Lumping Nonlinear Kinetics: Apparent Overall Order of Reaction

The analysis of Astarita and Ocone (1988) of the lumping of nonlinear kinetics in continuous mixtures offers a framework for examining the apparent overall behavior of a multicomponent mixture given the underlying intrinsic kinetics. Specific solutions of the governing equations are given for some special cases of underlying intrinsic kinetics. It is shown that the apparent overall order of reaction may be both larger and smaller than the underlying one, depending on the initial concentration distribution and on the distribution of kinetic parameters.

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Introduction

Astarita and Ocone (1988) have recently published an analysis of the lumping of nonlinear kinetics in continuous mixtures. The crucial point of their analysis is the idea that, for nonlinear kinetics, reactions in a multicomponent mixture cannot be assumed to have independent kinetics, and that therefore the nonlinearity needs to be modeled through a nonlinearity factor that depends on the whole spectrum of concentrations of all species. Astarita and Ocone give very few examples where the overall lumped kinetics are explicitly calculated in terms of the underlying intrinsic kinetics and of the initial distribution of concentrations. The purpose of the present paper is to furnish the results of some such detailed calculations.

In particular, the following question is addressed. First consider the case where there is only one component. The instantaneous order of reaction can be defined as $n' = d \ln(-dc/dt)/d \ln c$ (notice that if the intrinsic kinetics are of n order, $n' = n$). Now consider a mixture where there are many components that undergo the same type of reaction, and let C be the total concentration of all such components. The apparent overall order is $N' = d \ln(-dC/dt)/d \ln C$. What is the relationship between N' and n'?

While this work was in progress, the preliminary draft of a paper by R. Aris was received in which a somewhat similar question is addressed. Aris, however, takes a different approach to the problem. Recognizing that an intrinsically linear kinetics may give rise to nonlinear apparent overall kinetics, he chooses to model an underlying nonlinear kinetics via a two-level lumping. Two component labels are introduced. The first is used to obtain a first-level lumping of intrinsically linear kinetics which is nonlinear; this is then lumped at a second and higher level by making use of the second component label. Aris's approach is different from the one taken in this paper, where the only level of alias considered is the first one. Possibly the results presented here could be included in the Aris formalism at the first level, thus making it possible for the first index to simulate reactions of any order.

Since the results to be given are essentially based on the approach of Astarita and Ocone (1988), this paper is very concise; the reader is referred to their paper for all background detail.

Analysis

Let x be the component label, and let $g(x, t)dx$ be the concentration at time t of species with labels in the interval between x and $x + dx$. Let $k(x)$ be the frequency factor of component x (or pseudofirst-order kinetic constant). Astarita and Ocone write the kinetic equation in the continuous mixture as:

$$-\partial g(x, t)/\partial t = k(x)g(x, t)R \tag{1}$$

where R is the nonlinearity factor, which depends on the whole spectrum of concentrations. In particular, let y be a dummy component label, and let $K(x, y)$ have dimensions of an inverse concentration. R is then given by a functional of the weighted concentration distribution $K(x, y)g(y, t)$, which in general may also depend parametrically on x. At this level of generality, actual solution of the kinetic equations for the continuous mixtures is impossible.

It is however possible to obtain a general solution if the following simplifying assumption is made: R depends on the weighted concentration distribution in the same way for all components; that is, R is a functional of $K(y)g(y, t)$ that does not depend parametrically on x, say:

$$R = F\{K(y)g(y, t)\} \tag{2}$$

Astarita and Ocone called the case where Eq. 2 holds true "uniform."

It is important to realize that the assumption of uniformity is a very strong one, and is probably an oversimplification in a variety of real situations. However, it does make it possible to obtain the results below, which are believed to be at least qualitatively correct in a more general context.

Let x^* identify one particular component. If Eq. 2 holds true, Eq. 1 can be applied to the generic component x and to the particular component x^*, and time can be eliminated to yield:

$$[1/k(x)] \ln [g(x, t)/g(x, 0)] = [1/k(x^*)] \ln [g(x^*, t)/g(x^*, 0)] = u(t) \quad (3)$$

which integrates to:

$$g(x, t) = g(x, 0) \exp [-k(x)u(t)] \quad (4)$$

The quantity $u(t)$ can be interpreted as a warped time scale. Now, without loss of generality, one can set $k(x) = k^*x$, with k^* the average value of k. This simplification only means that x has been scaled to be proportional to k. It is now convenient to define the dimensionless time $\tau = k^*t$, and to define $v(\tau) = k^*u(t)$, so that v is a dimensionless warped time. With these definitions, Eq. 4 becomes:

$$g(x, \tau) = g(x, 0) \exp (-xv) \quad (5)$$

The quantity v is delivered by the solution of the following differential equation:

$$dv/d\tau = F\{K(x)g(x, 0) \exp (-xv)\}, \quad v(0) = 0 \quad (6)$$

Given an initial concentration distribution $g(x, 0)$ and a specific form for the functional $F\{\}$, Eq. 6 can always be integrated to yield $v(\tau)$. This, however, as will be seen in the following, need not be done in a variety of cases.

