On Apparent Second-Order Kinetics

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The lumping of a complex mixture into a continuum first proposed by DeDonder (1931) has found a number of applications since it was propounded in the context of reaction (Gavalas and Aris, 1966). A particularly simple form was applied to cracking (Aris, 1968) and it was shown that parallel first-order cracking of a continuum could simulate any reaction order between one and two. Specifically let

$$c(k,0)\,dk = \frac{\alpha^\alpha}{\Gamma(\alpha)}\left(\frac{k}{\hat{k}}\right)^{\alpha-1}\frac{\exp(-\alpha k/\hat{k})}{\hat{k}}\,dk, \quad \alpha \geq 1 \tag{1}$$

be the initial fraction with first-order rate constant in $(k, k + dk)$. Then at any later time

$$c\,(k, t) = c(k, 0)\,e^{-kt} \tag{2}$$

and the total remaining fraction is

$$C(t) = \int_0^\infty c(k, t)\,dk = (1 + \hat{k}t/\alpha)^{-\alpha} \tag{3}$$

But then

$$\frac{dC}{dt} = -\hat{k}\,(1 + \hat{k}t/\alpha)^{-\alpha-1} = -\hat{k}C^\beta \tag{4}$$

where

$$\beta = (\alpha + 1)/\alpha \tag{5}$$

is the apparent order of reaction. As α increases from 1 to infinity, β decreases from 2 to 1. Apparent second-order reaction, a phenomenon somewhat implausible in itself, becomes plausible on the assumption of an exponential distribution

$$c(k, 0) = [\exp - (k/\hat{k})]/\hat{k} \tag{6}$$

or something like it.

Indeed we need only suppose $c(o, 0) \neq 0$ to get an asymptotic second-order reaction, as the following argument shows. Let the initial distribution have a McLaurin series,

$$\begin{aligned} c(k, 0) &= c(o, 0) + kc'(o, 0) + \tfrac{1}{2}k^2c''(o, 0) + - \\ &= \sum_{n=0}^{\infty}\frac{1}{n!}k^n c^{(n)}(o, 0). \end{aligned} \tag{7}$$

Then

$$\begin{aligned} C(t) &= \int_0^\infty c(k, 0)\,e^{-kt}\,dk \\ &= \frac{1}{t}\int_0^\infty c\left(\frac{u}{t}, 0\right)e^{-u}\,du \\ &= \frac{1}{t}\int_0^\infty \sum \frac{c^{(n)}(o, 0)}{n!t^n}u^n\,e^{-u}\,du \\ &= \sum_{n=0}^{\infty}\frac{c^{(n)}\,(o, 0)}{t^{n+1}} \end{aligned} \tag{8}$$

If $c^{(n)}\,(o, 0) < KT^n$, this converges for $t > T$, but in any case gives us an asymptotic series of which the leading term is $C(t) \sim c(o, 0)/t$; hence

$$\frac{dC}{dt} \sim \frac{-1}{c(o, 0)}C^2 \tag{9}$$

and the equivalent second-order rate constant is $1/c(o, 0)$. Thus the presence of a finite fraction that is virtually unreactive leads always to apparent second-order kinetics for this "lump." This is not surprising as the behavior after a long time is clearly governed by the most refractory components.

If $c(o, 0) = 0$ but

$$c(k, 0) = k^{\alpha-1}(\gamma_0 + \gamma_1 k + \cdots), \quad \alpha > 1, \quad \gamma_0 \neq 0 \tag{10}$$

then

$$C(t) = \frac{1}{t^\alpha}\int_0^\infty \left(\gamma_0 + \gamma_1 \frac{u}{t} + \cdots\right) u^{\alpha-1} e^{-u}\, du$$

$$\sim \frac{\Gamma(\alpha)}{t^\alpha}\gamma_0 + \cdots \tag{11}$$

Hence

$$\frac{dC}{dt} \sim -\frac{\alpha}{[\Gamma(\alpha)\gamma_0]^{1/\alpha}} C^\beta \tag{12}$$

with β again given by Eq. 5 and an apparent rate constant depending on α and γ_o.

Luss and Hutchinson (1970) used inequalities to get bounds on the solution

$$C(t) = \int_0^\infty c(k, 0)\, e^{-kt}\, dk$$

and looked in particular at the case where $c(k, 0) \equiv 0$ for sufficiently small k.

It is tempting to think of extending the theory to a mixture whose components individually react according to some rate constitutive equation other than first order, i.e., for an isothermal closed system,

$$\frac{d}{dt} c(k, t) = -kr[c(k, t)], \quad r(c) \geq 0, \quad r(0) = 0 \tag{13}$$

Then, formally, if $x(u) = g(u; v)$ is the solution of

$$\frac{dx}{du} = -r(x), \quad x(0) = v, \tag{14}$$

we have

$$c(k, t) = g[kt; c(k, 0)] \tag{15}$$

and

$$\begin{aligned} C(t) &= \int_0^\infty g[kt; c(k, 0)]\, dk \\ &= \frac{1}{t}\int_0^\infty g\left[u; c\left(\frac{u}{t}, 0\right)\right] du \\ &\sim \frac{1}{t}\int_0^\infty g\,[u; c(o, 0)]\, du \end{aligned} \tag{16}$$

again giving apparent second-order kinetics if the integral converges and $c(o, 0) \neq 0$.

The fallacy in this is that it has lost sight of the fact that it is $c(k, t)\, dk$, not $c(k, t)$, which is a concentration, and $r(cdk)/dk$ can only be interpreted for a first-order rate expression, $r(c) = kc$. To put it another way, we may say that although

$$C(t) = \int_0^\infty g[kt, c(k, 0)]\, dk \tag{17}$$

defines a valid nonlinear integral transform of $c(k, 0)$ into $C(t)$, which reduces to the Laplace transform in case $g(u, v) = ve^{-u}$, there is no way of obtaining the single-component identity

$$\int_0^\infty g(kt; \bar{c}\delta\,[k - \bar{k})]\, dk = g(\overline{kt}; \bar{c}) \tag{18}$$

except in the first-order case. Were this possible it would be useful to develop the theory of the transform defined by Eqs. 14 and 17.

Our conclusion is that in a complex mixture with a nonzero concentration of virtually unreactive species the "lump" will seem to disappear asymptotically in a second-order fashion. This conclusion may have a bearing on catalyst evaluation work. A catalytic system that does not activate certain refractory components of the feed might well be evaluated as apparently of the second order. But if the performance of the catalyst is improved (for instance, by the incorporation of a more effective promoter) so that there is no longer a refractory component, then an apparent order less than two would have to be used in evaluating the improved catalyst.

Notation

$c(t)$ = total concentration of all reacting material
$c(k, t)\, dk$ = concentration of material with rate constant in $(k, k + dk)$
$g(u; v)$ = solution of Eq. 14
k = rate constant used as a continuous variable
$\hat{k}$ = mean value of k
$r(c)$ = general rate law
t = time

Greek Letters

α = parameter in initial distribution
$\beta = (\alpha + 1)/\alpha$
γ_1 = coefficients in the expansion of $c(k, 0)$
$\delta(t)$ = Dirac delta function

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Manuscript received Dec. 31, 1986, and revision received Feb. 4, 1987.