Lumping Coupled Nonlinear Reactions in Continuous Mixtures

A lumping procedure proposed previously is applied to two types of continuous reaction mixtures: one in which the constituents undergo reactions of a Langmuir-Hinshelwood (LH) type, the other in which the constituents undergo reactions of a bimolecular type. It is shown that both mixtures initially can behave qualitatively like lumped first-order reactions. At large times, the behavior of the lumps can be described by power law kinetics, with the bimolecular lump displaying a higher overall reaction order. In particular, if the feed contains a nonzero amount of unconvertible species, the LH lump at large times decays at a second-order rate, whereas the bimolecular lump decays at a third-order rate. To complement the asymptotic results, expressions describing the behavior of the lumps at any time are derived.

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Introduction

Due to its practical importance, the subject of lumping a large number of reactions has received considerable attention (Weekman, 1979, and references therein; Li, 1984; Coxson and Bischoff, 1987a,b; Ho and Aris, 1987; Astarita and Ocone, 1988; Chou and Ho, 1988). In a previous paper we proposed a procedure for lumping nonlinear reactions in continuous mixtures. The focus there was on independent reactions (for instance, parallel nth-order reactions).

Astarita and Ocone have recently treated a similar problem but dealt with coupled reactions. As a prototype of coupled nonlinear kinetics, they considered reactions of a Langmuir-Hinshelwood type and of a bimolecular type. They showed that lumping of these kinetics has a mathematical structure qualitatively similar to that of lumping of first-order kinetics. The new feature is that the behavior of the lump is governed by functional-differential equations. The possibility of expanding the functionals into a series of integrals was also explored.

In this study we apply the lumping procedure proposed previously (Chou and Ho, 1988) to the two types of reaction mixtures considered by Astarita and Ocone. Our intent is to gain some additional insights into the behavior of these two kinetically complex mixtures. Specifically, we consider the following isothermal closed system containing N different types of reactants

$$\frac{dc_i}{dt} = -k_i c_i f\left(\sum_{j-1}^{N} K_j c_j\right) \tag{1}$$

where c_i is the concentration of reactant i, and f is a function of $\Sigma_{j-1}^{N} K_j c_j$. The sum is over all reactants. Admittedly, kinetics of this type is rather restrictive in that the function f has the same value for all reactants and depends only on the weighted sum of *all* concentrations, and that the reactions are irreversible. Despite these restrictions, we believe the problem is worth investigating because it should provide some qualitative insights into the behavior of more complex systems.

The specific form of f depends on the reaction chemistry involved. We shall consider two simple model systems. One is a Langmuir-Hinshelwood (LH) kinetic model for which f is

$$f = \frac{1}{1 + \sum_{j-1}^{N} K_j c_j} \tag{2}$$

The other is a bimolecular reaction system with

$$f = \sum_{j-1}^{N} K_j c_j \tag{3}$$

We shall lump the above reactions by treating the system as a continuum. We show that an apparent kinetics can be derived for the lump (or macroscopic observer) under certain circumstances. Where appropriate, we shall compare and contrast our results with prior results for mixtures of parallel first-order reactions (Aris, 1968; Krambeck, 1984); we do so because the problem at hand may be viewed as that of determining the influence of f on the behavior of first-order reaction mixtures.

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General Considerations

Discrete description

Equation 1 indicates that we are dealing with a multiparameter system, for k_i and K_i may both vary (nonlinearly) from species to species. This is analogous to the reversible reactions considered by Chou and Ho (1988). Without loss of generality, we can arrange the sequence of k_i in such a way that $k_i > k_j$ for $i > j$. (The case where $k_i = k_j$ for $i > j$ has been discussed by Chou and Ho.) Once this is done, the sequence of K_i is also specified. In other words, K_i bears a fixed relation to i, and K_i may or may not be greater than K_j for $i > j$. The k_i vs. i and K_i vs. i relations allow us to determine how the K_i's are related to the k_i's. The concentration of the reactant lump is simply the sum over individual concentrations

$$C(t) = \sum_{i=1}^{N} c_i(t) \tag{4}$$

The concentration of the reactant lump in the feed is $C(0)$.