If $g()$ has been normalized with respect to the initial total concentration, its integral at time zero is unity:

$$\int g(x, 0)\, dx = 1 \quad (7)$$

The normalized total concentration at time t, that is, the total concentration at time t divided by the initial total concentration, is:

$$C(\tau) = \int g(x, \tau)\, dx = \int g(x, 0) \exp (-xv)\, dx \quad (8)$$

Equation 8 shows that the total concentration at time t is a Laplace transform of the initial one, with v playing the role of the transform parameter. Differentiation of Eq. 8 yields:

$$-dC/d\tau = (dv/d\tau) \int xg(x, 0) \exp (-xv)\, dx \quad (9)$$

Equation 9 shows that the rate of change of the total concentration is proportional to $dv/d\tau$ and to the first moment of the concentration distribution.

Now consider the case where the initial concentration distribution is a gamma one, say:

$$g(x, 0) = \alpha^\alpha x^{\alpha-1} \exp (-\alpha x)/\Gamma(\alpha) \quad (10)$$

with $\alpha \geq 1$. For $\alpha = 1$, one gets an exponential distribution: the highest concentration is that of the component with $k = 0$, that is, the most refractory one. When α approaches ∞, the gamma distribution approaches $\delta(x - 1)$; that is, one recovers the single-component case. Substitution of Eq. 10 into Eqs. 8 and 9 yields:

$$C(\tau) = [\alpha/(\alpha + v)]^\alpha \quad (11)$$

$$-dC/d\tau = (dv/d\tau)C^{(\alpha+1)/\alpha} \quad (12)$$

Equation 12 contains the basic result of Aris (1968). In fact, in the linear case R is a constant which without loss of generality can be set to unity, and hence $dv/d\tau = 1$. The apparent overall order of reaction $N' = d \ln (-dC/d\tau)/d \ln C$ is in that case $(\alpha + 1)/\alpha$: for an exponential distribution $N' = 2$, while of course for the single-component case ($\alpha = \infty$), $N' = 1$.

All the results obtained so far are independent of the particular form of the functional $F\{\}$ in Eq. 2. In order to proceed, one does need to assign a specific form to $F\{\}$. Consider the case where R is given by:

$$R = \left[\int K(y)g(y, t)\, dy\right]^{n-1} \quad (13)$$

This corresponds to the case where the single-component kinetics are of n order. In fact, suppose there is only one component, so that $g(x, \tau) = g(\tau)\delta(x - 1)$. One obtains $-dg(\tau)/d\tau = g^n/K(1)^{n-1}$. Equation 13, of course, does not describe *parallel* n-order reactions in the case of a finite number of components larger than one: the essence of the nonlinearity factor is that it describes possible interactions between different reactants.

It is now convenient to define $z = (\alpha + v)x$. After some algebra one obtains:

$$(dv/d\tau) = \left\{[C/\Gamma(\alpha)] \int K[z/(\alpha + v)]z^{\alpha-1}e^{-z}\, dz\right\}^{n-1} \quad (14)$$

One does need now to assume a form for $K(x)$, and the following is chosen:

$$K = K^*(\alpha x)^\beta \Gamma(\alpha)/\Gamma(\alpha + \beta) \quad (15)$$

where K^* is the (dimensionless) average value of K, which, for the case at hand, could be set to unity without loss of generality. (This is due to the monomial nature of Eq. 13, so that a nonunity value of K^* could be normalized by rescaling k^*.)

Equation 15 should be discussed in some detail. First of all, parameter β is subject to the condition $\alpha + \beta > 0$. The form of $K(x)$ is so chosen that the integral of $K(x)g(x, 0)$ converges, and in fact has a value of K^* ($=1$). Because of Eq. 5, the form chosen also guarantees that the integral converges at all times. It is important to notice that β may be both positive and negative. A positive value means that the ordering of components in the direction of increasing frequency factors $k(x)$ is also an ordering in increasing $K(x)$, and vice versa for a negative β. Substitution of Eq. 15 into Eq. 14 yields:

$$dv/d\tau = C^{(n-1)(\alpha+\beta)/\alpha} \quad (16)$$

Therefore $-dC/d\tau$ is proportional to C^N, and the apparent overall order of reaction N is calculated to be:

$$\alpha N = n\alpha + 1 + \beta(n - 1) \tag{17}$$

Before analyzing this result in general, some interesting special cases are discussed in the following.

