Reactions in Continuous Mixtures

A continuous mixture is one which is so complex that it is no longer worthwhile to distinguish individual chemical species; instead, an index, such as the simulated boiling point, is chosen and c_i, the concentration of the species A_i, is replaced by $c(x)dx$, the concentration of material with index in the interval $(x, x + dx)$. It has been long known that the total concentration of a suitably distributed mixture, each of whose components disappears by a first-order reaction with constant $k(x)$, will appear to disappear according to a higher order of reaction. The generalization of this to a mixture that requires two indices for its description is worth considering for three reasons: First, there may well be materials that are so complex as to require this. Second, the second index may be considered to distribute reaction time. Third, this approach seems to answer the mathematical question of how to generalize from the continuum of first-order reactions to one of parallel Nth-order reactions.

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Introduction

The notion of a continuous mixture has proved its value in many ways since it was first introduced by de Donder (1931). It arises when the number of distinct species is very large and the difference between adjacent species is relatively slight. Under such circumstances a continuous variable, such as boiling point or chromatographic retention time, is used to describe the composition. This notion has been applied to distillation (Amundson and Acrivos, 1955), to the thermodynamics of the distribution of isomers (Alberty and Oppenheimer, 1984) and other thermodynamical questions (Briano and Glandt, 1984), to polymerization (Zeman and Amundson, 1965), froth flotation (Loveday, 1966), the heterogeneity of catalytic sites (Malhotra and Sadana, 1987), and to reactions in continuous mixtures in general (Aris and Gavalas, 1965; Aris, 1968; Luss and Hutchinson, 1971; Gohkeri and Luss, 1971; Kemp and Wojciechowski, 1974; Weekman, 1979; Krambeck, 1984; Astarita and Ocone, 1988; Chou and Ho, 1989; Prasad et al., 1986a, b).

To the best of my knowledge, the work of Prasad et al. contains the first mention of the use of two indices, for, in their description of coal liquefaction they take the number of carbon atoms and the number of oxygen atoms to be their two index parameters. They review various models in the context of coal liquefaction and are successful in fitting kinetic kernels (Prasad, 1986). There may also be other materials of sufficient complexity to merit description with two indices, and reactions in such mixtures are worth considering in a more general light. One authority, with much experience in the oil industry, has said that "in any real case, sufficiently complex for a continuous description, I think it is highly unlikely that one could ever determine the initial distribution of reaction rates and that the finest analysis technique will only resolve the mixture into components that still have a continuum of reaction rates" (Krambeck, personal communication, 1984).

It is in the cracking of crude oil that the continuum of parallel reactions in a continuous mixture has found its principal application (Weekman, 1979). It explains how so essentially first-order a process as cracking can give data best correlated by a second-order reaction, for this is just the kinetics of the disappearance of the total concentration of a mixture with exponentially distributed first-order rate constants. Indeed, Krambeck (1984) has shown that, whenever the distribution does not go to zero at the irrefrangible end of the spectrum, the disappearance of the "lump" is as if by second-order reaction. The argument is simple and convincing when the basic reaction is of the first order, for such a reaction is essentially a spontaneous individual process, as when a bond breaks thermally, independent of other species that may be present. It matters not whether the species be discrete or a slice of a continuum; each "does its own thing." It is less easy to see how a continuum of parallel reactions of the second order can be justified. Second-order reaction implies a cooperation between molecules and although this cooperation might reasonably be confined to each of several species when the species are discrete, so that a number of parallel second-order reactions result, this is less plausible when the species are continuous and can scarcely avoid interacting with their neighbors. It is the recognition of this that led Astarita and Ocone (1988) to look at kinetics represented by kinetic laws of the type

$$\frac{d}{dt} c(x, t) = k(x) c(x, t) F \left[\int K(x, z) c(z, t)\, dz \right]$$

Here $c(x, t)dx$ is the concentration of material with index in the slice $(x, x + dx)$ whose rate constant is $k(x)$; $K(x, z)$ describes the interaction of the species. The authors obtain some striking results for uniform systems, as they call those for which K is independent of x (Astarita and Ocone, 1988; Astarita, 1989). Their second-order reaction would imply that each slice reacted with every other, K being a stoichiometric coefficient function. Only if $K = \delta(z - x)$ would we have a continuum of independent parallel second-order reactions. In spite of the physical objections, the mathematical challenge of setting this up properly remains. Ho and Aris (1987) have shown how not to do it. Astarita and Ocone have shown how to do something a little different and probably more sensible physically. We shall see that it can be done quite generally by having a double-indexed mixture with parallel first-order reactions. The first-order kinetics ensures the individuality of the reactions and the distribution in one index simulates a reaction of the Nth order that is distributed by the second index. If we relax the requirement of first-order kinetics and permit uniform Astarita kinetics, we find that, by using his latest results on apparent reaction rate, we can justify the lumping of reactions with quite general nonlinear kinetics. Various special cases will be examined in detail.

Since the dimensionless time for a first-order reaction is the product of the reaction time t and a first-order rate constant k, there is no reason why $k(x)t$ should not be interpreted as $k(x)t(x)$, that is, the reaction time may be distributed over the index space as well as the rate constant. Alternatively, with two indices k might be distributed over one and t over the other as $k(x)t(y)$. We can thus consider a continuum of reactions in a reactor with specified residence time distribution and this is entirely equivalent to the single reaction with the apparent kinetics of the continuum under the segregation hypothesis of residence time distribution theory, a topic that is in the elementary texts. Three indices would be required to distribute the reaction time with a doubly-distributed continuous mixture.

To these three *a priori* reasons for considering the generalization to two indices a fourth may be added *a posteriori*. We shall encounter, in important specific cases, one or two of the rarer special functions associated with the confluent hypergeometric function.

General Formulation for a Single Index

It is better to define the continuous mixture in terms of an index variable (Aris and Gavalas, 1966; Astarita and Ocone, 1988) rather than to use the dimensional rate constant k. Let x be an index variable, which without loss of generality we can take to be in the interval $[0, \infty)$. The initial concentration of material characterized by indices in the interval $(x, x + dx)$ is

$$c(x, 0)dx = c_0 f(x)dx \tag{1}$$

where c_0 is a concentration. Thus $f(x) \geq 0$.

$$\int_0^\infty f(x)\, dx = 1 \tag{2}$$

and without loss of generality we can scale x so that we also have

$$\int_0^\infty x f(x)\, dx = 1 \tag{3}$$

The distribution $f(x)$ will have one or more shaping parameters and we shall have occasion to use the gamma distribution

$$f(x) = \frac{\alpha^\alpha x^{\alpha-1}}{\Gamma(\alpha)} e^{-\alpha x} = \phi_\alpha(x), \quad \alpha > 0 \tag{4}$$

which, as $\alpha \rightarrow \infty$, approaches $\delta(x - 1)$. We suppose that this initial distribution decays in such a way that

$$\frac{\partial}{\partial t} c(x, t) = -k(x)c(x, t) \tag{5}$$

where $k(x)$ is a monotonic increasing function on $[0, \infty)$ with $k(0) = 0$ and $k(x) \rightarrow \infty$ as $x \rightarrow \infty$. Thus

$$\begin{aligned} c(x, t) &= c_0 u(x, t) \\ &= c_0 f(x) e^{-k(x)t} \end{aligned} \tag{6}$$

and

$$U(t) = \int_0^\infty c(x, t)\, dx/c_0 = \int_0^\infty f(x) e^{-k(x)t}\, dx \tag{7}$$