Continuum description

The basic premise in lumping continuous reactions is that one can always pick a continuous variable to label the reacting species (Aris and Gavalas, 1966). For convenience and without loss of generality, we choose k as the label and K naturally should be treated as a function of k. If, for certain mixtures, k is not a good choice, we can always use another convenient label to define the mixture (Chou and Ho, 1988). To *approximate* Eq. 4 by an integral, according to Chou and Ho (1988), we write

$$C(t) = \int_0^\infty c(k,t)D(k)\,dk \tag{5}$$

where $c(k, t)$ is a well-behaved function which takes the value of $c_i(t)$ at point k_i. $D(k)$ is a reactant-type distribution function which ensures that Eq. 5 closely approximates Eq. 4. Mathematically, D may be regarded as the Jacobian of the discrete-to-continuum coordinate transform. Physically, $D(k)dk$ is the total number of reactant types with rate constants between k and $k + dk$. The D function can be used to calculate other properties of the continuous mixture. A detailed discussion of the physical significance of this function can be found elsewhere (Chou and Ho, 1988).

Note that $C(t) \leq C(0)$ where $C(0)$ is the total reactant concentration in the feed and is given by

$$C(0) = \int_0^\infty c(k,0)D(k)\,dk \tag{6}$$

Of course, we must assume that $c(k, 0)D(k)$ is of such a form that the above integral exists and is finite. Note that here we consider only the case of the reactant label k going to infinity in the lumping integral. As discussed by Chou and Ho (1988), this may be an oversimplification of physical reality in some cases, but it simplifies the mathematics considerably. Shibata et al. (1987) have lumped continuous mixtures by finite integral and compared the results with those obtained by improper integral.

Similarly, we can approximate the coupling term $\Sigma_j K_j c_j$ by an integral of the form

$$\int_0^\infty K(k)c(k,t)D(k)\,dk \tag{7}$$

Again, we need to assume that the integrand is of such a form as to ensure the integrability of Eq. 7.

General behavior of the lumps

To satisfy the requirement of coordinate invariance (Chou and Ho, 1988), we rewrite Eq. 1 in the "continuum coordinate" as

$$\frac{dc(k,t)}{dt} = -kc(k,t)\mathcal{F} \tag{8}$$

where $\mathcal{F}$ is a dimensionless, time-dependent function of the form

$$\mathcal{F} = \mathcal{F}\left[\int_0^\infty K(k)c(k,t)D(k)\,dk\right] > 0 \tag{9}$$

Note that $\mathcal{F}$ is independent of k for the reaction mixtures considered here. (Recall that f is independent of i.) Also note that $\mathcal{F}$ and f have the same analytic form but different arguments.

Paralleling the development of Astarita and Ocone (1988), we obtain from Eq. 8 that

$$c(k,t) = c(k,0)e^{-ku(t)} \tag{10}$$

where $u(t)$ is defined as

$$u(t) \equiv \int_0^t \mathcal{F}(t')\,dt' \tag{11}$$

Note that in the case of parallel first-order reactions, $u = t$.

The problem is now reduced to that of finding $u(t)$, a timelike variable with $u(0) = 0$. For a given feed [i.e., given $D(k)$, $c(k, 0)$, and $K(k)$], $u(t)$ can be obtained by solving the following integro-differential equation

$$\frac{du(t)}{dt} = \mathcal{F}\left[\int_0^\infty K(k)c(k,0)D(k)e^{-ku}\,dk\right] \tag{12}$$

Once $u(t)$ is obtained, the total concentration C is calculated as

$$C(t) = \int_0^\infty c(k,0)D(k)e^{-ku}\,dk \tag{13}$$

Hence, C represents the Laplace transform of $c(k, 0)D(k)$ and can be viewed as a function of u. Note also that the lumping integral, Eq. 13, is structurally similar to that for first-order reactions; in the latter case t takes the place of u in Eq. 13.