1. $n = 1$. Here one of course recovers the Aris (1968) result that $N = (\alpha + 1)/\alpha$.
2. $\alpha = \infty$. This is the single-component limit, and one gets, as expected, $N = n$.
3. $\beta = 1$. One obtains a generalization of the Aris result, namely, that $N/n = (\alpha + 1)/\alpha$. This is a result that could not be guessed by some sort of intuitive analysis.
4. $\alpha = \beta = 1$. One obtains the surprisingly simple result that $N = 2n$. For an exponential distribution and $\beta = 1$, the apparent overall order is exactly twice the underlying order. Astarita and Ocone considered the case $n = 2$, $\alpha = \beta = 1$ and calculated $N = 4$, which is of course a special case of this result.
5. β has its minimum possible value compatible with Eq. 15, say $\beta = -\alpha$. One obtains $N = (\alpha + 1)/\alpha$. In a plot of N vs. β at fixed α, every value of n is a straight line; all lines originate at $\beta = -\alpha$, $N = (\alpha + 1)/\alpha$; and their slope is positive for $n > 1$ and negative for $n < 1$, Figure 1.

Astarita and Ocone speculated that $N > n$ invariably, based on a heuristic argument: as time progresses, species with large values of $k(x)$ disappear first, and hence the mixture becomes progressively more refractory, so that the apparent order would appear to be larger than the intrinsic one. The argument has some validity as far as $k(x)$ is concerned, but it entirely overlooks the effect of $K(x)$, and indeed Figure 1 shows that N may not only be less than n but even negative if $n < 1$.

First of all, notice that at fixed β, $N(\alpha)$ is a monotonous function, since the derivative $dN/d\alpha = -[1 + \beta(n - 1)]/\alpha^2$. It follows that, if $N(1) > n$, then $N \geq n$ for all α's, and vice versa. Notice however that $N(1)$ is given by:

$$N(1) = n + 1 + \beta(n - 1) \tag{18}$$

which not only is not necessarily larger than n, but is not even guaranteed to be positive. The two cases $n > 1$ and $n < 1$ need to be analyzed separately.

The case $n > 1$ is the simpler one. The slope in Figure 1 is positive, and therefore $N > (\alpha + 1)/\alpha$. This however does not guarantee that $N > n$, unless $n < (\alpha + 1)/\alpha$.

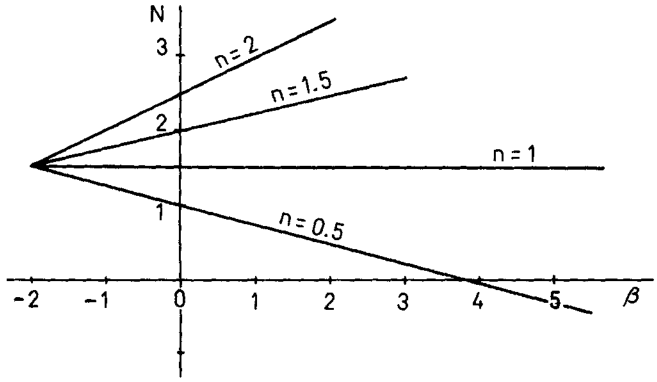

Figure 1. N vs. β for $\alpha = 2$.
Parameter of straight lines is the underlying order n

In the case $n < 1$, N will invariably become less than n at sufficiently large β, unless $\alpha = \infty$. Furthermore, as β grows even more, N will eventually become negative.

It is now of interest to discuss the physical significance of the results obtained. The sign of β is interpreted as follows: If β is positive, components with a larger k also have a larger K, and vice versa in the case of negative β. Now components with a larger k will tend to disappear first; if β is positive, this means that components with a larger K will also disappear first. If $n > 1$, this means that both the average frequency factor and the nonlinearity factor R will decrease as the reaction proceeds, and hence the apparent order will exceed the intrinsic one. However, if $n < 1$, as time progresses the average frequency factor will decrease, but the nonlinearity factor will increase, and either one of the two effects may predominate; at very large β's, the increase of R is sure to predominate, and hence the overall reaction will appear to accelerate, leading to a negative apparent order. Analogous (and specular) considerations apply of course to the case of negative β.

In order to discuss the physical significance of the parameter β it is useful to consider a different underlying kinetics, that is, that of a Langmuir isotherm dominated kinetics, for which the nonlinearity factor R can be written as:

$$R = \left[\int K(x)g(x, t)\,dx + 1\right]^{-1} \tag{19}$$

The Langmuir isotherm kinetics represent a realistic case where the intrinsic apparent order of reaction is less than unity. Apparent intrinsic orders larger than unity generally arise from mechanisms complicated enough to result in nonmass-action kinetics, except for $n = 2$.