If t can be eliminated between $U(t)$ and

$$\dot{U}(t) = -\int_0^\infty k(x) f(x) e^{-k(x)t}\, dx \tag{8}$$

to give a kinetic law for the "lump"

$$\dot{U} = -F(U),\ U(0) = U_0 = 1 \tag{9}$$

we say that this kinetic law is an alias of the underlying first-order kinetics generated by the distributions $f(x)$, $k(x)$. Since $k(x)$ is monotonic, we can regard $f(x)$ as $f^*(k)$ with $f^*(k)dk = f(x)k'(x)dx$ when necessary. This transformation is the essential feature of Ho's treatment (Chou and Ho, 1988). Let

$$\hat{k} = \int_0^\infty k(x) f(x)\, dx \tag{10}$$

so that $\hat{k}$ has the dimensions of reciprocal time and

$$\hat{k}t = \tau \tag{11}$$

is the dimensionless time. If

$$k(x) = \hat{k} h(x) \tag{12}$$

where $h(x)$ is monotonic and $\int_0^\infty h(x) f(x) dx = 1$, then

$$U(\tau) = \int_0^\infty f(x) \exp - [\tau h(x)]\, dx \tag{13}$$

In most cases it is possible to take $h(x) = x$ and

$$U(\tau) = \int_0^\infty f(x) e^{-x\tau}\, dx \tag{14}$$

and $U(\tau)$ is therefore the Laplace transform of $f(x)$ with x playing the role of the traditional t variable and τ that of s or p, the Laplace transform variable.

If we approach the problem from the other direction and ask what distribution will produce a given alias, we have first to solve Eq. 9 and then find the distribution f of which it is the Laplace transform. Now (formally)

$$\begin{aligned} U(\tau) &= \sum_{j=0}^{\infty} (-)^j \frac{\tau^j}{j!} \int_0^\infty x^j f(x)\,dx \\ &= 1 - \tau + \sum_{i=2}^{\infty} m_i \frac{(-\tau)^i}{i!} \end{aligned} \tag{15}$$

by the normalizations, Eqs. 2 and 3, and m_i is the ith moment of $f(x)$ about the origin. There is thus an implicit restriction on the function F of Eq. 9, namely that

$$F(1) = 1 \tag{16}$$

We also see immediately that there are certain kinetic laws that cannot be generated. For example the so-called zero-order reaction that just takes place at a constant rate so long as there is any reactant present. Thus F is a constant and by Eq. 1 must be 1, giving

$$U(\tau) = 1 - \tau, \quad 0 \le \tau \le 1 \tag{17}$$

But there is no $f(x) \ge 0$ with $m_0 = m_1 = 1$ and $m_i = 0, i \ge 1$. For an nth-order reaction with $n \ge 1$ however

$$F(U) = U^n \tag{18}$$

and

$$U(\tau) = \{1 + \tau(n-1)\}^{-1/(n-1)} \tag{19}$$

Inversion of this transform gives the gamma distribution

$$f(x) = \phi_\alpha(x), \quad \alpha = 1/(n-1) \tag{20}$$

which is the well known result, $n = (\alpha + 1)/\alpha$. $U(\tau)$ is shown in Figure 1 for several values of n.

The apparent nth-order rate constant can be obtained from Eq. 19 by writing it in the dimensional form

$$c_0 U = c_0\{1 + (n-1)\hat{k}t\}^{-1/(n-1)} \tag{21}$$

and comparing this with the solution of

$$\frac{dc}{dt} = -k_n c^n, \quad c(0) = c_0 \tag{22}$$

which is

$$c(t) = c_0\{1 + (n-1)k_n c_0^{n-1} t\}^{-1/(n-1)} \tag{23}$$

Thus,

$$k_n = \hat{k} c_0^{1-n} \tag{24}$$

This points up the desirability of using the dimensionless index variable x and of having the liberty of choosing $h(x)$ in Eq. 12. If $h(x) = x$ then k, the first-order constant, is being linearly distributed. If it is desirable to distribute k_n linearly then $h(x) = x[f(x)]^{n-1}$.

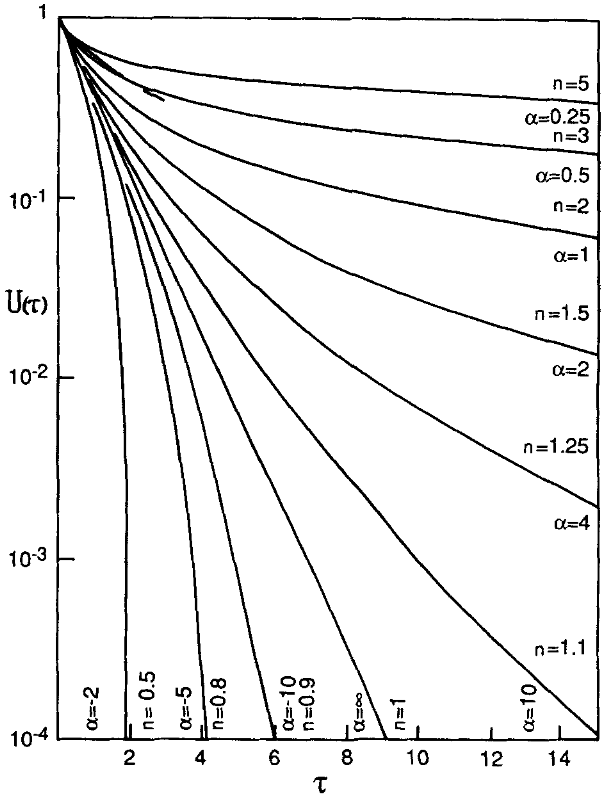

Figure 1. Fractional concentration as a function of time for reactions of various orders.

Parallel Reaction in a Doubly-Distributed Continuum

Let $H(x, y)$ and $h(x, y)$ be nonnegative functions that satisfy

$$\int_0^\infty \int_0^\infty H(x, y)\,dx\,dy = 1 \tag{25}$$

$h(0, y) = h(x, 0) = 0, \partial h/\partial x > 0, \partial h/\partial y > 0$ and

$$\int_0^\infty \int_0^\infty h(x, y) H(x, y)\,dx\,dy = 1 \tag{26}$$

Then, if $c_0 u(x, y, t)\,dxdy$ is the concentration of material in the index interval $(x, x + dx)x(y, y + dy)$,

$$u(x, y, 0) = H(x, y) \tag{27}$$

we have

$$U(\tau) = \int_0^\infty \int_0^\infty H(x, y) e^{-\tau h(x,y)}\,dx\,dy \tag{28}$$

In particular, if $H(x, y) = f(x)g(y)$, where f and g satisfy the normalizations, Eqs. 2 and 3, and $h(x, y) = xy$, $U(\tau)$ becomes

$$\begin{aligned} U(\tau) &= \int_0^\infty f(x) \left[\int_0^\infty g(y) e^{-\tau xy}\,dy\right] dx \\ &= \int_0^\infty f(x) V(\tau x)\,dx \end{aligned} \tag{29}$$

where $V(\tau)$ is the course of the reaction

$$\dot{V} = -G(V) \tag{30}$$

the kinetic alias generated by the distribution g.