For the Langmuir-Hinshelwood case,

$$\frac{du}{dt} = \mathcal{F} = \frac{1}{1 + \int_0^\infty K(k)c(k,0)D(k)e^{-ku}\,dk} \tag{14}$$

and du/dt is positive and increases monotonically as u increases.

For the bimolecular case,

$$\frac{du}{dt} = \mathcal{F} = \int_0^\infty K(k)c(k,0)D(k)e^{-ku}\,dk \tag{15}$$

and du/dt decreases as u increases. It can be shown for both mixtures that u and t are one-to-one corresponding and that $u \longrightarrow \infty$ as $t \longrightarrow \infty$ and *vice versa.* The integral in Eqs. 14 and 15 can be regarded as the Laplace transform of $K(k)c(k, 0)D(k)$.

Asymptotic Kinetics at Large Times

The behavior of the lump after a long time can be determined asymptotically because it is governed by the most refractory species. Suppose that the feed mixture has a nonzero and finite amount of virtually unconvertible species [i.e., $c(0,0)D(0) \neq 0$ nor ∞], the long-time behavior of the lump can be conveniently seen by invoking the limiting-value theorem of the Laplace transform. Accordingly, Eq. 13 is reduced to the following form

$$C(t) \approx \frac{c(0,0)D(0)}{u(t)} \quad \text{for large } u \text{ or } t \tag{16}$$

It immediately follows that

$$\frac{dC}{dt} \approx -\frac{1}{c(0,0)D(0)}\frac{du}{dt}C^2 \quad \text{for large } u \text{ or } t \tag{17}$$

The time-dependent term du/dt comes from the coupling term $\mathcal{F}$. In the case of first-order kinetics, $du/dt = 1$.

We now need to obtain an asymptotic expression for du/dt at large t. Again by the limiting-value theorem and using Eq. 16, we obtain

$$\int_0^\infty K(k)c(k,0)D(k)e^{-ku}\,dk \approx \frac{K(0)c(0,0)D(0)}{u} \approx K(0)C(t) \quad \text{for large } u \text{ or } t \tag{18}$$

To proceed further, we must specify the kinetics, as described below.

LH mixtures

For large t it is easily shown from Eqs. 14 and 18 that

$$\frac{du}{dt} \approx \frac{1}{1 + \dfrac{K(0)c(0,0)D(0)}{u}} \approx 1 \tag{19}$$

and from Eq. 17 that

$$\frac{dC}{dt} \approx -\frac{1}{c(0,0)D(0)}C^2 \quad \text{for large } t \tag{20}$$

Thus, as long as $c(0,0)D(0) \neq 0$ nor ∞ and $K(0)$ is finite, the lump at large t will disappear at a second-order rate with an effective rate constant of $1/c(0,0)D(0)$—regardless of the forms of $c(k,0)$, $D(k)$, and $K(k)$. This behavior is identical to that of lumped first-order reactions (Krambeck, 1984). This is to be expected because at large t competitive adsorption no longer plays a role. In other words, the coupling term $\mathcal{F}$ loses its influence at large times; the problem naturally degenerates to that of lumping first-order reactions.

It should be emphasized that the asymptotic second-order kinetics is expected only after a long time. A follow-up question then arises: How long do we have to wait before the system attains the second-order rate? A partial answer to this question is given below by means of an order-of-magnitude analysis.

