Lumped Kinetics of Many Parallel *n*th-Order Reactions

The kinetics of lumped *n*th-order reactions are examined both asymptotically and numerically. The lumped kinetics in most cases are *M*th order at large times. There exist two critical values for *n*, denoted by n^* and n_*, which are expressed explicitly as functions of the feed properties. It is shown that (1) $M = n$ when $n > n^*$, (2) *M* is linear in *n* when $n_* < n < n^*$, and (3) *M* does not exist when $n = n^*$ or $n \leq n_*$. Whenever the feed contains some unconvertibles, *M* is independent of *n* for $-\infty < n < n^*$. The overall effective rate constant is not continuous at $n = n^*$ nor at $n = n_*$. Unexpectedly, when $n > n^*$ the lump's long-time behavior is governed by *all* species, not just by the most refractory species. Although the asymptotic kinetics are developed for long times, they are useful for fitting the whole-time behavior of the lump by an *m*th-order model. This is true even when *M* does not exist in the asymptotic regime. Numerical experiments show that *M* and *m* behave similarly in many respects. For example, as *n* increases, they both become closer to *n* and less dependent on the feed properties. Some published data are rationalized in light of the present results.

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Introduction

When modeling the kinetics of industrial processes, one often is compelled to group the reacting species into several representative lumps because the number of species in the feed mixture is too large for individual consideration (Weekman, 1979, and references therein). Many theoretical studies have been undertaken to address the question of what constitutes an exact or approximate lumping and the conditions under which such lumpings can be achieved (Wei and Kuo, 1969; Kuo and Wei, 1969; Bailey, 1972; Liu and Lapidus, 1973; Li, 1984; Li and Rabitz, 1989). An exact lumping procedure, as discussed in those studies, may be loosely defined as one that preserves the basic kinetic structure of the underlying unlumped system. For example, it may be desirable that the lumped and the underlying unlumped kinetics have the same functional form. Systematic ways of selecting the lumps and the distribution of species among lumps have been discussed (Lee, 1978; Coxson and Bischoff, 1987a, b).

In many processes, however, the only lump that is of ultimate interest, or is measurable, is the total concentration of the reactants or of some specific classes of species. In other words, the process is basically designed for the conversion of a single total lump. Such is the case, for instance, in catalytic cracking and in hydrodesulfurization (HDS) of petroleum feedstocks. It is then of practical importance to develop an overall apparent kinetics for the conversion of the *total* lump. In this case and similar cases, there is no *a priori* reason why the lumped and the unlumped kinetics should have the same functional form, especially since the feed mixtures by their very nature may contain species of widely different reactivities. In practice, it is common to empirically fit the kinetic data by an *m*th-order power law model.

Aris (1968) was the first to address the theoretical aspects of total lumping based on the idea that a sufficiently large multicomponent mixture can be approximated by a continuum (de Donder, 1931; Aris and Gavalas, 1966). His analysis was restricted to first-order reactions. Recently, some progress has been made on extending Aris's treatment to nonlinear reactions (Ho and Aris, 1987; Astarita and Ocone, 1988; Chou and Ho, 1988, 1989; Astarita, 1989; Aris, 1989; Astarita and Nigam, 1989). The basic problem addressed in these studies can be

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posed as this: If the individual unlumped kinetics is of the form $r(c)$, can one find a lumped kinetics of the form $R = R(C)$ in terms of r and the properties of the mixture? Here C is the concentration of the lump and c the concentration of the individual reactant. This problem has been tackled along two lines. In one approach, one derives R by specifying *a priori* the functional forms for the feed properties; that is, one considers a fully characterized mixture (FCM). Alternatively, one derives R at extreme conditions with only partial information on the feed properties; that is, one considers a partially characterized mixture (PCM). Some of the recent results along these two lines are highlighted as follows.

Consider an FCM in which the feed composition-reactivity spectrum follows a gamma distribution. Then for first-order kinetics in a batch or plug-flow reactor, $R \propto C^m$, where $1 \le m \le 2$ (Aris, 1968). Thus, high-order kinetics, a phenomenon somewhat implausible in the context of a single reaction, can be formally justified in the context of processing complex reaction mixtures. Moreover, the result shows that total lumping results in an increase in the reaction order. Subsequently, Luss and coworkers (Luss and Golikeri, 1975; Golikeri and Luss, 1972, 1974; Hutchinson and Luss, 1970) uncovered many behavioral features of complex first-order reaction mixtures. For instance, the behavior of the lump depends on the mixing characteristics of the system. Indeed, van Dongen et al. (1980) have experimentally demonstrated that the overall order of HDS in plug-flow reactors is higher than that in stirred-tank reactors by 0.5. This is hardly surprising. An overall lumped kinetics represents an averaging over the reactivity and composition spectra, and the average should be different in reactors with different mixing characteristics. Chou and Ho (1988) treated reversible first-order reactions. The lump reacts at a high-order rate and ultimately reaches an apparent equilibrium level.

The interactive kinetics (e.g., bimolecular reactions) considered by Astarita and Ocone (1988) is very versatile. Aris (1989) showed with what he called the α, β, Γ distribution that for any unlumped kinetics r, one can always find R in the form $R = R(C)$. The converse is also true—for a given $R = R(C)$, one can always find the corresponding $r = r(c)$. In some situations the interactive kinetics lead to $R \propto C^m$. Astarita (1989) has shown that m can be smaller than the order of the underlying reactions, and in fact even negative. In the case of a CSTR, unfortunately, this simple result does not apply; $R(C)$ in general cannot be found (Astarita and Nigam, 1989).

A PCM in the present context means that one has some information on the most refractory part of the feed. A problem of practical interest is the lump's behavior at large times (or in the high-conversion regime). This is because in oil refining one almost always wants to run the reactor at the highest permissible conversion. In exploring or developing new catalysts, it is important that competing catalysts be compared at high conversions.

For first-order reactions, $R \propto C^2$ at large times whenever the feed contains some unconvertibles (Krambeck, 1984). One can calculate the overall rate constant based on the amount of unconvertibles. This is also true for reversible first-order reactions, irreversible nth-order reactions with $n < 2$, and a particular type of Langmuir-Hinshelwood (LH) reactions (Chou and Ho, 1988, 1989). Chou and Ho (1989) also estimated the waiting time for the LH system to attain the asymptotic second-order rate. For bimolecular reactions, $R \propto C^3$ (Chou and Ho, 1989). Since the only restriction here is the presence of some unconvertibles, these asymptotic power law kinetics do seem to have some fundamental generality in certain contexts. The asymptotic second-order kinetics also holds for first-order reaction mixtures free of unconvertibles (Ho and Aris, 1987).

There is yet another approach, which involves the derivation of upper and lower bounds on R based on the initial rate. For parallel nth-order reactions in discrete mixtures, Luss and Hutchinson (1971) obtained an upper bound for $n \ge 0.5$ and a lower bound for any n. The gap between these bounds is small initially, but becomes wide at large times.

This study is aimed at developing a fairly complete picture of the asymptotic and the global behavior of a large number of parallel nth-order reactions. We first develop a general long-time asymptotic theory that includes as special cases the results of prior studies. We prove that, except for some special cases, the lumped kinetics at large times to leading order are Mth order, with M depending on n and the properties of the most refractory part of the feed. Some of the results are not intuitively obvious. Next we perform numerical experiments to fit the global kinetics by an mth-order kinetic model, including cases where the asymptotic kinetics do not follow a power law form. We show that M and m behave quite similarly in many respects.

Formulation

Consider a mixture containing a total of N different types of reactants in an isothermal batch or plug-flow reactor. Each reactant disappears at an nth-order rate. Since N is very large, we treat the mixture as a continuum and label the reactants by a dimensionless real variable x in the interval $[0, \infty)$. We then have the following component mass balance equation for species x:

$$\frac{dc(x;t)}{dt} = -k(x)c(x;t)^n$$

$$t = 0, c(x;t) = c(x;0) \tag{1}$$

where $c(x;t)$ is the concentration of reactant x at time t and $k(x)$ is the rate constant. The nth-order reaction assumption is not a serious one even when adsorption on a nonideal catalyst surface is considered (Carberry, 1976). Note also that n is assumed to be constant for all x; this is not a particularly strong assumption for many petroleum processes (Venuto and Habib, 1978; Ho, 1988). For instance, in hydrodenitrogenation (HDN) of many petroleum feeds, n is practically zero (Shabtai and Yeh, 1988; Smith and Satterfield, 1986; Ho, 1988, and references therein). Here each species denitrogenates at its own zero-order rate, independent of its concentration and neighboring species. Mathematically, this represents the simplest linear system. Yet, as will be seen later, the collective behavior of these species can be quite complex.

We consider first $n > 1$. $c(x;t)$ is of the form

$$c(x;t) = \frac{c(x;0)}{\left[1 + \frac{1}{\beta} c(x;0)^{1/\beta} k(x) t\right]^{\beta}} \tag{2}$$

in which

$$\beta \equiv 1/(n-1) \tag{3}$$

Then the total concentration of the reactants $C(t)$ is (Chou and Ho, 1988)

$$C(t) = \int_0^\infty c(x; t)D(x)\,dx = \int_0^\infty \frac{c(x; 0)D(x)\,dx}{\left[1 + \frac{1}{\beta}c(x; 0)^{1/\beta}k(x)t\right]^\beta} \tag{4}$$

$D(x)$ is a reactant-type distribution function. The slice $D(x)dx$ is the total number of reactant types with x between x and $x + dx$. It should be emphasized that $c(x; t)$ in Eq. 4 is a concentration rather than a concentration density.

The system in question can be scaled as follows. Let

$$c(x; 0) = c_0 f(x),\ D(x) = Ng(x),\ k(x) = \hat{k}h(x)$$

$$\tau = \hat{k}c_0^{n-1}t,\ U = C(t)/C(0) \tag{5}$$

where τ is the dimensionless time and U is the dimensionless total concentration. On physical grounds c_0 should be much smaller than $C(0)$. The above scaling for t is chosen for notational convenience. One may choose $\tau = \hat{k}C(0)^{n-1}t$.

We may refer to $g(x)$ as the lumping density that satisfies

$$\int_0^\infty g(x)\,dx = 1 \tag{6}$$

Without loss of generality, we let

$$\int_0^\infty f(x)g(x)\,dx = 1 \tag{7}$$

That is to say, we scale C with Nc_0 [$= C(0)$], which is a finite (experimentally measurable) number. We assume that $f(x)$ and $g(x)$ remain bounded as $x \to \infty$. In fact, both functions for practical purposes can be assumed to approach zero rapidly as $x \to \infty$. Their behaviors near $x = 0$ are discussed later.

It often pays to pick x which is a measure of reactivity, since after all we are interested in the overall reactivity of the mixture. This amounts to a change of variables $x' = k(x)$ in Eq. 4, which is permissible as long as $k(x)$ is monotonic. Thus, without loss of much generality, we simply let $h(x) = x$. This assumption, for first-order and Astarita's kinetics (Astarita and Ocone, 1988; Astarita, 1989), allows one to take advantage of existing theorems for the Laplace transform. We should also make a fine distinction here: The reactant with $x = 0$ is unconvertible. A reactant with a small x is refractory; the closer its x value is to zero, the more refractory is the reactant.