Ho and Aris (1987) argued that any formulation of reaction in continuous mixtures must satisfy the single-component identity (SCI), namely that it should reduce to the kinetics of a single component when the mixture is pure. This is true of Eq. 29, for with $f(x) = \delta(x - x_o)$, $U(\tau) = V(x_o\tau)$. The corresponding $H(x, y) = \delta(x - x_o)g(y)$ is not "pure" in the second index, so to speak. The requirement should be enlarged to a discrete component each satisfying the kinetic law given by G. We see that this is

$$H(x, y) = \Sigma u_i \delta(x - x_i) g(y)$$

giving

$$U(\tau) = \Sigma u_i V(\tau x_i)$$

Astarita kinetics satisfy the SCI, but not necessarily the discrete-component identity (DCI). For example, putting $g(x, 0) = f(x) = \Sigma u_i \delta(x - x_i)$ in the uniform kinetic law

$$-\frac{\partial}{\partial t} g(x, t) = k(x) g(x, t) \left\{ \int_0^\infty K(y) g(y, t)\, dy \right\}^{n-1}$$

gives

$$-\dot{g}_i(t) = k_i g_i \{\Sigma u_j k_j g_j\}^{n-1}, \quad g_i(0) = u_i$$

When $n = 2$ this represents the second-order reaction scheme $\alpha_{ik} A_i + A_k \longrightarrow$ products with certain constraints on the stoichiometry and kinetic constants. When there is a single component this reduces to a second-order reaction. This cooperative element in the Astarita kinetics is, of course, no defect—indeed it may be its strength.

Examples

We can have parallel nth-order reactions ($n > 1$) from the y continuum by taking

$$g(y) = \frac{\beta^\beta y^{\beta - 1} e^{-\beta y}}{\Gamma(\beta)}, \quad \beta = 1/(n - 1) \tag{31}$$

to give

$$V(\tau x) = \{1 + \tau x/\beta\}^{-\beta} \tag{32}$$

Thus,

$$\begin{aligned} U(\tau) &= \int_0^\infty f(x)\{1 + \tau x/\beta\}^{-\beta}\, dx = \left(\frac{\beta}{\tau}\right)^\beta \int_0^\infty f(x) \left\{\frac{\beta}{\tau} + x\right\}^{-\beta} dx \\ &= \left(\frac{\beta}{\tau}\right)^{\beta - 1} \int_1^\infty z^{-\beta} f\left[\frac{\beta}{\tau}(z - 1)\right] dz \\ &= \left(\frac{\beta}{\tau}\right)^\beta G_\beta \left\{ f(x); \frac{\beta}{\tau} \right\} \end{aligned} \tag{33}$$

where G_β is the generalized Stieltjes transform of order β (Erdelyi et al., 1954; Widder, 1941).

If for $f(x)$ we use the gamma distribution $\phi_\alpha(x)$ and put $\sigma = \tau/\alpha\beta$, we have

$$U(\tau) = e^{1/2\sigma} \sigma^\kappa W_{\kappa,\mu}(1/\sigma) \tag{34}$$

where

$$\kappa = \frac{1}{2}(1 - \alpha - \beta), \quad \mu = \frac{1}{2}(\alpha - \beta) \tag{35}$$

and $W_{\kappa,\mu}$ is Whittaker's form of the confluent hypergeometric function. An even more aposit form is the Tricomi function (Spanier and Oldham, 1987):

$$\begin{aligned} \psi(a; c; z) &= \frac{\Gamma(1 - c)}{\Gamma(1 + a - c)} {}_1F_1(a; c; z) \\ &\quad + \frac{\Gamma(c - 1)}{\Gamma(a) z^{c-1}} {}_1F_1(1 + a - c; 2 - c; z) \end{aligned} \tag{36}$$

in terms of which

$$\begin{aligned} U(\sigma) &= \sigma^{-\alpha} \psi(\alpha; 1 + \alpha - \beta; 1/\sigma) \\ &= \sigma^{-\beta} \psi(\beta; 1 + \beta - \alpha; 1/\sigma) \end{aligned} \tag{37}$$

a form that has the advantage of showing the invariance under the interchange of α and β. The integral forms of U are

$$\begin{aligned} U(\tau) &= \frac{\alpha^\alpha}{\Gamma(\alpha)} \int_0^\infty \frac{x^{\alpha - 1} e^{-\alpha x}}{(1 + \tau x/\beta)^\beta}\, dx \\ &= \left(\frac{\alpha\beta}{\tau}\right)^\beta e^{(\alpha\beta/\tau)} \frac{1}{\Gamma(\beta)} \int_1^\infty z^{-\alpha} (z - 1)^{\beta - 1} e^{-\alpha\beta z/\tau}\, dz \end{aligned} \tag{38}$$

and equivalent forms obtained by interchanging α and β. When α or β is an integer, say $\beta = b$, we have a finite expansion

$$\begin{aligned} U(\tau; \alpha, b) &= \left(\frac{\alpha b}{\tau}\right)^b \frac{e^{\alpha b/\tau}}{(b - 1)!} \int_1^\infty z^{-\alpha} (z - 1)^{b - 1} e^{-(\alpha b/\tau) z}\, dz \\ &= \left(\frac{\alpha b}{\tau}\right)^b e^{\alpha b/\tau} \sum_{j=0}^{b-1} \frac{(-1)^j}{j!(b - 1 - j)!} \int_1^\infty z^{-\alpha + j} e^{-(\alpha b/\tau) z}\, dz \end{aligned} \tag{39}$$

If $\alpha = a$, an integer, the last integral is $E_{a-j}(ab/\tau)$, E being the exponential integral

$$E_p(s) = \int_1^\infty t^{-p} e^{-st}\, dt; \quad p \geq 1 \tag{40}$$

The formula will produce negative p, so we understand

$$\begin{aligned} E_0(s) = \alpha_0(s) = (1 - e^{-s})/s, \quad E_{-p}(x) &= \alpha_p(s) \\ &= \sum_{k=1}^{p} \frac{p!}{k!} \frac{e^{-s}}{s^{p-k+1}} + \frac{p!}{s^p} \alpha_0(s) \end{aligned} \tag{41}$$

Thus

$$U(\tau; a, b) = \left(\frac{ab}{\tau}\right)^b e^{ab/\tau} \sum_{j=0}^{b-1} \frac{(-1)^j}{j!(b-1-j)!} E_{a-j}(ab/\tau) \quad (42)$$

and in particular

$$U(\tau; 1, 1) = \frac{1}{\tau} e^{1/\tau} E_1(1/\tau) \quad (43)$$

$$U(\tau; 2, 1) = \frac{2}{\tau} e^{2/\tau} E_2(2/\tau)$$
$$= \frac{2}{\tau} e^{2/\tau}\{E_0(2/\tau) - E_1(2/\tau)\} = U(\tau; 1, 2) \quad (44)$$

In general the second form in Eq. 38 can be expanded as

$$U(\tau; \alpha, \beta) = \left(\frac{\alpha\beta}{\tau}\right)^\beta e^{(\alpha\beta/\tau)} \sum_{j=0}^{\infty}$$
$$\cdot \frac{(-1)^j}{\Gamma(j+1)\Gamma(\beta - j - 1)} E_{\alpha-\beta+1-j}\left(\frac{\alpha\beta}{\tau}\right) \quad (45)$$

where E for a nonintegral index is the incomplete gamma function

$$E_\gamma(s) = s^{\gamma-1}\Gamma(1-\gamma; s) = \int_1^\infty t^{-\gamma} e^{-st}\, dt \quad (46)$$