Let $z(k) = c(k,0)D(k)$ have a McLaurin series; Eq. 13 can be rewritten as

$$\begin{aligned} C(t) &= \int_0^\infty z(k)e^{-ku}\,dk \\ &= \frac{1}{u}\int_0^\infty z\left(\frac{\kappa}{u}\right)e^{-\kappa}\,d\kappa \\ &= \frac{1}{u}\int_0^\infty \sum_{m=0}^\infty \frac{z^{(m)}(0)}{m!u^m}\kappa^m e^{-\kappa}\,d\kappa \\ &= \sum_{m=0}^\infty \frac{z^{(m)}(0)}{u^{m+1}} \end{aligned} \tag{21}$$

If $z^{(m)}(0) < MW^m$, this series converges for $u > W$. Retaining only the first two terms, we obtain

$$C[u(t)] \approx \frac{z(0)}{u} + \frac{z'(0)}{u^2} \tag{22}$$

Hence the system will attain the second-order rate when

$$u \gg \frac{z'(0)}{z(0)} \tag{23}$$

To express the above inequality in terms of t, one needs to know the functional dependence between u and t. Such a dependence is highly system-dependent. We illustrate an example of the u-t relation for a simple LH system in a later section.

Bimolecular reaction mixtures

As before, we need to estimate du/dt at large u or t. In contrast to the LH case, here the coupling term should have a significant effect on the lumped kinetics. From Eqs. 15 and 18, we see that du/dt decays like $K(0)C$ for large t. Equation 17 may thus be rewritten as

$$\frac{dC}{dt} \approx -\frac{K(0)}{c(0,0)D(0)}C^3 \quad \text{for large } t \tag{24}$$

which is an apparent third-order reaction for the lump.

It should be pointed out that the foregoing system may well serve as a qualitative probe of lumping of independent second-order reactions. The latter is not amenable to the asymptotic treatment described above (Chou and Ho, 1988). It has been conjuctured that a continuum of independent second-order reactions may plausibly display an overall order higher than two (Chou and Ho, 1988).

Kinetics at All Times

The investigation has so far been restricted to the limiting case of large t and $c(0, 0)D(0) \neq 0$ nor ∞. 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 $c(k, 0)$, $D(k)$, and $K(k)$. Let $c(k, 0)$, $D(k)$, and $K(k)$ be described by the following functions

$$D(k) = qk^{\eta}e^{-\zeta k} \tag{25}$$

$$c(k, 0) = pk^{\alpha}e^{-\beta k} \tag{26}$$

$$K(k) = \bar{K}k^{\delta}e^{-\tau k} \tag{27}$$

To ensure the convergence of $\int_0^\infty D(k)\, dk$, $\int_0^\infty c(k, 0)D(k)\, dk$, and $\int_0^\infty K(k)c(k, 0)D(k)\, dk$, we impose that

$$\begin{gathered}\eta > -1, \quad \alpha + \eta > -1, \quad \alpha + \eta + \delta > -1 \\ \zeta > 0, \quad \beta + \zeta > 0, \quad \beta + \zeta + \tau > 0\end{gathered} \tag{28}$$

Note that p and q are determined by certain requirements of coordinate invariance (Chou and Ho, 1988). The total number of reactants must remain invariant under the i-to-k coordinate transform. The normalization constant q is then determined by

$$N = \int_0^\infty D(k)\, dk = \frac{q\Gamma(\eta + 1)}{\zeta^{\eta+1}} \tag{29}$$

Also, the total reactant concentration in the feed remains invariant under the coordinate transform. By means of Eqs. 6, 25, and 26, we find that

$$C(0) = \frac{pq\Gamma(\mu)}{\nu^{\mu}} \tag{30}$$

where

$$\mu \equiv \alpha + \eta + 1 > 0, \quad \nu \equiv \beta + \zeta \tag{31}$$

and Γ is the gamma function. The normalization constant p can then be determined from Eqs. 29 and 30 as

$$p = \frac{C(0)\Gamma(\eta + 1)\nu^{\mu}}{N\zeta^{\eta+1}\Gamma(\mu)} \tag{32}$$

The functions represented by Eqs. 25–27 are simple and yet versatile. Take the function in Eq. 25 as an example. It has an absolute maximum at $k = \eta/\zeta$. η and ζ measure the sharpness and asymmetry of the distribution. When $\eta = 0$, one obtains an exponential distribution and $D(0) \neq 0$; that is, the mixture contains unconvertible species. In the limits of $\eta \rightarrow \infty$ and $\zeta \rightarrow \infty$, with $\eta/\zeta \rightarrow$ constant, the function becomes a delta function centered at η/ζ.