Equation 4 in dimensionless form, with the scalings in Eq. 5, becomes

$$U(\tau) = \int_0^\infty \frac{f(x)g(x)\,dx}{\left[1 + \frac{1}{\beta}f(x)^{1/\beta}\tau x\right]^\beta} \quad \text{for } \beta > 0 \tag{8}$$

When $\beta < 0$ (or $n < 1$), we need to consider the phenomenon of reactant exhaustion. Equation 8 is then rewritten as

$$U(\tau) = \int_0^\infty f(x)g(x)[1 - \tau/\tau^*(x)]^{|\beta|}\,dx \quad \text{for } \beta < 0 \quad \{x: \tau < \tau^*\} \tag{9}$$

where the function $\tau^*(x)$ is the exhaustion time at which reactant x is completely consumed. That is, the integral in Eq. 9 is only over reactants that have not been depleted by time τ, with $\tau < \tau^*$. Unless all the reactants have the same exhaustion time, the behavior of the reactant lump will not be that of a zero-order reaction. The function $\tau^*(x)$ is obtained by finding the root(s) of the denominator in Eq. 8:

$$\tau^*(x) = |\beta| f(x)^{1/|\beta|}(1/x) \tag{10}$$

The case where τ^* is bounded is not of interest to us because U is identically zero when $\tau > \max \tau^*$. What we are interested in is the situation in which τ^* remains unbounded.

When $|\beta| = \infty$ ($n = 1$), the integrand in Eq. 8 reduces to the usual exponential form and $U(\tau)$ simply becomes the Laplace transform of $f(x)g(x)$; that is,

$$U(\tau) = \int_0^\infty f(x)g(x)\exp(-x\tau)\,dx \tag{11}$$

We will show that in most cases the behavior of the lump at large times is governed by the most refractory species, as might be expected intuitively. Therefore, we need to know the behaviors of $f(x)$ and $g(x)$ near $x = 0$. Following Ho and Aris (1987) we let

$$\begin{aligned} g(x) &\sim x^\mu(g_0 + g_1x + \cdots) \sim g_0x^\mu \\ f(x) &\sim x^\nu(f_0 + f_1x + \cdots) \sim f_0x^\nu \end{aligned} \quad \text{as } x \to 0 \tag{12}$$

in which $f_0 \neq 0$ and $g_0 \neq 0$. Physically, $c(x; 0)$ should be a small and finite quantity; we thus let $\nu \geq 0$. Since g is meaningful only in the context of an integral, we are content with the requirement $1 + \mu > 0$, which ensures that g is integrable. These two conditions guarantee the integrability of $f \cdot g$. When $\nu = 0$ the unconvertible has a finite concentration. When $\mu \leq 0$, the mixture has a finite number of reactant types whose x values are arbitrarily close to zero.

Equations 8–12 define the starting point for this study. We next determine the long-time asymptotes for $U(\tau)$ under various conditions and find a function R such that $dU/d\tau \sim -R(U)$ as $\tau \to \infty$. It turns out that in most cases $R \sim U^M$. Under some exceptional conditions, no M can be found. To see the usefulness of the asymptotic results, we shall fit the global behavior of the lump by an mth-order kinetic model. Throughout this work M denotes the asymptotic reaction order for large τ and m denotes the order of a power law model approximating the lump's global behavior for all τ.

Large Time Behavior of $U(\tau)$

Case A: $\beta > 0$ (i.e., $n > 1$)

There are three subcases, discussed individually below.

Theorem 1. If

$$0 < \beta < 1 + \mu \tag{13}$$

then

$$U(\tau) \sim \frac{I_\beta}{\tau^\beta} \quad \text{as } \tau \to \infty \tag{14}$$

where I_β, a functional of $g(x)$, is given by

$$I_\beta \equiv \beta^\beta \int_0^\infty \frac{g(x)}{x^\beta}\, dx \tag{15}$$

Proof. Equation 8 can be rewritten as

$$\tau^\beta U(\tau) = \int_0^\infty \frac{f(x)g(x)\, dx}{\left[\frac{1}{\tau} + \frac{1}{\beta} x f(x)^{1/\beta}\right]^\beta} \tag{16}$$

Equation 14 is obtained by simply dropping the $1/\tau$ term in the denominator of Eq. 16. This is permissible when $\tau \to \infty$ (monotone convergence) as long as I_β converges. Note that we have assumed that g goes to zero rapidly as $x \to \infty$. To ensure convergence at $x = 0$ we replace $g(x)$ by its asymptotic form, Eq. 12, and impose the condition $\beta < 1 + \mu$. If $f(x) = 0$ on some interval, then we take $g(x) = 0$ on this interval. (This of course makes physical sense.) The proof of Theorem 1 is thus completed.

Remarks. Note here that $f(x)$, or $c(x;0)$, plays no role in determining the behavior of I_β. When $\mu = 0$, the condition Eq. 13 becomes $0 < \beta < 1$, implying $n > 2$.

When $\beta \geq 1 + \mu$, the integral I_β diverges. In this case, the term $1/\tau$ in the denominator of Eq. 16 cannot be neglected due to the existence of a boundary layer near $x = 0$. This leads to the next theorem.

Theorem 2. If

$$\beta > 1 + \mu > 0 \tag{17}$$

then to leading order as $\tau \to \infty$

$$U(\tau) \sim \frac{g_0 f_0^\eta \beta^{z+1}}{(\beta + \nu)} B(z, w) \frac{1}{\tau^z} \tag{18}$$

where

$$z \equiv \frac{\beta(1 + \mu + \nu)}{\nu + \beta} > 0 \tag{19}$$

$$\eta \equiv 1 - z/\beta \tag{20}$$

$$w \equiv \beta - z = \beta\eta > 0 \tag{21}$$

and $B(z,w)$ is the beta function, defined as

$$B(z, w) \equiv \int_0^\infty \frac{\xi^{z-1}\, d\xi}{(1 + \xi)^{z+w}} = \int_0^1 \xi^{z-1}(1 - \xi)^{w-1}\, d\xi \quad z, w > 0 \tag{22}$$

Proof. We split the righthand side of Eq. 8 into two terms:

$$U(\tau) = \int_0^\epsilon \frac{f(x)g(x)\, dx}{\left[1 + \frac{1}{\beta} f(x)^{1/\beta} x\tau\right]^\beta} + \int_\epsilon^\infty \frac{f(x)g(x)\, dx}{\left[1 + \frac{1}{\beta} f(x)^{1/\beta} x\tau\right]^\beta} \equiv I_1 + I_2 \tag{23}$$

in which ϵ is a small number. I_1 is an integral over the refractory region, while I_2 is over the reactive region. It can be seen that $I_2 = 0(1/\tau^\beta)$ as $\tau \to \infty$. In I_1 we replace $f(x)$ and $g(x)$ by their asymptotic forms as $x \to 0$, Eq. 12, with errors that are small as $\epsilon \to 0$ (see Appendix A for a rigorous justification of this claim). To blow up the region near $x = 0$, we rescale x by letting

$$\xi = \frac{1}{\beta} f_0^{1/\beta} x^{(1+\nu/\beta)} \tau \tag{24}$$

Then I_1 becomes

$$I_1 = \frac{g_0 f_0^\eta \beta^{z+1}}{(\beta + \nu)} \frac{1}{\tau^z} \int_0^{b(\tau)} \frac{\xi^{z-1}\, d\xi}{(1 + \xi)^\beta} \tag{25}$$

where

$$b(\tau) \equiv f_0^{1/\beta} \epsilon^{(1+\nu/\beta)} (\tau/\beta) \tag{26}$$

Note that $b(\tau) \to \infty$ as $\tau \to \infty$ for fixed ϵ.

For fixed ϵ and sufficiently large τ, I_1 can be reduced to

$$I_1 = \frac{g_0 f_0^\eta \beta^{z+1}}{(\beta + \nu)} B(z, w) \tau^{-z}[1 + o(1)] \tag{27}$$

where $o(1)$ represents terms that go to zero as $\tau \to \infty$ or $\epsilon \to 0$. $B(z,w)$ is finite because w and z are both positive. Since $\beta > 1 + \mu$, we have $z < \beta$, which says that of the two terms, I_1 and I_2, the former is the dominant one as $\tau \to \infty$. We thus prove the theorem.

Remarks. Here the refractory (or the boundary layer) region is more important than the reactive region. There is no boundary layer effect in Theorem 1; both regions are important. We discuss this point in detail later. Finally, when $\mu = \nu = 0$, then $z = 1$ and hence $U(\tau) = 0(1/\tau)$ in the limit $\tau \to \infty$, a result obtained by Chou and Ho (1988).

We now consider the case $\beta = 1 + \mu$. Again we show that the boundary layer near $x = 0$ is the dominant region.

Theorem 3. If

$$\beta = 1 + \mu > 0 \tag{28}$$

then as $\tau \to \infty$

$$U(\tau) \sim \frac{g_0 \beta^{z+1}}{(\beta + \nu)} \frac{\ln \tau}{\tau^z} \tag{29}$$

Proof. When $\beta = 1 + \mu$, Eq 23 becomes

$$U(\tau) = \frac{g_0\beta^{z+1}}{(\beta+\nu)}\frac{1}{\tau^z}\int_0^{b(\tau)}\frac{\xi^\mu\, d\xi}{(1+\xi)^{1+\mu}}[1 + o(1)] + 0(1/\tau^\beta) \quad (30)$$

Convergence of the above integral depends on the behavior of the integrand at large ξ. Note that here $z = \beta$. Asymptotically, Eq. 30 for fixed ϵ reduces to

$$U(\tau) \sim \frac{g_0\beta^{z+1}}{(\beta+\nu)}\frac{1}{\tau^z}\int^{b(\tau)}\xi^{-1}\, d\xi + 0(1/\tau^\beta) \sim \frac{g_0\beta^{z+1}}{(\beta+\nu)}\frac{\ln\tau}{\tau^z} \quad \text{as } \tau\to\infty \quad (31)$$

which is Eq. 29.

Remarks. As before when $\nu = \mu = 0$, $z = 1$. Since this is the case for Aris's (1989) assumption $f(x) = \exp(-x)$, we recover his result for $\beta = 1$ ($n = 2$) and $g_0 = 1$; that is,

$$U(\tau) \sim \frac{\ln\tau}{\tau} \quad \text{as } \tau\to\infty \quad (32)$$

Aris also gave higher order terms. Theorem 3 shows that the leading logarithmic term first found by Aris is not an isolated phenomenon.

Case B: $\beta < 0$ (i.e., $n < 1$)

As discussed earlier, the total concentration is given by Eqs. 9 and 10, where the integral is only over reactants that have not been totally depleted. If $\tau^*(x)$ is bounded, then all reactants will be depleted after a finite time. $\tau^*(x)$ can be unbounded only for small values of x. By Eq. 12 we have

$$\tau^*(x) \sim |\beta| f_0^{1/|\beta|} x^{(\nu/|\beta|-1)} \quad \text{as } x\to 0 \quad (33)$$

To ensure that U will not become completely depleted in a finite time (i.e., τ^* is unbounded), we impose, in addition to $\beta < 0$, that

$$|\beta| > \nu \quad (34)$$

The inverse of Eq. 33 is

$$\chi(\tau) \sim \left[\frac{\tau}{|\beta| f_0^{1/|\beta|}}\right]^{1/(\nu/|\beta|-1)} \quad (35)$$

The asymptotic behavior of $U(\tau)$ is given by the following theorem.