Other special cases are:

$$\alpha = \beta, \quad U(\tau; \alpha, \alpha) = \Gamma(1-\alpha) e^{\alpha^2/2\tau} k_{-2\alpha}(\alpha^2/2\tau) \quad (47)$$

where k is Bateman's function

$$k_\mu(x) = \frac{2}{\pi}\int_0^{\pi/2} \cos(x \tan t - \mu t)\, dt \quad (48)$$

$\alpha = \beta + 1/2,$

$$U(\tau; \alpha; \alpha - 1/2) = \left[\frac{\alpha(2\alpha-1)}{\tau}\right]^{\alpha-1/2}$$
$$\cdot e^{\alpha(2\alpha-1)/4\tau} D_{1-2\alpha}\left[\frac{\sqrt{\alpha(2\alpha-1)}}{\sqrt{\tau}}\right] \quad (49)$$

where $D_\nu(x)$ is the parabolic cylinder function; $\alpha = 1, \beta = 1/2,$

$$U(\tau; 1; 1/2) = \left(\frac{\pi}{2\tau}\right)^{1/2} e^{1/2\tau} \operatorname{erfc}\left(\frac{1}{2\tau}\right)^{1/2} \quad (50)$$

From the asymptotic expansion of the Tricomi function we get

$$U(\tau) = 1 - \tau + \frac{(\alpha+1)(\beta+1)}{\alpha\beta}\frac{\tau^2}{2!}$$
$$- \cdots = \sum_{j=0}^{\infty} (-)^j \frac{(\alpha)_j(\beta)_j}{(\alpha\beta)^j}\frac{\tau^j}{j!} \quad (51)$$

which passes to the limit of $e^{-\tau}$ as a α and $\beta \rightarrow \infty$. On the other hand the power series expansions that give the behavior for large τ depend on the relative magnitudes of α and β. If

$$\beta > \alpha + 1, U(\tau) \sim \frac{\Gamma(\beta-\alpha-1)}{\Gamma(\beta)}\left(\frac{\alpha\beta}{\tau}\right)^\alpha\left(\beta - \alpha - 1 - \alpha\frac{\alpha\beta}{\tau}\cdots\right)$$
$$\beta = \alpha + 1, U(\tau) \sim \left(\frac{\alpha\beta}{\tau}\right)^\alpha\left\{\frac{1}{\Gamma(1+\alpha)} - \frac{1}{\Gamma(-\alpha)}\frac{\alpha\beta}{\tau}\ln\frac{\alpha\beta}{\tau}\right\}\cdots$$
$$\alpha < \beta < \alpha + 1, U(\tau) \sim \frac{\Gamma(\beta-\alpha)}{\Gamma(\beta)}\left(\frac{\alpha\beta}{\tau}\right)^\alpha + \frac{\Gamma(\alpha-\beta)}{\Gamma(\alpha)}\left(\frac{\alpha\beta}{\tau}\right)^\beta\cdots$$
$$\alpha = \beta, U(\tau) \sim \left(\frac{\alpha^2}{\tau}\right)^\alpha\left\{\frac{1}{\Gamma(\alpha)}\ln\tau - \frac{2\gamma - \psi(\alpha)}{\Gamma(\alpha)}\right\}\cdots \quad (52)$$

When $\beta < \alpha$ we can reverse the roles of α and β. It is clear that, except when $\alpha = \beta$, $U(\tau)$ is asymptotically $0(\tau^{-\alpha})$ if $\alpha < \beta$ and $0(\tau^{-\beta})$ if $\beta < \alpha$. Thus, if $m = (\alpha + 1)/\alpha$, $n = (\beta + 1)/\beta$, the total concentration ultimately disappears as if by a qth-order reaction where q is the greater of m and n. If $\alpha = \beta$, the asymptotic kinetic law cannot be written down explicitly. $F(U)$ is obtained by eliminating τ between $F = A\tau^{-\alpha-1}\{\alpha \ln \tau - 1\}$ and $U = A\tau^{-\alpha} \ln \tau$ where $A = \alpha^{2\alpha}/\Gamma(\alpha)$. If the instantaneous order is defined as $\mu = d \ln F/d \ln U$, then

$$\mu = m\left\{1 - \frac{1}{\ln\tau(\alpha\ln\tau - 1)}\cdots\right\} \sim m \quad (53)$$

as we would expect. Figure 2 shows $U(\tau; \alpha, 1)$ for several values of α. The curve for $\alpha = \infty$ is the same as that for the second-order reaction ($n = 2$) in Figure 1. The broken lines in Figure 2 are for nth-order reaction $n = (\alpha + 2)/\alpha$ which show a certain degree of approximation.

Generalized Background Kinetics

Astarita and Ocone's uniform kinetics (1988) may be used for the background kinetics (with distribution parameter y). It will

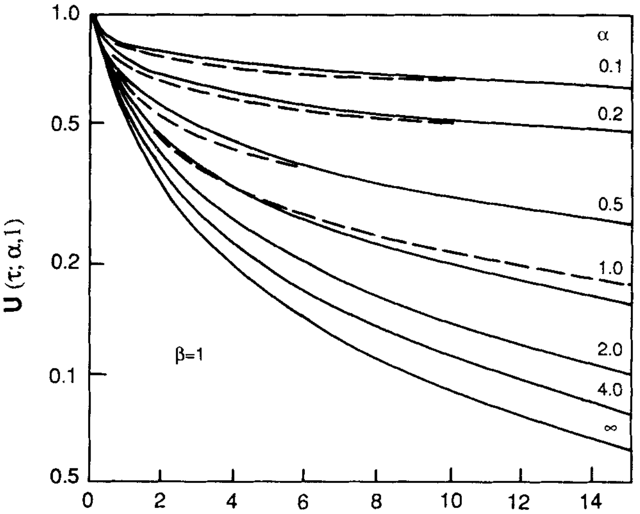

Figure 2. $U(\tau; \alpha, \beta)$ for $\beta = 1$ and various α.

be recalled that they showed that kinetics of the form

$$-\dot{u}(y,\tau) = yu(y,\tau)R\left[\int_0^\infty K(z)u(z,\tau)\,dz\right] \tag{54}$$

were patient of the solution

$$u(y,\tau) = u(y,0)e^{-y\omega(\tau)} \tag{55}$$

where

$$\dot{\omega}(\tau) = R\left(\int_0^\infty K(z)u(z,0)e^{-z\omega(\tau)}\,dz\right) \tag{56}$$

For any initial distribution R is a function of ω, and $\omega(\tau)$, the eigenzeit, can be found implicitly by quadrature,

$$\tau = \int_0^{\omega(\tau)} d\omega/\tilde{R}(\omega) \tag{57}$$

where $\tilde{R}$ is the righthand side of Eq. 56 expressed as a function of ω. In particular, Astarita's uniform kinetics with what might be called the α, β gamma distributions

$$u(y,0) = \frac{\alpha^\alpha y^{\alpha-1}}{\Gamma(\alpha)}e^{-\alpha y},$$

$$K(z) = \frac{\Gamma(\alpha)}{\Gamma(\alpha+\beta)}(\alpha z)^\beta \quad \alpha, \alpha+\beta > 0 \tag{58}$$

have the beautiful property of being able to imitate any overall reaction kinetics. We have

$$\begin{aligned} U(\tau) &= \int_0^\infty u(y,0)e^{-y\omega}\,dy \\ &= \frac{\alpha^\alpha}{\Gamma(\alpha)}\int y^{\alpha-1}e^{-y(\alpha+\omega)}\,dy = \left\{1 + \frac{\omega(\tau)}{\alpha}\right\}^{-\alpha} \end{aligned} \tag{59}$$

and

$$\begin{aligned} \int_0^\infty K(z)u(z,\tau)\,dz &= \frac{\alpha^{(\alpha+\beta)}}{\Gamma(\alpha+\beta)}\int_0^\infty z^{\alpha+\beta+1}e^{-z(\alpha+\omega)}\,dz \\ &= \left\{1 + \frac{\omega(\tau)}{\alpha}\right\}^{-(\alpha+\beta)} = U^{(\alpha+\beta)/\alpha} \end{aligned} \tag{60}$$