Defining a dimensionless concentration $U(t) \equiv C(t)/C(0)$ and substituting Eqs. 25–27 and 30 into Eq. 13 yields

$$U(t) = \left[\frac{\nu}{u(t) + \nu}\right]^{\mu} \tag{33}$$

It follows that

$$\frac{dU}{dt} = -\frac{\mu}{\nu}\frac{du}{dt}U^{(1+1/\mu)} \tag{34}$$

Again, here we remark that $du/dt = 1$ for first-order kinetics. We now wish to express du/dt in terms of U. The two kinetic models are discussed individually below.

LH mixtures

Upon integration of Eq. 14 and with use of Eqs. 25–27 and 33, we obtain

$$\frac{du}{dt} = \frac{1}{1 + \lambda\left(U^{-1/\mu} + \dfrac{\tau}{\nu}\right)^{-(\mu+\delta)}} \tag{35}$$

where

$$\lambda \equiv pq\bar{K}\frac{\Gamma(\mu + \delta)}{\nu^{\mu+\delta}} \tag{36}$$

Substituting Eq. 35 into Eq. 34, we get the following overall kinetics for the lumped LH mixture

$$\frac{dU}{dt} = -\frac{\mu}{\nu}\left[\frac{U^{(1+1/\mu)}}{1 + \lambda\left(U^{-1/\mu} + \dfrac{\tau}{\nu}\right)^{-(\mu+\delta)}}\right] \tag{37}$$

which looks quite different from the underlying LH kinetics. This results from the fact that the constituent reactants can have widely different reactivities and adsorptivities. Nevertheless, Eq. 37 may be loosely regarded as consisting of a kinetic term and an inhibition (adsorption) term. A closer connection can be made with the underlying LH kinetics if we let the lump be made up of species of equal adsorptivity. Then $\delta = \tau = 0$, and Eq. 37 becomes

$$\frac{dU}{dt} = -\frac{\mu}{\nu}\left[\frac{U^{(1+1/\mu)}}{1 + \bar{K}C(0)U}\right] \tag{38}$$

Thus, when reactants of equal adsorptivity are lumped together, the apparent behavior of the lump can look like that of an LH reaction with a higher apparent order. Of course, a limiting case is where all the reactants have the same reactivity and adsorptivity. (The reactants are therefore kinetically indistinguishable.) In this case D becomes a delta function, and the rate equation for the lump degenerates to that for the individual reactant ($\mu \rightarrow \infty$ and $\mu/\nu \rightarrow$ constant in Eq. 38). This single-component identity (Ho and Aris, 1988), while conceptually obvious, is central to the working of any continuum lumping procedure.

As mentioned before, the lump of first-order reactions decays at a power law rate with an overall order of $1 + 1/\mu$ and an effective rate constant of μ/ν. To see how the rate represented by Eq. 37 is related to the decay rate of the first-order case, we next examine the asymptotic cases of small and large times.

During the initial stages of the reaction, the system is governed by a small amount of very reactive species. [Note that $c(k, 0)$ and $D(k)$ both approach zero as $k \rightarrow \infty$.] Due to an averaging effect, $\mathcal{F}$ would change slowly relative to changes in the concentrations of those very reactive species. Thus, as a first approximation, the individual reactions may be regarded as pseudofirst-order. And the lump should behave in some way similarly to the lump of first-order reactions.