Theorem 4. If

$$\beta < 0 \quad \text{and} \quad |\beta| > \nu \quad (36)$$

then as $\tau\to\infty$

$$U(\tau) \sim \frac{g_0 f_0^\eta |\beta|^{z+1}}{(|\beta|-\nu)} B(z, 1+|\beta|)\frac{1}{\tau^z} \quad (37)$$

Proof. When $\tau\to\infty$, the integral in Eq. 9 can be replaced asymptotically by the integral from $x = 0$ to $x = \chi(\tau)$. We also replace $f(x)$ and $g(x)$ by their asymptotic forms, Eq. 12. Let

$$\xi = \frac{\tau}{|\beta| f_0^{1/|\beta|}} x^{1-\nu/|\beta|} \quad (38)$$

Then Eq. 9 becomes

$$U(\tau) \sim \frac{g_0 f_0^\eta |\beta|^{1+z}}{(|\beta|-\nu)}\frac{1}{\tau^z} \int_0^1 (1-\xi)^{|\beta|}\xi^{[(\mu+\nu+\nu/|\beta|)/(1-\nu/|\beta|)]}\, d\xi \quad (39)$$

from which Eq. 37 follows.

Remarks. When $\mu = \nu = 0$, Eq. 37 reduces to that obtained by Chou and Ho (1988). In this case Eq. 37 and Eq 18 have identical form after judicious placement of absolute value signs.

For completeness we should include Ho and Aris's (1987) result for $|\beta| = \infty$ (or $n = 1$). In this case Eq. 11 reduces to

$$U(\tau) \sim \int_0^\infty f_0 g_0 x^{\mu+\nu}\exp(-x\tau)\, dx = \frac{f_0 g_0 \Gamma(1+\mu+\nu)}{\tau^{1+\mu+\nu}} \quad \text{as } \tau\to\infty \quad (40)$$

When $\mu = \nu = 0$, $U(\tau) = 0(1/\tau)$ as $\tau\to\infty$, which is Krambeck's result (1984).

It should be pointed out that Eq. 40 can be obtained from Eq. 18 or Eq. 37 by taking the limit as $\beta\to\infty$ or $\beta\to-\infty$, respectively. This can be proved by noting that

$$\lim_{\beta\to\infty}\beta^z B(z, \beta - z) = \lim_{\beta\to-\infty}|\beta|^z B(z, 1+|\beta|) = \Gamma(z) \quad (41)$$

where in taking the limit we have used $B(z,w) = \Gamma(z)\Gamma(w)/\Gamma(z+w)$ and Stirling's formula for the gamma function.

Before proceeding further, we should get some feel for the accuracy of the leading asymptotic approximation. The exact results under different conditions were obtained by numerically integrating Eq. 8 or 9. It is to these that the asymptotic results are compared.

Evaluation of Asymptotic Results

Consider a fully characterized mixture with f and g given by

$$f(x) = \frac{\Gamma(p)(p+q)^{p+q-1}}{p^p\Gamma(p+q-1)} x^{q-1}e^{-qx} \quad (42)$$

$$g(x) = \frac{p^p x^{p-1}e^{-px}}{\Gamma(p)} \quad (43)$$

A simple comparison can be made analytically for $|\beta| = \infty$ ($n = 1$) and $p = q = 1$: Eq. 11 gives $U(\tau) = 2/(\tau+2)$, while Eq. 40 gives $U(\tau) = 2/\tau$.

In terms of percent conversion of the lump vs. time, Figure 1 compares the asymptotic result (solid line) with the exact

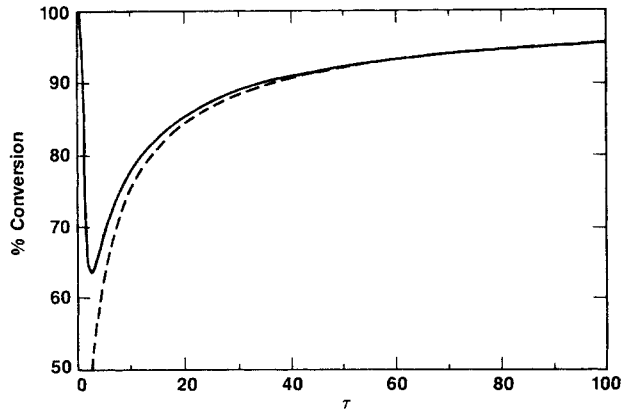

Figure 1. $U(\tau)$ for $\beta = p = q = 1$ in Eqs. 42 and 43.
----calculated by exact numerical integration

calculation (dashed line) for $\beta = p = q = 1$ ($n = 2$). This is the case considered by Aris (1989); that is, $U(\tau) \sim -\ln\tau/\tau$. As Figure 1 shows, the domain of validity covers the region of greater than 65% conversion. The asymptotic result, going through a minimum, lies above the exact result. This is a characteristic of the $\beta = 1 + \mu$ case due to the logarithmic term. Figure 2 shows the results for $\beta = 1$ and $p = q = 2$ (case VI). We also did similar calculations for other cases and found that the asymptotic results compare well with the exact calculations at high conversions. Except for the $\beta = 1 + \mu$ case, the asymptotic results all fall below the exact results, (e.g., Figure 2). Finally, it should be stressed that the asymptotic approximations are accurate only up to terms of $0(1/\tau)$. And the domain of validity depends on $f(x)$, $g(x)$, and the underlying kinetics.

Asymptotic Kinetics at Large Times

Having established the asymptotics, it is of practical interest to find a rate equation for the lump; that is, we seek a function $R(U)$ such that

$$\frac{dU}{d\tau} \sim -R(U) \quad \text{as} \quad \tau \to \infty \tag{44}$$

We know that as $\tau \to \infty$, U either is $0(1/\tau^{\lambda})$ or $0(\ln\tau/\tau^{\lambda})$ where $\lambda > 0$. In what follows we assume that the asymptotic expression for U can be differentiated to give the asymptotic form for $dU/d\tau$ (or U'). This assumption is justified in Appendix B. It is trivial to show that if

$$U \sim \frac{\sigma}{\tau^{\lambda}} \quad \text{and} \quad U' \sim -\frac{\lambda\sigma}{\tau^{1+\lambda}}, \text{ then } R(U) \sim \frac{\lambda}{\sigma^{1/\lambda}} U^{(\lambda+1)/\lambda} \tag{45}$$

That is to say, the lumped kinetics, asymptotically, has an order of $M = (\lambda + 1)/\lambda$ and an overall effective rate constant equal to $\lambda/\sigma^{1/\lambda}$.

For the special case of $U(\tau) = 0(\ln\tau/\tau^{\lambda})$, the following theorem tells us that the asymptotic kinetics *is not* of a power law form.

Table 1. Summary of Results

Case No.	Conditions n	Condition β	U as $\tau \to \infty$	$dU/d\tau$ as $\tau \to \infty$	Remarks
I	$n \le 1 - \frac{1}{\nu}$	$-\nu \le \beta < 0$	0	0	Depletion in finite time
II	$1 - \frac{1}{\nu} < n < 1$	$\beta < -\nu$	$\frac{g_0 f_0^{\eta} \lvert\beta\rvert^{z+1}}{(\lvert\beta\rvert - \nu)} \frac{B(z, 1 + \lvert\beta\rvert)}{\tau^z}$	$-z\left[\frac{g_0 f_0^{\eta} \lvert\beta\rvert^{z+1}}{\lvert\beta\rvert - \nu} B(z, 1 + \lvert\beta\rvert)\right]^{-1/z} \cdot U^{1+1/z}$	$\mu = \nu = 0$ (Chou & Ho, 1988)
III	$n = 1$	$\lvert\beta\rvert = \infty$	$\frac{f_0 g_0 \Gamma(z)}{\tau^z}$	$-z[f_0 g_0 \Gamma(z)]^{-1/z} \cdot U^{1+1/z}$	(i) Ho & Aris (1987) (ii) $\mu = \nu = 0$ (Krambeck, 1984) (iii) $z = \mu + \nu + 1$
IV	$1 < n < 1 + \frac{1}{(1+\mu)}$	$\beta > 1 + \mu$	$\frac{g_0 f_0^{\eta} \beta^{z+1}}{(\beta + \nu)} \frac{B(z, \beta - z)}{\tau^z}$	$-z\left[\frac{g_0 f_0^{\eta} \beta^{z+1} B(z, \beta - z)}{(\nu + \beta)}\right]^{-1/z} \cdot U^{1+1/z}$	$\mu = \nu = 0$ (Chou & Ho, 1988)
V	$n = 1 + \frac{1}{(1+\mu)}$	$\beta = 1 + \mu$	$\frac{g_0 \beta^{z+1}}{(\beta + \nu)} \frac{\ln\tau}{\tau^z}$	$-z^{1+1/z}\left[\frac{(\nu + \beta)}{g_0 \beta^{z+1} \lvert\ln U\rvert}\right]^{1/z} \cdot U^{1+1/z}$	(i) $z = \beta$ (ii) $\beta = 1, g = 1, f = e^{-x}$ (Aris, 1989)
VI	$n > 1 + \frac{1}{(1+\mu)}$	$0 < \beta < 1 + \mu$	$\frac{\beta^{\beta}}{\tau^{\beta}} \int_0^{\infty} \frac{g(x)\,dx}{x^{\beta}}$	$-\left[\int_0^{\infty} \frac{g(x)\,dx}{x^{\beta}}\right]^{-1/\beta} \cdot U^{1+1/\beta}$	$1 + \frac{1}{\beta} = n$

$\beta \equiv 1/(n-1)$, $z \equiv \beta(\mu + \nu + 1)/(\nu + \beta)$, $\eta \equiv 1 - z/\beta$, $1 + \mu > 0$
$f(x)$, feed concentration; $g(x)$, lumping density
$f(x) \sim f_0 x^{\nu}$ and $g(x) \sim g_0 x^{\mu}$ as $x \to 0$

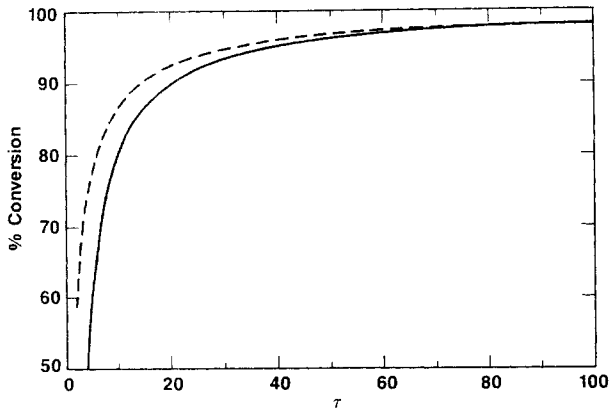

Figure 2. $U(\tau)$ for $\beta = 1$ and $p = q = 2$ in Eqs. 42 and 43.
----calculated by exact numerical integration

Theorem 5. If

$$U \sim \frac{\sigma \ln \tau}{\tau^{\lambda}} \quad \text{and} \quad U' \sim \frac{d}{d\tau}\left(\frac{\sigma \ln \tau}{\tau^{\lambda}}\right) \quad \text{as } \tau \to \infty \tag{46}$$

then

$$R(U) \sim \frac{\lambda^{(\lambda+1)/\lambda}}{\sigma^{1/\lambda}} \frac{U^{(\lambda+1)/\lambda}}{|\ln U|^{1/\lambda}} \quad \text{as } \tau \to \infty \tag{47}$$