Now

$$\begin{aligned} -\dot{U} &= \left\{\int_0^\infty yu(y,\tau)\,dy\right\}R\left[\int K(z)u(z,\tau)\,dz\right] \\ &= \left\{1 + \frac{\omega(\tau)}{\alpha}\right\}^{-(\alpha+1)}R[U^{(\alpha+\beta)/\alpha}] \\ &= U^{(\alpha+1)/\alpha}R[U^{(\alpha+\beta)/\alpha}] = G(U) \end{aligned} \tag{61}$$

so that the kinetics G is imitated if $R(W)$ is taken to be $W^{-(\alpha+1)/(\alpha+\beta)}G[W^{-\alpha/(\alpha+\beta)}]$. The eigenzeit itself is given implicitly by

$$\frac{\tau}{\alpha} = \int_1^{1+\omega(\tau)/\alpha} dw/R[w^{-(\alpha+\beta)}] = \int_{[1+\omega(\tau)/\alpha]^{-\alpha}}^{1} du/G(u) \tag{62}$$

The incorporation of Astarita's uniform kinetics into the separable form of a doubly-distributed reaction is now possible. The specification of $g(y)$ in $u(x,y,0) = f(x)g(y)$, together with K and R, defines the kinetics G that will then be distributed by x, g, k, and R also define $\omega(\tau)$ and

$$\begin{aligned} U(z) &= \int_0^\infty f(x)\int_0^\infty g(y)e^{-y\omega(x\tau)}\,dy\,dx \\ &= \int_0^\infty f(x)V(x\tau)\,dx \quad \text{where } -\dot{V} = G(V) \end{aligned} \tag{63}$$

Since $\tau = kt$ we can regard $x\tau$ as either $(xk)t$ or $k(xt)$. In the first case $f(x)$ distributes the rate constant about the mean k (since $\int_0^\infty xf(x)\,dx = 1$); in the second it distributes the reaction time about the mean t. The gamma distribution again comes to the fore, since a popular configuration is the chain of N stirred tanks for which

$$f(x) = \frac{N^N x^{N-1}}{(N-1)!}e^{-xN} \tag{64}$$

We can in this way distribute reactions of order less than 1 using Astarita's striking result (1989) for $R(w) = w^{\gamma-1}$. By Eq. 61 this will imitate an nth-order reaction where

$$n = \{\alpha + 1 + (\gamma - 1)(\alpha + \beta)\}/\alpha \tag{65}$$

and, since, α, β, and γ are restricted only by $\alpha > 0$, $\beta > -\alpha$, $\gamma > 0$, n can be less than 1 and even negative. Thus

$$U(\tau) = \int_0^{\xi(\tau)} f(x)\{1 - (1-n)x\tau\}^{1/(1-n)}\,dx \tag{66}$$

with

$$\xi(\tau) = 1/(1-n)\tau$$

is the extension to orders less than 1. This formula is the same as Eq. 38 when, as there, $\beta = 1/(1-n)$ and allowance is made for the concentrations reaching zero in a finite time. For computational purposes a function can conveniently be made zero when negative by averaging it with its absolute value.

Discrete Distributions

Before going on to consider other distributions of the rate constant $k(x)$, it is worth drawing attention to a class of discrete distributions that asymptotically mimic nth-order reactions. Let a discrete mixture of nth-order reactants be described by the vector of concentrations $c_1(t), \ldots, c_p(t), \ldots, c_P(t)$ where c_p is governed by

$$\frac{dc_p}{dt} = -k_p c_p^n, \; c_p(0) = c_{po} \tag{67}$$

Thus

$$c_p(t) = \{[c_{po}]^{1-n} + (n-1)k_p t\}^{-\beta}, \quad \beta = 1/(n-1) \tag{68}$$

and the total concentration

$$C(t) = \sum_{p=0}^{P} c_p(t) \tag{69}$$

The irrefrangible component, $k_o = 0$, corresponds to $p = 0$ and the fraction of the total reactive material is

$$U = [C(t) - c_o]/C(0) = \sum_{p=1}^{P} c_p(t) \Big/ \sum_{p=0}^{P} c_{po} \tag{70}$$

Without loss of generality the k_p can be assumed to be rational and so made integral multiples of some increment Δk; that is, $k_p = j_p \Delta k$. We may replace the sums over p by sums over j from 0 to ∞ by setting to zero the c_{jo} for any j not equal to a j_p and recover everything thus far, but we may also have a denumerable infinity of components provided the summations coverage.

Consider the initial distribution

$$c_{jo} = c_o\{1 + j(n-1)\Delta k/\hat{k}_n\}^{-\beta}, \quad k_j = j\Delta k \tag{71}$$

Setting

$$u_o = \hat{k}/(n-1)\Delta k \tag{72}$$

we have

$$C(0) = c_o u_o^\beta \zeta(\beta; u_o) \tag{73}$$

where

$$\zeta(\beta; u) = \sum_{j=0}^{\infty} (u + j)^{-\beta} \tag{74}$$

is the so-called Hurwitz function. Substituting this in the formula for $c(t)$ gives

$$U(\tau) = u^\beta \zeta(\beta; u+1)/u_o^\beta \zeta(\beta; u_o) \tag{75}$$

where

$$u = u_o/(1 + \tau) \quad \text{and} \quad \tau = \hat{k}_n c_o^{n-1} t \tag{76}$$

We may pass to the continuous case by letting $\Delta k \rightarrow 0$. In this case u and $u_o \rightarrow \infty$ and $u^\beta \zeta(\beta; u) \sim u/(\beta - 1) + 1/2 + \cdots$ and

$$U(\tau) \sim \frac{1}{1+\tau} \quad \text{as} \quad \Delta k \rightarrow 0 \tag{77}$$

Again the apparent reaction order is 2. Of course if Δk is kept fixed, the apparent reaction is n, for, with only $u \rightarrow \infty$,

$$U(\tau) \sim \frac{1}{(1+\tau)^\beta} \frac{\zeta(\beta)}{\zeta(\beta; u_o)} \tag{78}$$

Distributions of $k(x)$

If instead of taking $\hat{k}h(x, y) = \hat{k}xy$ we were to take it as $k(x)y$, then $V(\tau x)$ in Eq. 29 would be

$$V = \int_0^\infty g(y)[\exp - k(x)ty]\, dy \tag{79}$$

If we again take $g(y) = \phi_\beta(y)$, $\beta = 1/(n-1)$

$$V = \{1 + k(x)t/\beta\}^{-\beta} \tag{80}$$

and

$$U(\tau) = \int_0^\infty f(x)\{1 + k(x)t/\beta\}^{-\beta}\, dx \tag{81}$$

Now, if $k_n = \hat{k}_n x$ then, by Eq. 24,

$$k(x)t = \hat{k}_n c_o^{n-1} t [f(x)]^{n-1} x = x[f(x)]^{1/\beta}\tau \tag{82}$$

where $\tau = \hat{k}_n c_o^{n-1} t$ is the dimensionless time. Thus

$$U(\tau) = \int_0^\infty \left\{[f(x)]^{-1/\beta} + \frac{\tau x}{\beta}\right\}^{-\beta} dx \tag{83}$$