Indeed, for small t with $u(t) \ll \nu$ [notice that $u(0) = 0$], we obtain from Eqs. 33 and 35 that

$$\frac{du}{dt} \approx \left[1 + \lambda\left(1 + \frac{\tau}{\nu}\right)^{-(\mu+\delta)}\right]^{-1} \equiv \phi < 1 \tag{39}$$

And Eq. 34 gives the same overall order as in the first-order case; that is,

$$\frac{dU}{dt} \approx -\frac{\mu}{\nu}\phi U^{(1+1/\mu)} \quad \text{for small } t \tag{40}$$

Note that ϕ is the minimum value of du/dt for $t > 0$ and is smaller than one. Hence, the initial effective rate constant is lower than that for lumped first-order reactions. The slowness of the initial rate is obviously the result of reactant inhibition and competitive adsorption.

On the other hand, as alluded to earlier, at large t the mixture should behave like lumped first-order reactions. Specifically, when t is large enough so that $u \gg \nu$, τ and $u^{\mu+\delta} \gg pq\bar{K}\Gamma(\mu + \delta)$, we have, by Eqs. 33 and 35, that

$$\frac{du}{dt} \approx 1 \tag{41}$$

Equation 34 then reduces to the familiar power law form for lumped first-order reactions (Aris, 1968); that is,

$$\frac{dU}{dt} \approx -\frac{\mu}{\nu} U^{(1+1/\mu)} \quad \text{for large } t \tag{42}$$

When $\mu > 1$ [in this case, $c(0, 0)D(0) = 0$; i.e., the feed contains no refractory species], the overall reaction order is between one and two at large times.

The overall reaction order for large times can be greater than two in Eq. 42 when $\alpha + \eta < 0$ (i.e., $\mu < 1$). This corresponds to a feed that is predominantly composed of unconvertible species. While theoretically insightful, this situation is not of much practical interest from the standpoint of catalyst and/or process development: if the whole feed is unconvertible, then it should deserve no attention.

The case $\alpha = \eta = 0$ or $\mu = 1$ (exponential distributions) represents a more realizable situation. In this type of feed, the unconvertible species has the highest but a finite concentration. Substituting $\mu = 1$ in Eq. 42, one obtains the asymptotic second-order kinetics as discussed earlier. We must emphasize that here a second-order overall rate is predicted only for *large* times. By contrast, the overall order for lumped first-order reaction is two at *all* times (Aris, 1968).

The $\mu = 1$ case can be further simplified if we set $\alpha = \eta = \delta = \tau = 0$. This simplification gives t as a simple, explicit function of u over $0 \leq u < \infty$. Specifically, from Eqs. 30, 31, 33, 35, and 36, one finds that

$$t = u + \nu\bar{K}C(0) \ln\left(1 + \frac{u}{\nu}\right) \tag{43}$$

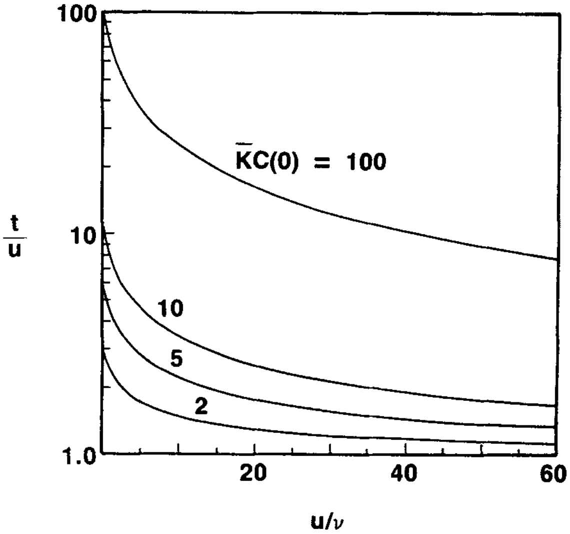

Figure 1. The *u-t* relation for a simple Langmuir-Hinshelwood system.

It follows that that t/u is bounded over the entire domain $0 \leq u < \infty$; that is,

$$1 < \frac{t}{u} \leq 1 + \bar{K}C(0) \tag{44}$$

Figure 1 plots t/u as a function of u/ν for various values of $\bar{K}C(0)$. With Eqs. 43, 44, and 23, one can estimate the waiting time for the system to attain the second-order rate.