Proof. Let

$$\theta = -\ln U \tag{48}$$

and

$$\phi = \ln \tau \tag{49}$$

Note that θ and ϕ both go to infinity as $\tau \to \infty$. We shall now express ϕ in terms of θ. Putting Eqs. 48 and 49 into Eq. 46 yields

$$\lambda = \frac{\theta}{\phi} + \frac{\ln \phi}{\phi} + \frac{\ln \sigma}{\phi} + o(1) \tag{50}$$

where $o(1)$ are terms that vanish as $\tau \to \infty$. We thus have

$$\frac{\theta}{\phi} = \lambda + o(1) \quad \text{when } \tau \to \infty \tag{51}$$

Therefore,

$$\ln \phi = \ln \theta - \ln \lambda + o(1) \quad \text{as } \tau \to \infty \tag{52}$$

Combining Eqs. 50 and 52 leads to

$$\lambda\phi = \theta + \ln \theta + \ln \frac{\sigma}{\lambda} + o(1) \tag{53}$$

Substituting Eqs. 48 and 49 into Eq. 53 gives

$$\tau^{\lambda} = \frac{1}{U}(\ln U^{-1}) \frac{\sigma}{\lambda}[1 + o(1)] \tag{54}$$

Differentiation of Eq. 46 yields

$$\frac{dU}{d\tau} \sim \frac{\sigma}{\tau^{1+\lambda}} - \frac{\lambda}{\tau}\left[\frac{\sigma \ln \tau}{\tau^{\lambda}}\right] \sim -\lambda \frac{\sigma \ln \tau}{\tau^{1+\lambda}} \tag{55}$$

which when combined with Eq. 54 gives Eq. 47.

Discussion of Asymptotic Results

The results obtained in the preceding sections show that in most situations the lumped kinetics to leading order takes a power law form at large times. However, exceptions do exist. Table 1 lists the leading terms for U and $dU/d\tau$ as $\tau \to \infty$. Except for some special cases, the behavior of the lump is basically governed by three parameters: n (or β), μ, and ν. Note that case III is a special case of either case II or IV, as already shown.

Physical considerations

There are six cases listed in Table 1, corresponding to the six regions of the (μ, ν, n) = parameter space depicted in Figure 3. Region I ($n \leq 1 - 1/\nu$) is characterized by total depletion in a finite time. The boundary ($n = 1 - 1/\nu$) between regions I and II ($1 - 1/\nu < n < 1$) is determined by ν, not by μ, since to be in region I, all reactants must deplete regardless of how they are distributed on the reactivity spectrum (or how they are lumped). Upon passing from region II to region I, the lump loses its asymptotic power law behavior. This occurs when n becomes very small, and consequently the overall rate accelerates as the individual reactions proceed, leading to total depletion after a finite time. Alternatively, at large ν the concentrations of the refractory species are low [$f(x)$ is concave upward near $x = 0$], which also favors total depletion.

Regions II, III ($n = 1$), and IV [$1 < n < 1 + 1/(1 + \mu)$] in Figure 3 are all characterized by power law behavior. However, in an experimental situation, crossing region III will not be noticed, since both the overall order and effective rate constants vary smoothly (they and their first derivatives with respect to n are continuous) as n passes through unity. Thus the boundary region III is experimentally "transparent". In this sense, regions II, III, and IV can be grouped together as one category, within which

$$M = (n\nu + \mu + 2)/(1 + \mu + \nu) \tag{56}$$

$$\text{for} \quad n_* \equiv 1 - 1/\nu < n < 1 + 1/(1 + \mu) \equiv n^* \tag{57}$$

that is, M is a linear function of n, Figure 4. It follows that for $n_* < n < n^*$

$$M > 1 \quad \text{and} \quad M > n \tag{58}$$

$M > 1$ implies that the lump will not deplete. That $M > n$ is hardly surprising, because as time progresses the reactive species will react so fast that the mixture becomes progressively more refractory, thus giving rise to a higher apparent order. Put differently, the overall rate may be regarded as nth order with a concentration-dependent rate "constant" that is asymptotic to U^{M-n}.

If we combine regions II, III, and IV as one group (they are

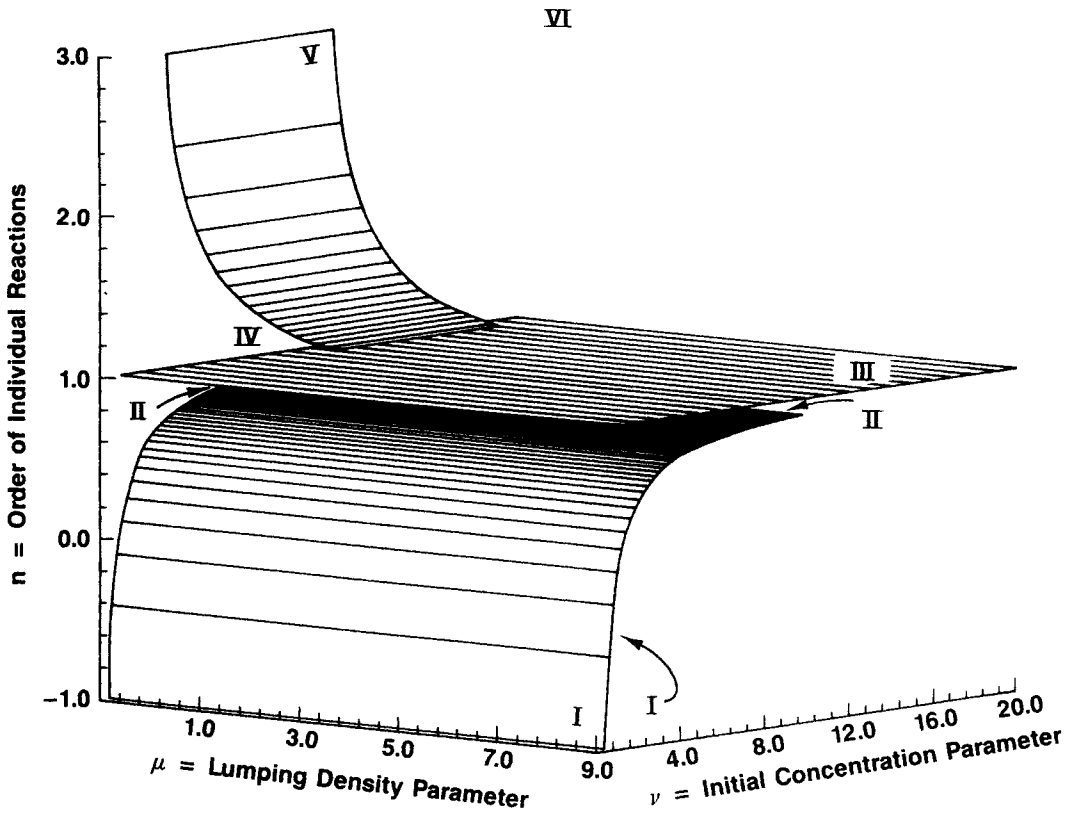

Figure 3. Parameter space with regions corresponding to case nos. in Table 1.

structurally similar), the lumped system is really characterized by four distinct cases. This is succinctly summarized in the Conclusions section. For practical calculations, however, it is necessary to divide the system into the six cases shown in Table 1.

Clearly the overall rates in regions II, III, and IV are all governed by the most refractory species (the asymptotic forms of f and g as $x \to 0$). This is an obvious advantage of the asymptotic analysis. That is, to evaluate the overall rate at large times, one needs only local information (near $x = 0$). In practice one seldom has a complete knowledge of the reactivity and composition spectra of the feed, while it is relatively easy to characterize the most refractory end of the spectra. Alternatively, the present results may be used to obtain information on the most refractory part of the feed (μ, ν, f_o, g_o) by fitting the U vs. τ data at large times. Here the mixture has a "short memory" in that the long-time data, asymptotically, are not affected by the reactive species.

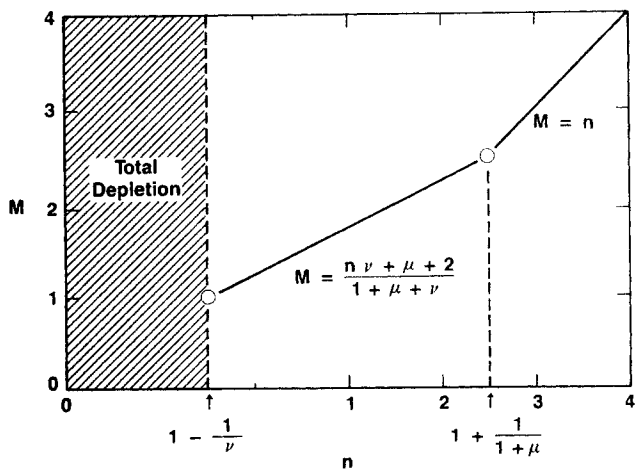

Figure 4. Relation between *M* and *n*.
No M can be found when $n = 1 + 1/(1 + \mu)$, denoted by O

As long as $n \geq 1$, none of the reactants will deplete in a finite time. So what is important here is how the reactants are distributed along the reactivity spectrum. This is why n^* depends on μ, not on ν. Here we also see the need of having the $g(x)$ function in the lumping integral.

In region VI the lump's long-term behavior depends on the refractory as well as the reactive species. This result is counterintuitive. Reactions in this region are characterized by high-order reactions. In fact, the order is so high that the decay rates of all species will decelerate rapidly as soon as the reactions start. Thus, even the most reactive species will remain influential after a long time. In other words, the mixture has a long memory. Here we are dealing with a lump whose constituents are relatively homogeneous. The result is that the overall rate, asymptotically, exhibits the same order as that of the individual reactions. But the effective rate constant, an average over the entire reactivity spectrum, weighs more heavily toward the refractory end. Note also that the overall effective constant depends on $g(x)$, not on $f(x)$. This again demonstrates the desirability of having $g(x)$ in the lumping integral. Specifically, for this region we have

$$M = n \quad \text{for} \quad n > n^* \tag{59}$$

Referring to Figure 4, the two linear functions represented by Eqs. 56 and 59, having different slopes, meet at $n = n^*$, although at this point (region V) M does not exist due to the additional logarithmic term. (This is indicated by the upper open circle in Figure 4.) In no case can the two slopes become equal since $1 + \mu > 0$. So the slope of the M-n relationship is discontinuous. Furthermore, the effective rate constants are discontinuous since the effective rate constant in region IV is governed by the refractory species, while that in region VI is governed by the refractory as well as the reactive species. For a fixed n, increasing μ will favor region VI because the number of refractory species decreases [$g(x)$ is concave upward], thereby making the reactive species relatively more important. Finally, in region VI local information on the feed mixture is not sufficient for evaluating the overall rate. This is somewhat discomforting. Nonetheless, we note that it suffices to characterize $g(x)$ without having to specify $f(x)$. And we know *a priori* that $M = n$, completely independent of the feed properties.

The overall rate in region V [$n = 1 + 1/(\mu + 1)$] is governed by the refractory species. It represents the transition from region IV to VI, or vice versa. The transition is by no means smooth. But it should be stressed that the asymptotic order in region IV matches that in region VI as region V is approached from either side.