We will drop the requirement on $f(x)$ expressed by Eq. 3 and insist only on Eq. 2 being satisfied. Then, if

$$f(x) = \frac{\beta - 1}{\beta}\left(1 + \frac{x}{\beta}\right)^{-\beta}, \beta > 1 \tag{84}$$

we have

$$U(\tau) = \frac{\beta - 1}{\beta} \int_0^\infty \left\{1 + \frac{x}{\beta} + \frac{\tau x}{\beta}\left(\frac{\beta - 1}{\beta}\right)^{1/\beta}\right\}^{-\beta} = \frac{1}{1 + \tau'} \tag{85}$$

where

$$\tau' = \tau\left(\frac{\beta - 1}{\beta}\right)^{1/\beta} \tag{86}$$

This is an exact second-order process in the modified time τ'. Now $c(x, 0) = c_o f(x)$ and $k(x)t = (\hat{k}_n c_o^{n-1} t) f(x)^{1/\beta} x$. But $c_{oo} = f(0) = (\beta - 1)/\beta$, so that $\tau' = \hat{k}_n c_{oo}^{n-1} t$ and the second-order alias depends on the concentration at the irrefrangible limit. The distribution of nth-order reactants, $1 < n < 2$, given by Eq. 71 can appear to be obeying a second-order rate law exactly. We notice that as $n \rightarrow 1$, $\beta \rightarrow \infty$, and $f(x) \sim e^{-x}$, which agrees with the best known case.

Similarly, a distribution of nth-order reactants with $n < 1$ can simulate a second-order reaction precisely. For again taking $\beta = 1/|n - 1| = 1/(1 - n)$, as in Eq. 46, we have

$$U(\tau) = \int_0^{\xi(\tau)} f(x)\left\{1 - \frac{\tau x}{\beta}[f(x)]^{-1/\beta}\right\}^\beta dx \tag{87}$$

where $\xi(\tau)$ satisfies

$$\tau\xi[f(\xi)]^{-1/\beta} = \beta \tag{88}$$

Then

$$f(x) = \frac{\beta + 1}{\beta}\left(1 - \frac{x}{\beta}\right)^\beta \tag{89}$$

gives

$$U(\tau) = \frac{\beta + 1}{\beta} \int_0^{\beta/(1+\tau')} \left\{1 - \frac{x(1 + \tau')}{\beta}\right\}^\beta dx \tag{90}$$

where

$$\tau' = \left(\frac{\beta + 1}{\beta}\right)^{-\beta} \quad \tau = \hat{k}_n c_{oo}^{n-1} t \tag{91}$$

is again the dimensionless time.

For a general distribution $f(x)$, and with $k(x)t = x[f(x)]^{1/\beta}\tau$, we have

$$U(\tau) = \int_0^\infty f(x)\left\{1 + \frac{\tau x}{\beta}[f(x)]^{1/\beta}\right\}^{-\beta}, \qquad \text{if } n > 1, \beta = 1/(n-1) \tag{92}$$

and

$$U(\tau) = \int_0^{\xi(\tau)} f(x)\left\{1 - \frac{\tau x}{\beta}[f(x)]^{-1/\beta}\right\}^{\beta}, \qquad \text{if } n < 1, \beta = 1/(1-n) \tag{93}$$

where $\xi(\tau)$ makes the expression in the bracket vanish. The values $n = 2$ and $n = 0$, which both make $\beta = 1/|n - 1| = 1$, are of special simplicity. In the case $n = 2$

$$U(\tau) = \int_0^\infty f(x)\{1 + \tau x f(x)\}^{-1}\,dx \tag{94}$$

and for $n = 0$

$$U(\tau) = \int_0^{\xi(\tau)} [f(x) - \tau x]\,dx \tag{95}$$

where $\xi(\tau)$ is the inverse function of

$$\tau = f(x)/x \tag{96}$$

The meaning of the single-component identity is of interest, for if we take

$$f(x) = \frac{\alpha^\alpha x^{\alpha-1}}{\Gamma(\alpha)} e^{-\alpha x} \tag{97}$$

and let $\alpha \rightarrow \infty$, the integral will be small unless x is near 1. But then $U(\tau) = 1/[1 + \tau f(1)]$ and this can be interpreted as a second-order reaction with time extended by a factor of $f(1)$. Then $\tau' = \hat{k}_2 c_o f(1)t = k_2(c_1)c_1 t$ where $k_2(c_1)$ is this rate constant associated with $x = 1$ and c_1 is the component concentration. This argument can be extended to a general β.

Asymptotic Behavior

It should be possible to say something about the asymptotic behavior of integrals like Eqs. 92 and 93 for a general $f(x)$ constrained by Eqs. 2 and 3, but the only case that has so far yielded to my attack is Eq. 94 with $f(x) = e^{-x}$. Letting $x = y/\tau$,

$$\begin{aligned}\tau U(\tau) &= \int_0^\infty e^{-y/\tau}\{1 + y - y(1 - e^{-y/\tau})\}^{-1}\,dy \\ &= \int_0^\infty \frac{e^{-y/\tau}}{1 + y} \cdot \sum_{r=0}^{\infty}\left(\frac{y}{1 + y}\right)^r (1 - e^{-y/\tau})^r\,dy\end{aligned} \tag{98}$$

and the fact that $y(1 - e^{-y/\tau})/(1 + y) < 1$ allows integration term by term. Also $1 - e^{-y/\tau} = y/\tau\,(1 - 1/2!\,y/\tau + 1/3!\,y^2/\tau^2 \ldots)$ so the rth term will be $O((\tau^{-r})$. Consider terms up to those of order τ^{-3}

$$\tau U = \int_0^\infty \frac{e^{-y/\tau}}{1 + y}\,dy + \frac{1}{\tau}\int_0^\infty \left(\frac{y}{1 + y}\right)^2 e^{-y/\tau}\,dy + \frac{1}{2\tau^2}\int_0^\infty \frac{y^3(y - 1)}{(1 + y)^3} e^{-y/\tau}\,dy + \cdots \tag{99}$$

Let $y = z - 1$; then the first integral is

$$e^{1/\tau}\int_1^\infty \frac{dz}{z} e^{-z/\tau} = e^{1/\tau}E_1(1/\tau) \sim e^{1/\tau}\left\{\ln\tau - \gamma + \frac{1}{\tau} + \frac{1}{4\tau^2}\ldots\right\}$$

The second is

$$e^{1/\tau}\int_1^\infty\left(\frac{1}{z^2} - \frac{2}{z} + 1\right)e^{-z/\tau}\,dz = e^{1/\tau} \cdot \left\{E_2\left(\frac{1}{\tau}\right) - 2E_1\left(\frac{1}{\tau}\right) + \tau(1 - e^{-1/\tau})\right\}$$

The third is

$$e^{1/\tau}\int_1^\infty\left(z - 5 + \frac{9}{z} - \frac{7}{z^2} + \frac{2}{z^3}\right)e^{z/\tau}\,dz = e^{1/\tau}\left\{2E_3\left(\frac{1}{\tau}\right) - 7E_2\left(\frac{1}{\tau}\right) + 9E_1\left(\frac{1}{\tau}\right) - 5\tau(1 - e^{-1/\tau}) + \tau e^{-1/\tau} + \tau^2(1 - e^{-1/\tau})\right\}$$

