\bar{k}, \underline{k}$ = upper and lower limits of $k$
$m(k)dk$ = total mass of species with rate constants in $(k, k + dk)$
$M(k)$ = total mass of all reactants in the feed, Eq. 15
$N$ = total number of reactant types
$n$ = order of reaction
$p, q$ = constants defined in Eq. 34
$r$ = reaction rate defined in Eq. 39
$t$ = time
$\mathbf{u}$ = vector defined in Eq. 39
$v$ = constant defined in Eq. 42
$x$ = a positive real number used to label the reactants in multiparameter reaction systems.

### *Greek letters*

$\alpha, \beta$ = constants defined in Eq. 34
$\delta$ = Dirac delta function
$\kappa$ = value of $k$ beyond which reactants are completely exhausted, Eq. 21
$\Gamma$ = Gamma function, Eq. 37
$\mu, \gamma$ = parameters defined in Eq. 38
$\lambda$ = parameter defined in Eq. 31
$\eta, \zeta$ = parameters defined in Eq. 34

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