Bimolecular reaction mixtures

Again, we let $D(k)$, $c(k, 0)$, and $K(k)$ be described by the functions shown in Eqs. 25 to 27, respectively. We then obtain the following expressions for the coupling term

$$\frac{du}{dt} = \frac{pq\bar{K}\Gamma(\mu + \delta)}{\nu^{\mu+\delta}}\left(U^{-1/\mu} + \frac{\tau}{\nu}\right)^{-(\mu+\delta)} \tag{45}$$

and for the overall kinetics

$$\frac{dU}{dt} = -\frac{\mu}{\nu}\lambda\left(U^{-1/\mu} + \frac{\mu}{\nu}\right)^{-(\mu+\delta)} U^{(1+1/\mu)} \tag{46}$$

where λ is defined in Eq. 36.

If the lump is made up of species of equal bimolecular rate constant K, then $\delta = \tau = 0$ in the above equations, and we obtain

$$\frac{dU}{dt} = -\frac{\tau}{\nu}\lambda U^{(2+1/\mu)} \tag{47}$$

That is, the decay of the lump can be exactly described by power law kinetics at all times—with an overall order at least equal to two. If we further let $\alpha = \eta = 0$ (i.e., $\mu = 1$, exponential distribution), the lumped system behaves like a third-order reaction. This is a special case of the results discussed in the preceding section.

As in the LH case, the individual reactions initially may be regarded as pseudofirst-order. For small t with $u(t) \ll \nu$, we have, from Eqs. 33 and 45, that

$$\frac{du}{dt} \approx \lambda \left(1 + \frac{\tau}{\nu}\right)^{-(\mu+\delta)} \equiv \psi \tag{48}$$

and that

$$\frac{dU}{dt} \approx -\frac{\mu}{\nu} \psi U^{(1+1/\mu)} \quad \text{for small } t \tag{49}$$

We thus obtain the same overall order as that for lumped first-order reactions, but with a different effective rate constant. Note that ψ is the maximum value of du/dt for $t \geq 0$.

On the other hand, for large t such that $u(t) \gg \nu$ and $u(t) \gg \tau$, Eqs. 33 and 45 yield

$$\frac{du}{dt} \approx \lambda \left(\frac{\mu}{\nu}\right)^{-(\mu+\delta)} \approx \lambda U^{(1+\delta/\mu)} \tag{50}$$

Therefore,

$$\frac{dU}{dt} \approx -\frac{\mu}{\nu} \lambda U^{[2+(\delta+1)/\mu]} \quad \text{for large } t \tag{51}$$

which is a high-order power law kinetics. When $\delta = 0$ and $\mu = 1$, Eq. 51 reduces to the asymptotic third-order kinetics discussed previously.

Conclusions

We have lumped two types of coupled nonlinear reactions in continuous mixtures. In one case, the individual reactions are of a Langmuir-Hinshelwood type, and in the other the individual reactions are of a bimolecular type. The kinetic behaviors of the reactant lumps under certain circumstances are examined. It is shown that both lumps at small times can behave qualitatively like the lump of first-order reactions with behavior that can be described by power law kinetics. At large times, the behavior of the lumps can also be described by power law kinetics, with the bimolecular lump exhibiting a higher overall order. In particular, if the feed mixture contains a nonzero amount of virtually unconvertible species, the Langmuir-Hinshelwood lump disappears at a second-order rate, whereas the bimolecular lump disappears at a third-order rate.

Expressions describing the kinetic behavior of these two lumps at any time have also been derived. These expressions bear little resemblance to those for individual reactants, unless the lump is made of species of equal adsorptivity in the Langmuir-Hinshelwood case or of equal bimolecular rate constant in the bimolecular case. These results may be useful to those who are faced with the problems of selecting proper kinetic models and/or lumps for complex reaction systems.