The leading terms in the three cases can be combined to give

$$(\ln\tau)\left(1 - \frac{1}{\tau} + \frac{2}{\tau^2}\ldots\right) - \gamma + \frac{7 + 2\gamma}{2\tau} - \frac{51 + 26\gamma}{4\tau^2}$$

This leads to the expansion:

$$\begin{aligned}U(\tau) &\sim \frac{\ln\tau - \gamma}{\tau} + \frac{2\ln\tau - 7 - 2\gamma}{2\tau^2} + 0(\tau^{-3}\ln\tau) \\ &= \frac{\ln\tau - 0.57721}{\tau} + \frac{\ln\tau - 4.07722}{\tau^2}\ldots\end{aligned} \tag{100}$$

Sequential Parallel Reactions

Let $A(x) \rightarrow B(x) \rightarrow C(x)$ be a parallel continuum of sequential reactions each of the first order. Then if $u(x, t)\,dx$, $v(x, t)\,dz$, and $w(x, t)\,dx$ are the three concentrations of material in the index slice $(x, x + dx)$,

$$\begin{aligned}\dot{u}(x, t) &= -k(x)u(x, t) \\ \dot{v}(x, t) &= k(x)u(x, t) - k'(x)v(x, t) \\ \dot{w}(x, t) &= k'(x)v(x, t)\end{aligned} \tag{101}$$

and $u(x, 0)$, $v(x, 0)$, $w(x, 0)$ can be specified. Thus

$$\begin{aligned}u(x, t) &= u(x, 0)e^{-k(x)t} \\ v(x, t) &= u(x, 0)\{\kappa(x) - 1\}^{-1}\{e^{-k(x)t} - e^{-k'(x)t}\} \\ &\quad + v(x, 0)e^{-k'(x)t} \\ w(x, t) &= u(x, 0) + v(x, 0) + w(x, 0) \\ &\quad - u(x, t) - v(x, t)\end{aligned} \tag{102}$$

where

$$\kappa(x) = k'(x)/k(x) \tag{103}$$

Thus

$$U(t) = \int_0^\infty u(x,0)e^{-k(x)t}\,dx$$

$$V(t) = \int_0^\infty u(x,0)\{\kappa(x) - 1\}^{-1}\{e^{-k(x)t} - e^{-k'(x)t}\}\,dx$$

$$+ \int v(x,0)e^{-k'(x)t}\,dx$$

$$W(t) = U(0) + V(0) + W(0) - U(t) - V(t) \tag{104}$$

For example if we use the Γ distribution we can without loss of generality take $k(x) = kx$ and set $\tau = kt$. In the first instance let κ be a constant and $v(x,0) = w(x,0) = 0$ with

$$u(x,0) = \frac{\alpha^\alpha x^{\alpha-1}}{\Gamma(\alpha)} e^{-\alpha x}, \quad \alpha > 0$$

Then

$$U(\tau) = (1 + \tau/\alpha)^{-\alpha} \tag{105}$$

and

$$V(\tau) = \{(1 + \tau/\alpha)^{-\alpha} - (1 + \kappa\tau/\alpha)^{-\alpha}\}/(\kappa - 1) \tag{106}$$

The relation between U and V can also be written

$$V = \{1 - [\kappa - (\kappa - 1)U^{1/\alpha}]^{-\alpha}\}U/(\kappa - 1) \tag{107}$$

$V(\tau)$ always goes through a maximum if $v(x,0) = 0$ as we are assuming here; it is at

$$U_{\max} = \left[\frac{\kappa - \kappa^{1/(\alpha+1)}}{\kappa - 1}\right]^\alpha \tag{108}$$

and has a value

$$V_{\max} = U_{\max}^{(\alpha+1)/\alpha}/\kappa \tag{109}$$

The limiting cases require separate forms and we have

$$\kappa = 1, \quad V = \alpha(1 - U^{1/\alpha})U \quad U_{\max} = \left(\frac{\alpha}{\alpha+1}\right)^\alpha, V_{\max} = \left(\frac{\alpha}{\alpha+1}\right)^{\alpha+1}$$

$$\alpha \leftarrow \infty, \quad V = (U - U^\kappa)/(\kappa - 1) \quad U_{\max} = \kappa^{-1/(\kappa-1)}, V_{\max} = \kappa^{-\kappa/(\kappa-1)}$$

$$\kappa = 1, \alpha \rightarrow \infty \quad V = U\ln(1/U) \quad U_{\max} = e^{-1} = V_{\max}$$

Figure 3 shows plots of $V(U)$ over a range of α for $\kappa = 1$ and Figure 4 for $\alpha = 1$ with κ varying.

The differential equation obeyed by U is, of course, that of a reaction of order $(\alpha + 1)/\alpha$; that governing V can be put in many forms by eliminating τ between V and $\dot{V}$. One such is:

$$\dot{V} = U^{\alpha+1/\alpha} - \frac{\kappa}{\kappa - 1}\{U^{\alpha+1/\alpha} - [U - (\kappa - 1)V]^{\alpha+1/\alpha}\} \tag{110}$$

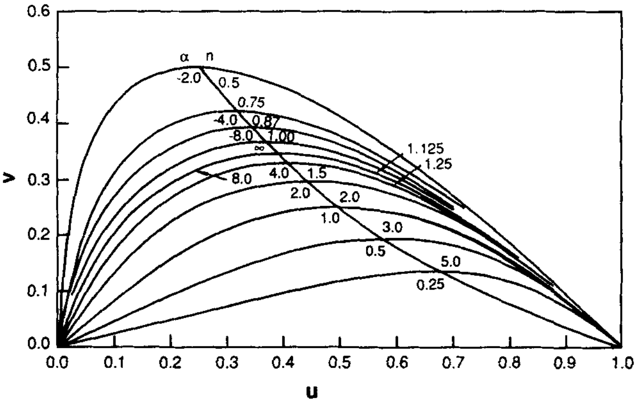

Figure 3. $V(U)$ for $\kappa = 1$ and various α.

Since V is not a monotonic function of U we cannot solve Eq. 107 to obtain $\dot{V}$ in the form $U^{(\alpha+1)/\alpha} - f(V)$. In the initial stages of reaction $f(V) = \kappa\alpha + 1/\alpha\ V$, and as we would expect this second reaction starts out as first order. As $U \longrightarrow 0$ and $V \sim \mu U$, $\mu = (1 - \kappa^{-\alpha})/(\kappa - 1)$, then $f(V) = k_0 V^{\alpha - 1/\alpha}$ where

$$k_0 = \kappa(\kappa - 1)^{1/\alpha}(\kappa^\alpha - 1)^{-(\alpha+1)/\alpha}(\kappa^{\alpha+1} - 1).$$

We have only considered the simplest case of constant $\kappa(x)$, but there are no reasons to limit the sequential reaction to this form save the wantonness of idle proliferation and the awkwardness of the resulting integrals. Thus if the second step were at a rate independent of x we would have $\kappa(x) = \kappa/x$ and with the usual distribution x,

$$V(\tau) = \int_0^\infty \frac{(\alpha x)^\alpha}{\Gamma(\alpha)} e^{-\alpha x} \frac{e^{-xz} - e^{-\kappa\tau}}{\kappa - x}\,dx$$

an integral that can be resolved into a series of incomplete gamma functions.