Finally, we note that for large values of ν and μ, the behavior of the lump is very sensitive to small changes in n when n is in the vicinity of unity. It may be remarked that in hydroprocessing catalysis, n may be changed by modifying the acidity of the catalyst support (Hensley et al., 1983).

Some special cases

When $\nu = 0$ (the unconvertible has a finite concentration), Eq. 56 becomes

$$M = \frac{(\mu + 2)}{(\mu + 1)} \quad \text{for} \quad -\infty < n < n^* \tag{60}$$

That is, M becomes independent of n and $M > 2$ if $\mu < 0$. On the latter point, we remark that Ozaki et al. (1976) reported an overall order greater than two for HDS of residual oils. The simplest subcase is when $\mu = 0$. Then $M = 2$ when $n < 2$ and $M = n$ when $n > 2$. But when $n = 2$, M does not exist. Moreover, the overall rate constant is not continuous at $n = 2$. In contemplating these peculiar results, one would ask: if the asymptotic kinetics does not take a power law form when $n = 2$, then how close can the overall rate be approximated by a power law model? What about the case of total absence of unconvertibles?

Another special case is when $n < 1$. Here M may not exist or may be larger than unity. The latter is not immediately obvious in light of Aris's (1968) result for first-order reactions. As mentioned, HDN of individual nitrogen compounds constitutes a practical example of the $n < 1$ case; the kinetics is often reported to be zero order. By contrast, HDN of most petroleum feeds exhibits an overall order between one and two (Heck and Stein, 1977; Stanulonis et al., 1981; Sonnemans, 1982; Ho, 1988). One may ask: If the individual reactant disappears at a zero-order rate, is it reasonable to expect an overall order higher than one or, in particular, as high as two? If the answer is affirmative, then under what circumstances should one expect this to occur?

It is to these questions that we direct ourselves in the sections that follow. Specifically, we exploit the $n = 2$ and $n = 0$ cases numerically. We determine the extent to which the overall global kinetics can be approximated by an mth-order power law model.

Numerical Investigation of Special Cases

For simplicity we assume that $g(x) = 1$ for $0 \le x < v$ and $g(x) = 0$ for $x > v$. Thus, the feed mixture contains a finite number of reactants whose x values are arbitrarily close to zero ($\mu = 0$). Also, as $x \to \infty$, we assume that $f(x)$ goes to zero so fast that, for a sufficiently large v, U for practical purposes can be calculated by

$$U(\tau) = \int_0^\infty u(x;\tau)\,dx \tag{61}$$

$$n = 2: \quad u(x;\tau) = \frac{f(x)}{[1 + f(x)\tau x]} \tag{62a}$$

$$n = 0: \quad u(x;\tau) = f(x)[1 - \tau/\tau^*(x)], \quad \{x: \tau < \tau^*\} \tag{62b}$$

We further assume that $f(x)$ takes the following form

$$f(x) = \frac{x^\alpha e^{-xs} s^{\alpha+1}}{\Gamma(\alpha + 1)} \tag{63}$$

which is slightly more flexible than Eq. 42. The above simplifications detract very little, if any, from the problem we wish to address here.

Lumping second-order kinetics

Knowing both f and g, we consider a fully characterized second-order mixture with U given by

$$U(\tau) = \int_0^1 \left[\frac{\Gamma(\alpha + 1)}{(-\ln y)^\alpha} - y\tau \ln y\right]^{-1} dy \tag{64}$$

In deriving this equation we have let $y = \exp(-xs)$ to eliminate the infinity in Eq. 61. The U vs. τ relation, computed from numerical integration of Eq. 64, is fitted by an empirical mth-order kinetic model. This means that we minimize the following objective function over a time interval of length ζ.

$$J = \int_0^\zeta [U(\tau) - U_m(\tau)]^2\,d\tau \tag{65}$$

where $U_m(\tau)$ represents the model prediction and is given by

$$U_m(\tau) = \begin{cases} [1 + (m-1)^{m-1}\kappa_m\tau]^{1/(1-m)} & m \neq 1 \\ \exp(-\kappa_1\tau) & m = 1 \end{cases} \tag{66}$$

And $U_m(\tau)$ satisfies $dU_m/d\tau = -\kappa_m U_m^m$ with $U_m(0) = 1$. Note that while fitting by power law model offers many advantages, one pays for these by having to accept that the best model parameters depend on the conversion level (or ζ). This can create problems in extrapolation and/or scaleup (Astarita, 1985). One would hope that such dependence on conversion will be a weak one.

To find the best fit we treat both m and κ_m as model

parameters. Hence we need to solve the following equations simultaneously:

$$\frac{\partial J}{\partial \kappa_m} = 0 \quad \text{and} \quad \frac{\partial J}{\partial m} = 0 \tag{67}$$

The asymptotic results should provide some guidance. For example, for $\alpha = 0$, $U(\tau) \sim (\ln \tau/\tau)$ at large τ. The function $\ln \tau$ is slowly varying at large τ. If one is to fit $\ln \tau/\tau$ by an mth-order model, m should be higher than two. At $\alpha = 0$ we also know that $M > 2$ when $n > 2$, and $M = 2$ when $n < 2$. We thus expect that m should be close to two.

We now turn to the numerical fitting. A 90% conversion of the lump for $\alpha = 1$ is obtained at $\zeta = 35.9$ To find the best fit over this conversion range, we solved Eq. 67 using the Newton-Raphson method with a numerically generated Jacobian matrix. The best fit yields $m = 2.241$, $\kappa_m = 0.3653$, and $J = 3.86 \times 10^{-5}$. The data and the model prediction are so close to each other that they cannot be distinguished by a plotted figure. Table 2 shows the numerical results. For practical purposes, the approximation may be viewed as arbitrarily accurate. As Table 3 shows, the dependences of m and κ_m on conversion are both relatively weak.

Table 4 lists the results for $\alpha = 0$ [implying $c(0,0) \neq 0$]. Again m and κ_m are not very sensitive to conversion. Collectively, Tables 3 and 4 indicate that m is a relatively weak function of α.

Finally, for curiosity we fitted U by an integer m. With $m = 2$ we get $\kappa_2 = 0.2992$ and $J = 7.54 \times 10^{-3}$ for $\alpha = 1$ and $\zeta = 35.9$. Letting $m = 3$ yields $\kappa_3 = 0.7026$ and $J = 4.98 \times 10^{-2}$. These J values are considerably larger than those for $m = 2.241$. But if one prefers an integer power, then $m = 2$ is the choice, as might be expected from the asymptotic results.

Summarizing, for $n = 2$ the overall rate is well approximated with an m modestly higher than two. We next look at the $n = 0$ case.

Table 2. Comparison between $U(\tau)$ and $U_m(\tau)$ for $\alpha = 1.0$

τ	$U(\tau)$	$U_m(\tau)$
0.0	1.0000	1.0000
0.1	0.9640	0.9649
0.2	0.9310	0.9325
0.3	0.9004	0.9024
0.4	0.8720	0.8743
0.5	0.8458	0.8482
0.6	0.8212	0.8238
0.7	0.7980	0.8008
0.8	0.7770	0.7793
0.9	0.7570	0.7590
1.0	0.7375	0.7399
1.5	0.6566	0.6583
2.0	0.5936	0.5945
2.5	0.5428	0.5430
3.0	0.5009	0.5006
4.0	0.4356	0.4345
5.0	0.3869	0.3852
6.0	0.3488	0.3469
8.0	0.2930	0.2910
10.0	0.2539	0.2519
15.0	0.1924	0.1910
20.0	0.1563	0.1555
30.0	0.1151	0.1152
35.9	0.0993	0.1006

Table 3. Results of Best Fit, $\alpha = 1$

ζ	Conversion	m	κ_m	J
	%			
0.69	20	2.444	0.3815	4.91×10^{-8}
3.0	50	2.314	0.3761	2.53×10^{-7}
35.9	90	2.241	0.3653	3.86×10^{-5}

Lumping zero-order kinetics

As before, we first see what we can learn from the asymptotic results. If the concentrations of refractory species are so high that $0 \leq \alpha < 1$, then $M = 2/(1 + \alpha)$, implying that no depletion will occur and that $1 < M \leq 2$, Figure 5. If, in addition, the unconvertible has a finite concentration ($\alpha = 0$), then $M = 2$. On the other hand, when $\alpha \geq 1$, the lump will deplete in a finite time. In no case will $M = 1$. Evidently, here α plays a pivotal role. Based on these, one should not be surprised at $m > 1$ when $\alpha < 1$, whether or not the feed contains unconvertibles. Also, one would expect that $m < 1$ when $\alpha \geq 1$. Since $f(x)$ and $g(x)$ are known, we can carry out the analysis further.

It follows from Eqs. 10 and 63 that the exhaustion time takes the form

$$\tau^*(x) = \frac{x^{\alpha-1} e^{-xs} s^{\alpha+1}}{\Gamma(\alpha + 1)} \tag{68}$$

which can exhibit three different behaviors, depending on α, as depicted in Figure 6. First when $\alpha = 1$, $\tau^*(x)$ decreases monotonically with increasing x. The maximum of $\tau^*(x)$, denoted by $\max \tau^*$, occurs at $x = 0$.

Second, $\alpha > 1$, the reactant with $x = x_r = (\alpha - 1)/s$ has the longest exhaustion time, given by

$$\max \tau^* = \frac{s^2(\alpha - 1)^{\alpha-1} e^{1-\alpha}}{\Gamma(\alpha + 1)} \tag{69}$$

Referring to Figure 6, here a fast-reacting species ($x = x_f$) with a high initial concentration can have the same exhaustion time as a slow-reacting species ($x = x_s$) with a low initial concentration. As long as $\alpha \geq 1$, the lump will preserve a fundamental property of the underlying reactions; that is, it will become completely depleted in a finite time (when $\tau = \max \tau^*$).

Third, $0 \leq \alpha < 1$, the feed mixture contains some very refractory species whose concentrations are such that their exhaustion times are indefinitely long. In other words, for any time τ, no matter how large, there exist some species whose x values are sufficiently small that they have not yet been consumed at time τ. This is true even for feeds having no unconvertibles (corresponding to $\alpha \neq 0$). We thus expect that $m \geq 1$.

Table 4. Results of Best Fit, $\alpha = 0$

ζ	Conversion	m	κ_m	J
	%			
1.04	20	2.339	0.2492	4.81×10^{-9}
4.57	50	2.331	0.2488	4.55×10^{-8}
56.55	90	2.270	0.2425	5.15×10^{-5}

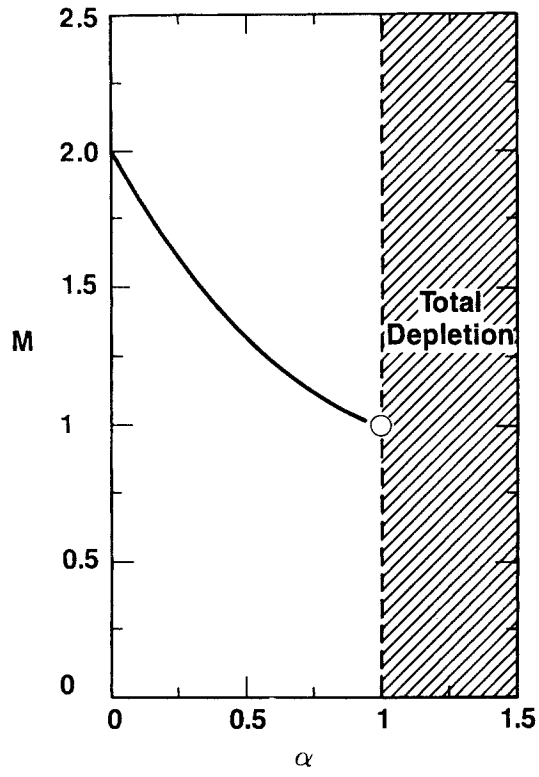

Figure 5. Relation between M and α for $n = \mu = 0$.
Total depletion occurs when $\alpha \geq 1$

Unlike the previous $n = 2$ case, here we can derive an analytical expression for U for each of the three cases. Figure 7 shows some of the qualitative behaviors of the concentration surfaces.