Acknowledgment

We are greatly indebted to Professor Astarita for sending us his manuscript "Lumping Nonlinear Kinetics," prior to publication (*AIChE J.*, **34**, p. 1299, 1988).

Notation

$C(t)$ = total concentration of reactants at time t
$C(0)$ = total concentration of reactant in feed
$c_i(t)$ = concentration of reactant of type i in discrete mixture
$c(k, t)$ = concentration of reactant with reactivity k in continuous mixture
$c(k, 0)$ = concentration of reactant with reactivity k in feed
$D(k)dk$ = number of species types with rate constants in $(k, k + dk)$
$D(k)$ = reactant-type distribution function, Eq. 5
f = function, Eq. 1
$\mathcal{F}$ = function, Eq. 8
i = reactant of type i
K_j = adsorption constant, or bimolecular rate constant, Eq. 1
k_i = rate constant for reactant of type i
k = rate constant used as a continuous variable
$\bar{K}$ = constant, Eq. 27
U = dimensionless total concentration, $U(t) \equiv C(t)/C(0)$
N = total number of reactant types
p, q = constants, Eqs. 25, 26
t = time
u = function, Eq. 11
z = function, $z(k) = c(k, 0)D(k)$

Greek letters

α, β = constants, Eq. 25
δ, τ = parameter, Eq. 27
η, ζ = parameters, Eq. 26
λ = parameter, Eq. 36
μ, ν = parameters, Eq. 31
ϕ = parameter, Eq. 39
ψ = parameter, Eq. 48
Γ = gamma function

Literature Cited

Aris, R., "Prolegomena to the Rational Analysis of Systems of Chemical Reactions. II: Some Addenda," *Arch. Rat. Mech. Anal.*, **27**, 356 (1968).

Aris, R., and G. R. Gavalas, "On the Theory of Reactions in Continuous Mixtures," *Phil. Trans. Roy. Soc.*, **A260**, 351 (1966).

Astarita, G., and R. Ocone, "Lumping Nonlinear Kinetics," *AIChE J.*, **34**, 1299 (1988).

Chou, M. Y., and T. C. Ho, "Continuum Theory for Lumping Nonlinear Reactions," *AIChE J.*, **34**, 1519 (1988).

Coxson, P. G., and K. B. Bischoff, "Lumping Strategy. 1: Introductory Techniques and Applications of Cluster Analysis," *Ind. Eng. Chem. Res.*, **26**, 1239 (1987a).

———, "Lumping Straetgy. 2: A System Theoretic Approach," *Ind. Eng. Chem. Res.*, **26**, 2151 (1987b).

Ho, T. C., and R. Aris, "On Apparent Second-Order Kinetics," *AIChE J.*, **33**, 1050 (1987).

Krambeck, F. J., "Computers and Modern Analysis in Reactor Design," *Inst. Chem. Eng. Symp. Ser.*, **87**, 733 (1984).

Li, G., "A Lumping Analysis in Mono- or/and Bimolecular Reaction Systems," *Chem. Eng. Sci.*, **39**, 1261 (1984).

Shibata, S. K., S. I. Sandler, and R. A. Behrens, "Phase Equilibrium Calculations for Continuous and Semicontinuous Mixtures," *Chem. Eng. Sci.*, **42**, 1977 (1987).

Weekman, V. W. Jr., "Lumps, Models, and Kinetics in Practice," *AIChE Monogr. Ser.*, **75**(11), (1979).

Note: Professor Aris has recently shown that the Astarita-Ocone kinetics is actually quite versatile (see p. 539 of this issue). He proved that in many situations the function f can be chosen so that the lump U obeys any prescribed overall kinetics $\hat{k}R(U)$ where $\hat{k}$ is the overall effective rate constant. A corollary of this is to say for any given f, one can always find an overall apparent kinetics $\hat{k}R(U)$ obeyed by the lump.

Manuscript received July 13, 1988 and revision received Oct. 5, 1988.