Mechanisms

Besides having the capital property of being able to imitate any kinetics—see Eq. 61—Astarita's uniform kinetics are often patient of a mechanistic derivation. Thus, for what Astarita and Ocone call uniform generalized Langmuir isotherm kinetic mechanism (UGLIKM), we might take $\theta(x)\,dx$ to be the frac-

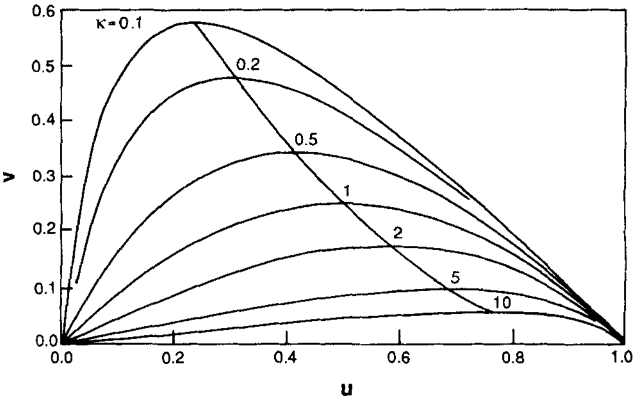

Figure 4. $V(U)$ for $\alpha = 1$ and various κ.

tion of catalytic surface occupied by the species $A(x)$ with index in $(x, x + dx)$. Then if the system is at pseudosteady state

$$r(x) = k_a(x)c(x, t)\left\{1 - \int_0^\infty \theta(x')\,dx'\right\} - k_d(x)\theta(x) = k_r(x)\theta(x)$$

where $k_a(x)$, $k_d(x)$, and $k_r(x)$ are the adsorption, desorption, ad reaction rate constants. Thus

$$\theta(x) = \left\{1 - \int_0^\infty \theta(x')\,dx'\right\} \cdot K(x)c(x, t), \quad K(x) = k_a(x)/\{k_d(x) + k_r(x)\}$$

whence

$$\Theta = \int_0^\infty \theta(x)\,dx = K(x)c(x, t)\Big/\left\{1 + \int_0^\infty K(z)c(z, t)\,dz\right\}$$

This leads straight to the UGLIKM kinetics and provides an interpretation for the kernel $K(x)$.

Progress on the same lines is possible for a nonuniform surface but it leads, as might be expected, to a nonuniform GLIKM. Thus if $c(x, t)\,dx$ is again the concentration of material with index in $(x, x + dx)$, $\Theta(y)\,dy$ is the fraction of surface sites characterized by y in $(y, y + dy)$ and $\theta(x, y)\,dx\,dy$ the fraction of y sites occupied by x material. Then

$$r(x,y)\,dx\,dy = k_a(x,y)c(x,t)\,dx\left\{\Theta(y)\,dy - \int \theta(x'y)\,dx'\,dy\right\} - k_d(x, y)\theta(x, y)\,dx\,dy = k_r(x, y)\theta(x, y)\,dx\,dy$$

If the p.s.s.h. holds

$$\theta(x, y) = K(x, y)c(x, t)\left\{\Theta(y) - \int K(x', y)\,dx'\right\}$$

giving

$$\int \theta(x', y)\,dx' = \Theta(y)\int K(x', y)c(x', t)\,dx'\Big/\left\{1 + \int K(x', y)c(x', t)\,dx'\right\}$$

Thus

$$r(x, y) = k_r(x, y)K(x, y)\Theta(y)c(x, t)\Big/\left\{1 + \int K(x', y)c(x', t)\right\}$$

and

$$r(x) = \int \frac{k_r(x, y')K(x, y')\Theta(y')}{1 + \int K(x', y')c(x', t)}\,dy'c(x, t)$$

Only if $k_r(x, y)K(x, y)\Theta(y)$ is simply separable—that is, the product of a function of x with a function of y—will the use of the eigenzeit lead to a solution.

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Literature Cited

Alberty, R. A., and I. Oppenheimer, "A Continuous Thermodynamics Approach to Chemical Equilibrium Within an Isomer Group," *J. Chem. Phys.*, **81**, 4603 (1984).

Amundson, N. R., and A. Acrivos, "On the Steady State Fractionation of Multicomponent and Complex Mixtures in an Ideal Cascade." I–VI, *Chem. Eng. Sci.*, **4**, 29; 68; 141; 159; 206; 249 (1955).

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

Astarita, G., "Lumping Nonlinear Kinetics: Apparent Overall Order of Reaction, *AIChE J.* **35**, 529 (1989).

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

Briano, J. G., and E. C. Glandt, "Statistical Thermodynamics of Polydisperse Fluids," *J. Chem. Phys.*, **80**, 3336 (1984).

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).

de Donder, Th., *L'Affinite*, 2^e pt., Gauthier-Villars, Paris (1931).

Erdelyi, A., ed., *Tables of Integral Transforms*, McGraw-Hill, New York (1954).

Golikeri, S. V., and D. Luss, "Diffusional Effects in Reacting Mixtures," *Chem. Eng. Sci.*, **26**, 237 (1971).

Ho, T. C., and R. Aris, "On Apparent Second-Order Kinetics," *AIChE J.*, **33**, 1050 (1987). The major part of this paper inadvertently repeated a result due to Krambeck (1984) and is only included here because it is more accessible. The authors should have been aware of the result and apologize for the duplication.

Kemp, R. D. D., and B. W. Wojciechowski, "The Kinetics of Mixed Feed Reactions," *Ind. Eng. Chem. Fundam.*, **13**, 332 (1974).

Krambeck, F. J., "Computers and Modern Analysis in Reactor Design," *Proc. ISCRE 8; Ind. Chem. Eng. Symp. Ser.*, **A260**, 351 (1984).

Loveday, B. K., "Analysis of Froth Flotation Kinetics," *Inst. Min. Metall. Trans.*, **C75**, 219 (1966).

Luss, D. G., and P. Hutchinson, "Lumping of Mixtures with Many Parallel *N*th-order Reactions," *Chem. Eng. J.*, **2**, 172 (1971).

Malhotra, A., and A. Sadana, "Effect of Activation Energy Microheterogeneity on First-order Enzyme Deactivation," *Biotech. Bioeng.*, **30**, 108 (1987).

Prasad, G. N., "Kinetic Modeling of Coal Liquefaction Reactions," Ph.D. Thesis, Monash Univ., Australia (1986).

Prasad, G. N., J. B. Agnew, and T. Sridhar, "Continuous Reaction Mixture Model for Coal Liquefaction. Theory," *AIChE J.*, **32**, 1277 (1986a).

———, "Continuous Reaction Mixture Model for Coal Liquefaction. II: Comparison with Experiments on Catalyzed and Uncatalyzed Liquifaction of Coals of Different Rank," *AIChE J.*, **32**, 1288 (1986b).

Spanier, J., and K. B. Oldham, *An Atlas of Functions*, Hemisphere, New York (1987).

Weekman, V. W., "Lumps, Models and Kinetics in Practice," *Chem. Eng. Prog. Monogr. Ser.* **75**(11), 3 (1979).

Widder, D. V., *The Laplace Transform*, Princeton Univ. Press, Princeton (1941).

Zeman, R. J., and N. R. Amundson, "Continuous Polymerization Models," *Chem. Eng. Sci.*, **20**, 331; 637 (1965).

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