$\alpha = 1$ behavior

With Eqs. 62b and 63, U can be calculated as

$$U(\tau) = \int_0^{\chi(\tau)} (xs^2e^{-xs} - x\tau)\, dx$$

$$= -s^2e^{-\chi s}(\chi/s + 1/s^2) + 1 - \frac{\chi^2\tau}{2} \qquad (70)$$

where $\chi(\tau)$ is the inverse of Eq. 68 and takes the form

$$\chi(\tau) = -\frac{1}{s}\ln(\tau/s^2) \qquad (71)$$

Substituting Eq. 71 into Eq. 70 yields U as a function of a new dimensionless time τ', defined as $\tau' \equiv \tau/s^2$.

$$U(\tau') = 1 - \tau'(1 - \ln\tau') - \frac{\tau'}{2}(\ln\tau')^2 \qquad (72)$$

Note that when $\tau' = 1$, $U(\tau')$ vanishes.

$\alpha < 1$ behavior

It can be shown that $U(\tau')$ is of the form

$$U(\tau') = \Gamma(\alpha + 1, \chi s) - \frac{(\chi s)^2}{2}\tau' \qquad (73)$$

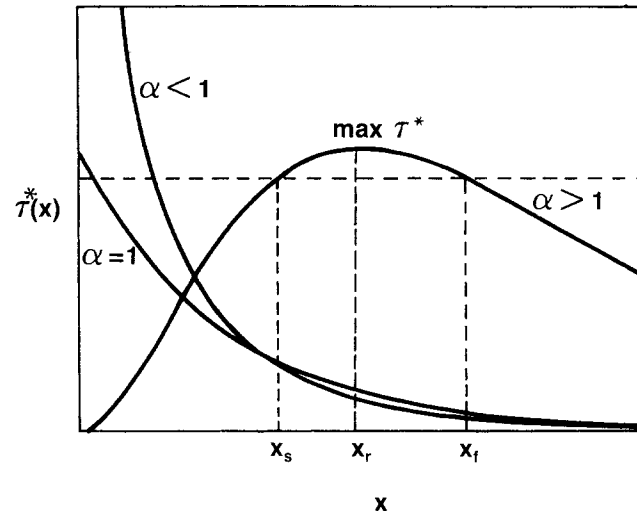

Figure 6. Distribution of exhaustion time as a function of x.

where $\Gamma(\alpha + 1, \chi s)$ is the incomplete gamma function, defined as

$$\Gamma(\alpha + 1, \chi s) = \frac{1}{\Gamma(\alpha + 1)}\int_0^{\chi s} e^{-\zeta}\zeta^{\alpha}\, d\zeta \qquad (74)$$

In this case χ is given implicitly by

$$\tau' = \frac{(\chi s)^{\alpha-1}e^{-\chi s}}{\Gamma(\alpha + 1)} \qquad (75)$$

Thus $U(\tau')$ is calculated by numerically solving Eqs. 73 and 75. As discussed earlier, here the presence of long-lasting species is expected to give rise to a high apparent order.

$\alpha > 1$ behavior

U is determined by

$$U(\tau) = \int_{\chi_1(\tau)}^{\chi_2(\tau)} [f(x) - x\tau]\, dx$$

$$= \Gamma(\alpha + 1, \chi_2 s) - \Gamma(\alpha + 1, \chi_1 s)$$

$$- \frac{\tau' e^{1-\alpha}(\alpha - 1)^{\alpha-1}}{2\Gamma(\alpha + 1)}(\chi_2^2 - \chi_1^2)s^2 \qquad (76)$$

where τ' is a new dimensionless time defined as $\tau' \equiv \tau/\max\tau^*$. Evidently, $\chi_1(t)$ and $\chi_2(t)$ are the two solutions of the following equation

$$\tau' = \frac{(\chi s)^{\alpha-1}e^{-\chi s}}{e^{1-\alpha}(\alpha - 1)^{\alpha-1}} \qquad (77)$$

As before, to calculate U requires solving both Eqs. 76 and 77. Like the $\alpha = 1$ case, here $U = 0$ at $\tau' = 1$. We next use an mth-order model to fit U.

Figure 8 shows $\ln U(\tau')$ vs. τ' for $s = 1$ and different α values over a wide conversion range (to 99%). The extent of deviation from linearity in these plots gives us an idea of how m compares

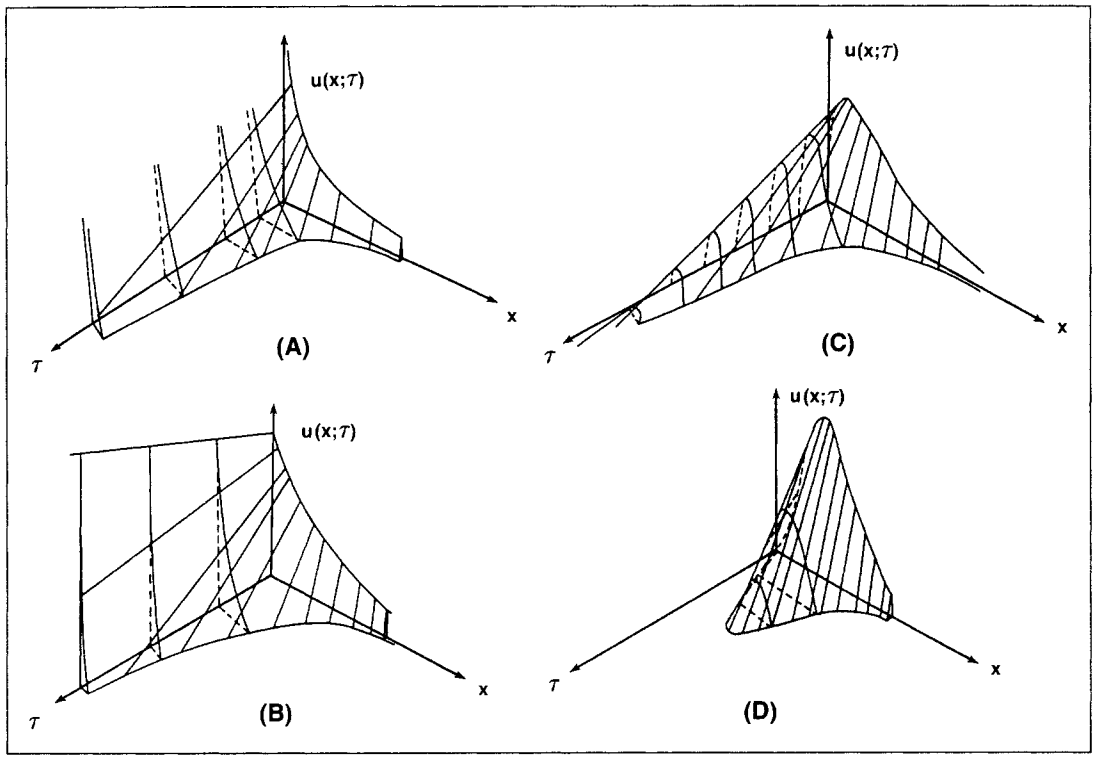

Figure 7. Time evolution of concentration surfaces for a large number of zero-order reactions.
A. $\alpha < 0$; B. $\alpha = 0$; C. $\alpha > 1$; D. $\alpha \gg 1$ and $s \gg 1$

with unity. For example, the curves for $\alpha = 0.5$ and 0.8 are concave upward, indicating that an m greater than one should be used. This is illustrated for $\alpha = 0.5$ in Figure 9 where U is fitted by $m = 2$. One sees a certain degree of approximation. It was considered unnecessary to carry out additional computation to find the best m (the computation, a time consuming process, is essentially the same as that described in the preceding section). The key point here is that m is definitely higher than unity over this conversion range, as suggested by the asymptotic results.

As shown before, $\alpha = 1$ means total depletion in a finite time. This says that $m < 1$. However, as Figure 8 shows, over a limited range of conversion, U may be fitted by $m = 1$ for practical purposes. Figure 10 shows total depletion after a finite time when $\alpha > 1$. In HDN catalysis, Hensley et al. (1983) have attributed this behavior to catalysts of strong acidity. They demonstrated that a high HDN can be achieved with a stacked bed in which the upstream catalyst has a higher m value than does the downstream catalyst.

The main message here is that zero-order reactions collectively can give rise to an apparent order of higher than unity. This occurs when the feed contains high concentrations of refractory species.

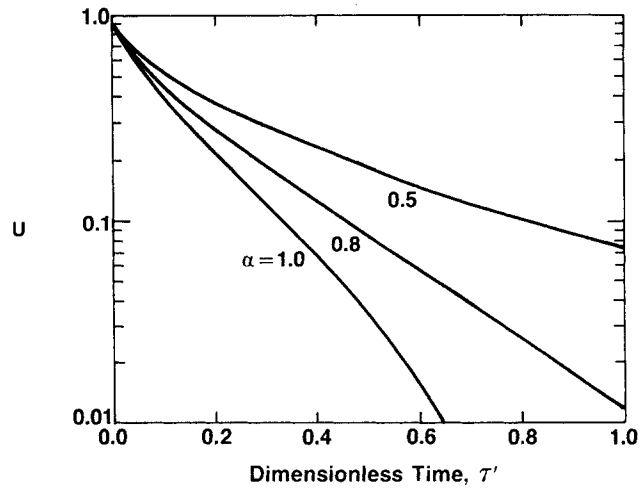

Figure 8. First-order kinetic plot for $s = 1$ and various α values

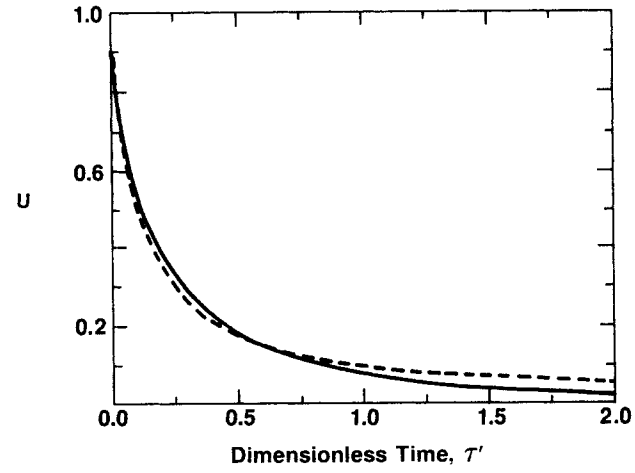

Figure 9. Approximation of $U(\tau')$ by a second-order kinetics; $\alpha = 0.5$

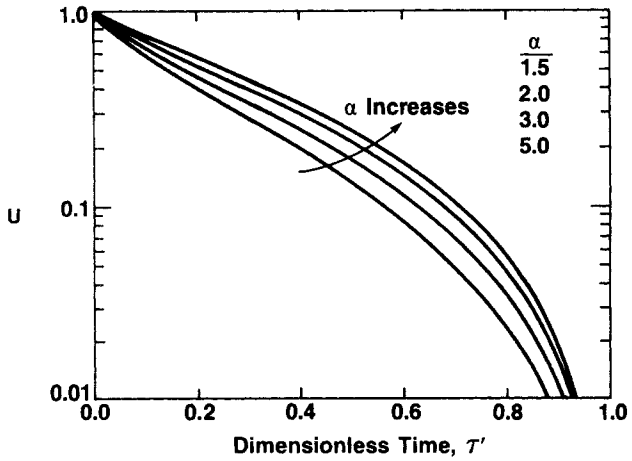

Figure 10. First-order kinetic plot for $\alpha > 1$.