Let $K(x)$ again be given by Eq. 15, with K^* now a quantity that cannot be set to unity arbitrarily, because of the binomial nature of the term within brackets in Eq. 19. One obtains, after some algebra:

$$-\frac{dC}{d\tau} = \frac{C^{(\alpha+1)/\alpha}}{1 + K^*C^{(\alpha+\beta)/\alpha}} \tag{20}$$

Again, for $\alpha = \infty$ one obtains $-dC/d\tau = C/(1 + K^*C)$ as expected for the single-component case. As time progresses, the second term in the denominator becomes negligible as compared to unity, and one recovers the Aris result $N = (\alpha + 1)/\alpha$, as one would expect when there is no more competition for active sites and hence the underlying kinetics become first order. When β has its minimum value of $-\alpha$, one also recovers the Aris result—which could not be easily foreseen.

For the case at hand, a positive β means that species with a high value of k are also species that compete fiercely for active sites, and indeed at large values of C the apparent overall order can become negative if $\beta > \alpha$: as components with large k's and large K's disappear, the remaining species compete less strongly for active sites, and this results in an acceleration of the overall rate. Notice that a negative N can only occur at large values of C, as one would expect from any realistic kinetic mechanism for an irreversible reaction.

The results obtained so far for the special cases of n-order and

Langmuir isotherm kinetics can be generalized as follows. Let the single-component kinetics be represented as follows:

$$-dc/dt = kcf(Kc);$$
$$-dc/d\tau = cf(Kc) \tag{21}$$

Let $w = Kc$ be the K-weighted concentration. Function $f(w)$ is assumed to be differentiable, in particular at the equilibrium point $w = 0$; Astarita and Ocone have discussed the thermodynamic significance of this assumption. At any given level of concentration, an instantaneous intrinsic order of reaction can be defined as:

$$n' = d\ln(-dc/d\tau)/d\ln c \tag{22}$$

Let f' be the derivative of f, and let q be wf'/f. Substitution of Eq. 21 into Eq. 22 yields:

$$n' = 1 + q \tag{23}$$

The linear case of course corresponds to $q = 0$, and hence $n' = 1$. The power law case is $f(w) = w^{n-1}$, and one obtains $n' = n$ as expected.

In the case of a continuous mixture for which Eq. 2 holds, let w be:

$$w = \int K(x)g(x,t)\,dx \tag{24}$$

Now suppose that the initial concentration distribution is a *gamma distribution* as given by Eq. 10, and that $K(x)$ is as given by Eq. 15. One calculates:

$$w = K^*C^{(\alpha+\beta)/\alpha} \tag{25}$$

Now suppose that the functional $F\{\}$ in Eq. 2 can be written as $f(w)$, which is an admissible form since it guarantees that the single-component case is recovered correctly; in the two cases discussed above, this assumption was indeed made. Equations 6 and 12 now yield:

$$-dC/d\tau = f(w)C^{(\alpha+1)/\alpha} \tag{26}$$

One can now define an overall instantaneous order of reaction N' as:

$$N' = d\ln(-dC/d\tau)/d\ln C \tag{27}$$

After some algebra with the equations above one obtains:

$$\alpha N' = \alpha + 1 + (\alpha + \beta)q \tag{28}$$

Several observations are in order.

1. If $\alpha = \infty$, $N' = n'$ as expected for the single-component case.
2. As time progresses, C approaches zero, and since $\beta > -\alpha$, so do w and q. It follows that N' approaches asymptotically $(\alpha + 1)/\alpha$, and n' approaches asymptotically the value of unity, no matter what the form of the function $f(w)$ may be.
3. If $\beta = 1$, one obtains again the generalization of the Aris result, that is, $N'/n' = (\alpha + 1)/\alpha$.
4. For an exponential distribution ($\alpha = 1$) one obtains $N'/n' = [2 + (1 + \beta)q]/(1 + q)$. As time progresses, this approaches asymptotically $N'/n' = 2$.

Notation

c = single-component concentration
C = overall concentration
$f()$ = function, Eq. 21
$F\{\}$ = functional, Eq. 2
$g()$ = concentration distribution
k = frequency factor
k^* = average value of k
K = weighting factor
K^* = average value of K
n = intrinsic order of reaction
n' = intrinsic instantaneous order of reaction
N = overall order of reaction
N' = overall instantaneous order of reaction
$q = wf'/f$
R = nonlinearity factor
t = time
u = warped time
v = dimensionless warped time
w = dimensionless weighted concentration, Eq. 24
x = component label
x^* = one particular component
y = dummy component label
$z = (\alpha + v)x$

Greek letters

α = initial distribution parameter
β = K distribution parameter
$\Gamma()$ = gamma function
$\delta()$ = delta function
τ = dimensionless time

Literature Cited

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