Asymptotic vs. Global Kinetics

The above results, together with those for the $n = 2$ case, indicate that the asymptotic kinetics are quite useful for fitting the global kinetics by an mth-order power law model. In fact, the behavior of m as a function of n and α qualitatively follows that of M. We discuss this in some detail below.

As mentioned before, total lumping results in an increase in the reaction order. The extent of this increase can be defined as follows:

$$\Delta_m(n, \alpha) \equiv m(n, \alpha) - n \tag{78}$$

$$\Delta_M(n, \alpha) \equiv M(n, \alpha) - n \tag{79}$$

With $n = 0$, 1, and 2, we now compare $m(n, \alpha)$ with $M(n,\alpha)$, and $\Delta_m(n, \alpha)$ with $\Delta_M(n, \alpha)$. Equation 56 leads to

$$M(n, \alpha) = \frac{n\alpha + 2}{\alpha + 1} \quad \text{when } 1 - 1/\alpha < n < 2 \tag{80}$$

and

$$M = n \quad \text{when } n > 2 \tag{81}$$

Hence $M \geq n$ as long as $n \neq 2$. It follows from Eqs. 79 and 80 that

$$\Delta_M(n, \alpha) = \frac{2 - n}{1 + \alpha} \quad \text{when } 1 - 1/\alpha < n < 2 \tag{82}$$

and

$$\Delta_M = 0 \quad \text{when } n > 2 \tag{83}$$

For a fixed α, Δ_M decreases linearly to zero as n increases. For a fixed n, the maximum of Δ_M occurs at $\alpha = 0$, implying the presence of a finite amount of unconvertibles. In this regard, Δ_M has been proposed as an index of feed refractoriness or catalyst effectiveness (Chou and Ho, 1988). We next look at $m(n,\alpha)$.

For $n = 1$, we have Aris's (1968) result:

$$m\ (1, \alpha) = \frac{\alpha + 2}{\alpha + 1} \tag{84}$$

The beauty here is that the lumped kinetics is exactly of the mth order, so $M(1,\alpha) = m(1,\alpha)$ and $\Delta_M(1,\alpha) = \Delta_m(1,\alpha)$. For instance, $\Delta_m(1,0) = 1$ and $\Delta_m(1,1) = 0.5$. The maximum of Δ_m occurs at $\alpha = 0$. In a sense, Eq. 80 can be viewed as a generalization of Eq. 84.

Now look at the $n = 2$ case. Here $m(n,\alpha)$ is an approximate reaction order determined by numerical fitting. At a total conversion of 90%, $m(2,0) = 2.270$ and $m(2,1) = 2.241$. By comparison, in the first-order case, $m(1,0) = 2$ and $m(1,1) = 1.5$. Hence m becomes more dependent on α as n decreases. This behavior is consistent with that of M: M becomes independent of α when $n > 2$, Eq. 81, while M behaves as $2/(1 + \alpha)$ when $n = 0$, Eq. 80.

For a fixed α, Δ_m also becomes smaller as n increases. Based on the results in Table 4, $\max \Delta_m(2,0) = 0.339$. This should be contrasted with $\Delta_m(1,0) = 1$ and $\Delta_m(0,0) > 1$. This behavior is entirely consistent with that of Δ_M: $\Delta_M = 0$ when $n > n^*$, $\Delta_M(1,0) = 1$, and $\Delta_M(0,0) = 2$.

Conclusions

We have examined the lumped behavior of nth-order reactions both asymptotically and numerically. On the asymptotic side, we have developed a complete theory for predicting the long-term behavior of the mixture under all possible conditions, with minimum information on the feed properties. There exist two critical values for n, n^* and n_*, both of which are explicitly expressed as functions of the feed properties. The lump, in most circumstances, disappears to leading order at an Mth-order rate. The main outcome of the long-time analysis is summarized as follows:

1. When $n > n^*$, $M = n$
2. When $n = n^*$, M does not exist
3. When $n_* < n < n^*$, M is linear in n and greater than n and 1
4. When $n \leq n_*$, the lump totally depletes in a finite time

We hope the theory can be tested against experiment in future studies.

On the numerical side, we have used an mth-order kinetic model to fit the global behaviors of two mixtures: one in which $n = 2$, the other $n = 0$. The former, corresponding to the $n = n^*$ case, can be well approximated with an m modestly higher than two. The latter can be approximated by an $m > 1$ when the feed has a high level of refractory species. Some published data are rationalized in light of these results.

Although the asymptotic kinetics are developed in the long-time limit, they are very useful for modeling the lumped kinetics with an mth-order power law form. Numerical experiments show that M and m behave similarly in many respects. For example, as n increases, they both become closer to n and less dependent on the feed properties.

Acknowledgment

We are grateful to Professor R. Aris for suggesting Figure 7 to us.

Notation

b = function, Eq. 26
$B(z,w)$ = beta function
$C(t)$ = total concentration of reactants at time t
$C(0)$ = total concentration of reactants in feed
c_0 = scaling constant, Eq. 5
$c(x;t)$ = concentration of reactant type of x at time t
$c(x;0)$ = concentration of reactant of type x in feed
$D(x)$ = reactant-type distribution function, Eq. 4

$f(x)$ = dimensionless initial concentration, Eq. 5
f_i = coefficients, Eq. 12; $i = 0, 1, \ldots$
$g(x)$ = lumping density function, Eqs. 5, 6
g_i = coefficients, Eq. 12; $i = 0, 1, 2, \ldots$
$h(x)$ = function, Eq. 5
I_β = functional, Eq. 15
J = objective function, Eq. 65
I_i = integrals, Eq. 25; i = 1, 2
$k(x)$ = reaction rate constant, Eq. 1
$\hat{k}$ = scaling constant, Eq. 5
M = asymptotic kinetic order for the lump at large times
m = order of empirical mth-order kinetic model, Eq. 66
n = reaction order of underlying kinetics
n^*, n_* = critical values of n, Eq. 57
n = total number of reactant types
p,q = parameters characterizing the shapes of $f(x)$ and $g(x)$, Eqs. 42, 43
R = rate expression for lumped kinetics
t = time
U = dimensionless total concentration, Eq. 5
u = function, Eqs. 61, 62
w = defined in Eq. 21
x = reactant label for continuous mixture, $x \in [0,\infty)$
y = defined as $y \equiv \exp(-xs)$
z = defined in Eq. 19

Greek letters

α = parameter in gamma distribution function, Eq. 63
β = defined as $\beta \equiv 1/(n = 1)$
Δ_m = increase in reaction order, $\Delta_m \equiv m - n$
Δ_M = increase in reaction order, $\Delta_M \equiv M - n$
ϵ = a small number, Eq. 23
χ = value of x beyond which all reactants are depleted, Eq. 70
Γ = gamma function
η = defined in Eq. 20
κ_m = rate constant of empirical mth-order kinetic model, Eq. 66
ν = defined in Eq. 12
μ = defined in Eq. 12
σ = defined in Eq. 45
τ = dimensionless time, Eq. 5
θ = defined in Eq. 48
λ = defined in Eq. 45
ϕ = defined in Eq. 49
τ^* = exhaustion time as a function of reactivity x, Eqs. 33, 68
ζ = final time of reaction, Eq. 65

Literature Cited

Aris, R., "Prolegomena to the Rational Analysis of Systems of Chemical Reactions. II: Some Addenda," *Arch. Rat. Mech. Anal.*, **27,** 35 (1968).
———, "Reactions in Continuous Mixtures," *AIChE J.*, **35,** 539 (1989).
Aris, R., and G. Gavalas, "On the Theory of Reactions in Continuous Mixtures," *Phil. Trans. Roy. Soc.*, **A260,** 351 (1966).
Astarita, G., "Scaleup: Overview, Closing Remarks, and Cautions," *Scaleup of Chemical Processes*, A. L. Bisio, R. L. Kabel, eds., Wiley, New York (1985).
———, "Lumping Nonlinear Kinetics: Apparent Overall Order of Reaction," *AIChE J.*, **35,** 529 (1989).
Astarita, G., and A. Nigam, "Lumping Nonlinear Kinetics in a CSTR," *AIChE J.*, **35,** 1927 (1989).
Astarita, G., and R. Ocone. "Lumping Nonlinear Kinetics," *AIChE J.*, **34,** 1299 (1988).
Bailey, J. E., "Lumping Analysis of Reactions in Continuous Mixtures," *Chem. Eng. J.*, **3,** 52 (1972).
Careberry, J. J., *Chemical and Catalytic Reaction Engineering*, McGraw-Hill, New York (1976).
Chou, M. Y., and T. C. Ho, "Continuum Theory for Lumping Nonlinear Reaction Mixtures," *AIChE J.*, **34,** 1519 (1988).
———, "Lumping Coupled Nonlinear Reactions in Continuous Mixtures," *AIChE J.*, **35,** 533 (1989).
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 Strategy. 2: A System Theoretic Approach," *Ind. Eng. Chem. Res.*, **26,** 2151 (1987b).
de Donder, Th., *L'Affinite*, pt. 2, Gauthier-Villars, Paris, Ch. 3 (1931).
Golikeri, S. V., and D. Luss, "Analysis of Activation Energy of Grouped Parallel Reactions," *AIChE J.*, **18,** 277 (1972).
———, "Aggregation of Many Coupled Consecutive First-Order Reactions," *Chem. Eng. Sci.*, **29,** 845 (1974).
Heck, R. H., and T. R. Stein, "Kinetics of Hydroprocessing Distillate Coal Liquids," *Amer. Chem. Soc. Symp. Ser.*, **22,** 948–961 (1977).
Hensley, A., L., Jr., A. M. Tait, J. T. Miller, and T. D. Nevitt, "Multiple Catalyst System for Hydrodenitrogenation of High Nitrogen Feeds," U.S. Patent 4406779, assigned to Standard Oil Co. (Indiana), (1983).
Ho, T. C., "Hydrodenitrogenation Catalysis," *Cat. Rev. Sci. Eng.*, **30,** 117 (1988).
Ho, T. C., and R. Aris, "On Apparent Second-Order Kinetics," *AIChE J.*, **33,** 1050 (1987).
Hutchinson, P., and D. Luss, "Lumping of Mixtures with Many Parallel First-Order Reactions," *Chem. Eng. J.*, **1,** 129 (1970).
Krambeck, F. J., "Computers and Modern Analysis in Reactor Design," *Inst. Chem. Eng. Symp. Ser.*, **87,** 733 (1984).
Kuo, J. C. W., and J. Wei, "A Lumping Analysis in Monomolecular Reaction Systems," *Ind. Eng. Chem. Fund.*, **8,** 124 (1969).
Lee, H. H., "Synthesis of Kinetic Structure of Reaction Mixtures of Irreversible First-Order Reactions," *AIChE J.*, **24,** 116 (1978).
Li, G., "A Lumping Analysis in Mono- or/and Biomolecular Reaction Systems," *Chem. Eng. Sci.*, **39,** 1261 (1984).
Li, G., and H. Rabitz, "A General Analysis of Exact Lumping in Chemical Kinetics," *Chem. Eng. Sic., 44, 1413 (1989).*
Liu, Y. A., and L. Lapidus, "Observer Theory for Lumping Analysis of Monomolecular Reactions Systems," *AIChE J.*, **19,** 467 (1973).
Luss, D., and S. V. Golikeri, "Grouping of Many Species, Each Consumed by Two Parallel First-Order Reactions," *AIChE J.*, **21,** 865 (1975).
Luss, D., and P. Hutchinson, "Lumping of Mixtures with Many Parallel n-th Order Reactions," *Chem. Eng. J.*, **2,** 172 (1971).
Ozaki, H., Y. Satomii, and T. Hisamitsu, "The Kinetics and Economics of Hydrodesulphurising Residual Oils," *Proc. World Pet. Cong., 6,* PD **18**(4), 97 (1976).
Shabtai, J., and G. J. C. Yeh, "Kinetics of HDN of SRC. II Liquids and Synfuel-simulating Blends," *Fuel,* **67,** 314 (1988).
Smith, C. M., and C. N. Satterfield, "Some Aspects of Vapor-Liquid Flow Ratio on Performance of a Trickle-Bed Reactor," *Chem. Eng. Sci.*, **41,** 839 (1986).
Sonnemans, J. W. M., "Hydrotreating of Cracked Feedstocks," Ketjen Catalyst Symp. (1982).
Stanulonis, J. J., J. A. Tabacek, and R. F. Vogal, U.S. Patents 4285836 and 4285807, issued to Gulf Oil (1981).
van Dongen, R. H., D. Bode, H. van der Eijk, and J. van Klinken, "Hydrodemetallization of Heavy Residual Oils in Laboratory Trickle-Flow Liquid Recycle Reactors," *Ind. Eng. Chem. Process Des. Dev.*, **19,** 630 (1980).
Venuto, P. B., and E. T. Habib, *Fluid Catalytic Cracking with Zeolite Catalysts*, Marcel Dekker, New York (1978).
Weekman, Jr., V. W., "Lumps, Models, and Kinetics in Practice," *AIChE Monog. Ser.*, **75,**(11) (1979).
Wei, J., and J. C. W. Kuo, "A Lumping Analysis in Monomolecular Reaction Systems," *Ind. Eng. Chem. Fund.* **8,** 114 (1969).

Appendix A. Details in Proof of Theorem 2

In the text, certain details in the proofs of some of the theorems are omitted. Here, details for Theorem 2 are given as an example.

Clearly I_2 is $0(\tau^{-\beta})$ as stated. Let δ, $0 < \delta < \frac{1}{2}$ be arbitrary. Choose ϵ so small that for $0 < x < \delta$

$$f(x) = f_0 x^\nu [1 + \delta_1(x)]$$
$$g(x) = g_0 x^\mu [1 + \delta_2(x)] \qquad \text{(A1)}$$

where

$$|\delta_1(x)| < \delta \quad |\delta_2(x)| < \delta \tag{A2}$$

That this can be done is assured by Eq. 12. Then keeping track of these errors, we have the equality

$$\tau^z I_1 = \frac{g_0 \beta^{z+1} f_0^\eta}{(\beta + \nu)} \int_0^{b(\tau)} [1 + \delta_1(x)][1 + \delta_2(x)] \left[\frac{1 + \xi}{1 + (1 + \delta_1)^{1/\beta}\xi}\right]^\beta \frac{\xi^{z-1}}{(1 + \xi)^\beta} d\xi \tag{A3}$$

Now let

$$\delta_3 = \left[\frac{1 + \xi}{1 + (1 + \delta_1)^{1/\beta}\xi}\right]^\beta - 1 \tag{A4}$$

For fixed δ_1, δ_3 is monotone in ξ. Hence

$$|\delta_3| < \max\left(0, \frac{-\delta_1}{1 + \delta_1}\right) < \frac{|\delta_1|}{1 - |\delta_1|} < \frac{|\delta|}{1 - |\delta|}, |\delta_3| < 2\delta \tag{A5}$$

where we have used $0 < \delta < 1/2$.

Therefore,

$$\tau^z I_1 = \frac{g_0 \beta^{z+1} f_0^\eta}{\beta + \nu} \int_0^{b(\tau)} (1 + \delta_4) \frac{\xi^{z-1}}{(1 + \xi)^\beta} d\xi \tag{A6}$$

where

$$1 + \delta_4 = (1 + \delta_1)(1 + \delta_2)(1 + \delta_3) \tag{A7}$$

and hence

$$|\delta_4| < 7\delta \tag{A8}$$

Now since $\tau^z I_2 \to 0$ as $\tau \to \infty$, $I = I_1 + I_2$, and $b(\tau) \to \infty$ as $\tau \to \infty$, we have

$$\begin{aligned} \overline{\lim_{\tau\to\infty}} \left| \tau^z I - \frac{g_0 \beta^{z+1} f_0^\eta}{\beta + \nu} \int_0^\infty \frac{\xi^{z-1}}{(1 + \xi)^\beta} d\xi \right| &= \overline{\lim_{\tau\to\infty}} \left| \tau^z I_1 - \frac{g_0 \beta^{z+1} f_0^\eta}{\beta + \nu} \int_0^{b(\tau)} \frac{\xi^{z-1}}{(1 + \xi)^\beta} d\xi \right| \\ &= \overline{\lim_{\tau\to\infty}} \left| \frac{g_0 \beta^{z+1} f_0^\eta}{\beta + \nu} \int_0^{b(\tau)} \delta_4 \frac{\xi^{z-1}}{(1 + \xi)^\beta} d\xi \right| \\ &\le 7\delta \frac{g_0 \beta^{z+1} f_0^\eta}{\beta + \nu} \int_0^\infty \frac{\xi^{z-1}}{(1 + \xi)^\beta} d\xi \end{aligned} \tag{A9}$$

in which the limit superior (denoted by the overbar) for a function $u(\tau)$ is defined as

$$\overline{\lim_{\tau\to\infty}} u(\tau) \equiv \lim_{\tau\to\infty} \sup_{\zeta > \tau} u(\zeta) \tag{A10}$$

Now the lefthand side of Eq. A9 does not depend on ϵ or δ. Thus letting $\delta \to 0$, we obtain

$$\lim_{\tau\to\infty} \tau^z I = \frac{g_0 \beta^{z+1} f_0^\eta}{\beta + \nu} \int_0^\infty \frac{\xi^{z-1}}{(1 + \xi)^\beta} d\xi \tag{A11}$$

which is equivalent to Eq. 18.

Appendix B. Asymptotics for U'

In deriving $R(U)$, we have assumed that the asymptotic expressions for U can be differentiated to give the asymptotic forms of U'. Although this is indeed the case here, it is not a mathematical necessity. It need not be true if higher order terms have rapid oscillations. For example, if

$$U(\tau) \equiv \frac{2}{\tau} + \frac{\cos(\tau^2)}{2\tau^3} \sim \frac{2}{\tau} \tag{B1}$$

Then

$$U'(\tau) = -\frac{[2 + \sin(\tau^2)]}{\tau^2} - \frac{3\cos(\tau^2)}{2\tau^4} \sim -\frac{[2 + \sin(\tau^2)]}{\tau^2} \tag{B2}$$

Hence the asymptotic expression in Eq. B2 is *not* obtained by differentiation of the asymptotc expression in Eq. B1. It turns out that pathologies like this do not occur in the present context. We provide proofs for only two representative cases where $\beta > 0$.

By differentiation of Eq. 8 under the integral sign, we obtain

$$U'(\tau) = -\int_0^\infty \frac{x f(x)^{1+1/\beta} g(x)\, dx}{\left[1 + \frac{1}{\beta} f(x)^{1/\beta} x\tau\right]^{\beta+1}} \tag{B3}$$

which can be rearranged to give

$$U'(\tau) = -\frac{\beta}{\tau}(U - V) \tag{B4}$$

where

$$V = \int_0^\infty \frac{f(x)g(x)\, dx}{\left[1 + \frac{1}{\beta} f(x)^{1/\beta} x\tau\right]^{\beta+1}} \tag{B5}$$

Note that Eq. B5 is quite similar to Eq. 8 for U, the only difference being that in Eq. B5 the denominator is raised to the power $\beta + 1$, whereas it is the power β in Eq. 8. Thus the asymptotics for V are derived in much the same way as those for U.

Case VI

Consider first case VI, $0 < \beta < \mu + 1$, corresponding to Theorem 1. From Eq. 14, $U = 0(\tau^{-\beta})$. However,

$$\tau^\beta V = \int_0^\infty \frac{f(x)g(x)\, dx}{\left(\frac{1}{\tau} + \frac{x}{\beta} f^{1/\beta}\right)^\beta \left(1 + \frac{x}{\beta} f^{1/\beta} \tau\right)} \tag{B6}$$

Note that the integrand in Eq. B6 is bounded above by $g(x)/x^{\beta}$, which is integrable. Also, as $\tau \to \infty$ the integrand vanishes for almost all x. Thus

$$\lim_{\tau \to \infty} \tau^{\beta} V = 0 \tag{B7}$$

by the dominated convergence theorem. From Eq. B7 and $U = 0(\tau^{-\beta})$ we get that $V/U \to 0$ as $\tau \to \infty$ and hence from Eq. B4

$$U' \sim -\frac{\beta}{\tau} U \tag{B8}$$

Now Eq. B8 is consistent with what is obtained by formally differentiating Eq. 14, so this differentiation is justified for $0 < \beta < \mu + 1$.

Case IV

We consider also case IV, $\beta > \mu + 1$, which corresponds to Theorem 2. Equation 18 may be written as

$$U(\tau) \sim \frac{G_0}{\tau^z} B(z, \beta - z) \tag{B9}$$

where

$$G_0 \equiv \frac{g_0 f_0^{\eta} \beta^{z+1}}{(\beta + \nu)} \tag{B10}$$

In this case the asymptotic expansion of V is obtained by following through the same steps that yielded the expansion shown in Eq. B9, this time giving

$$V(\tau) \sim \frac{G_0}{\tau^z} B(z, \beta + 1 - z) \tag{B11}$$

Combining Eqs. B4, B9, and B11 yields

$$U'(\tau) \sim \frac{-\beta}{\tau} \frac{G_0}{\tau^z} [B(z, \beta - z) - B(z, \beta + 1 - z)]$$

$$= -\frac{z}{\tau} \frac{G_0}{\tau^z} B(z, \beta - z) \tag{B12}$$

where we have used the identity

$$B(z, \beta + 1 - z) = \left(1 - \frac{z}{\beta}\right) B(z, \beta - z) \tag{B13}$$

Now Eq. B12 is consistent with formal differentiation of Eq. B9, so differentiation is justified in this case.

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