On the Continuum Approximation of Large Reaction Mixtures

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In analyzing a reaction mixture of very many components, treating the mixture as a continuum can produce results of generality. In many practical situations (e.g., hydrodesulfurization), it is highly desirable to predict the overall behavior of the mixture at large times (high conversions) with minimum information on the mixture property. For irreversible first-order reactions in a plug-flow reactor, it was previously shown that the continuum approximation cannot be valid at arbitrarily large times. This work is an investigation of the validity of the approximation for mixtures with complex kinetics. It is found that the approximation can be conditionally or universally valid, depending on kinetics, reactor type, pore diffusion, and mixture properties. The validity conditions for a variety of situations, nontrivial as they may seem, take a power-law form. Backmixing and pore diffusion widen the range of validity. The underlying physics and some dichotomies/subtleties are discussed. The results are applied to catalytic hydroprocessing in petroleum refining. © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 1894–1906, 2010

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Introduction

Many sectors of the world economy have been and will continue to be largely hydrocarbon-based in coming decades. Complex hydrocarbon mixtures such as petroleum fractions, coal/shale, bitumen, and biomass have a vast number of reacting species. Currently, it is not possible to measure the concentration of all species routinely and robustly. In many practical situations, one is interested in the aggregate, rather than the individual, behavior of these species. For instance, in hydrodesulfurization (HDS), only the reduction of total sulfur really matters. The same is true of hydrodenitrogenation (HDN) and hydrodemetallation (HDM). Fluid catalytic cracking is designed primarily for the overall conversion of high boiling (>340°C) to low boiling (<340°C) hydrocarbon species. In polymerization, the overall degree of polymerization is often the main concern.

The problem of finding the overall kinetics and behavior of a reaction mixture containing N types of species can be broadly stated as follows. Let $c_i(t)$ ($i = 1, 2, \cdots, N$) be the concentration of reactant type i with rate constant k_i and $C(t) = \Sigma_i c_i$ be the total concentration of all reactants at reaction time (or space-time) t. The concentration of the ith reactant in the feed is $c_{if} = c_i(0)$. Each reactant disappears at the rate r_i. The aim is to predict the dependence of $C(t)$ on feed properties and reactor type. It is also of interest to know if an overall kinetics $R(C)$ can be found for the mixture as a whole. To this end, one often treats a large mixture (very large N) as a continuum for mathematical tractability.[1–2] In practice, chemical-analytical characterization data for petroleum fractions are frequently obtained as a continuous function of one or more macroscopic properties such as boiling point, molecular weight, carbon number, solubility, and/or polarity.[3] There are refining process models based on the notion of continuous mixtures.[4–8] The continuum approach has also been used to solve thermodynamic problems in engineering applications.[9–10] A major difference between continuum thermodynamics and continuum kinetics is that the latter must be discussed in the context of reactor design.

For rational design of hydrocarbon conversion catalysts/processes, it is highly desirable to be able to determine $C(t)$ and $R(C)$ *a priori*, which requires complete information on feed properties and reactivity spectra. In practice, however, practitioners do not usually have the luxury of fully

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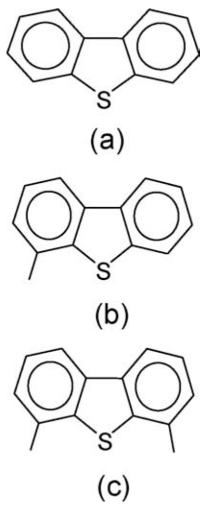


Figure 1. Structures of dibenzothiophene (a), 4-methyldibenzothiophene (b), and 4,6-dimethyldibenzothiophene (c).

charactering petroleum feedstocks. A pragmatic approach is to find $C(t)$ and $R(C)$ at large times (or high conversions) using the continuum approach. Such asymptotic kinetics in many cases is insensitive to the details of feed properties, so one can gain fundamental insights into the mixture's generic behavior. Moreover, they can be used to construct semiempirical models.[11] Indeed, the asymptotic approach has proved very useful for catalyst and process developments.[3] This is hardly surprising as many refining processes are designed to achieve a high conversion. In exploring or developing new catalysts, it is important that competing catalysts be evaluated at high conversions.[12]

Useful as the continuum approximation may be, one may not escape the feeling that the continuum concept applied to reaction kinetics is perhaps on a less firm foundation relative to its use, say, in fluid mechanics. A large reaction mixture will becomes progressively less crowded as reactant molecules react away with time; the longer the time, the more likely it is that a continuum model will be invalid. Consider a discrete mixture with $r_i = k_i c_i$ in an isothermal plug flow reactor (PFR), so $C(t) = \sum_i c_{if} \exp(-k_i t)$. The rate constant k_i can be viewed as the reactivity of species i. After a sufficiently long time, the mixture behaves as if there were only one reacting species decaying exponentially, since the concentrations of all other species are exponentially smaller. This counters the asymptotic power-law decay predicted by the continuum theory.[13–14] This apparent paradox can be reconciled by the fact that the asymptotic kinetics is valid only over an intermediate regime — one in which time is large enough for the asymptotic kinetics to be valid, but short enough for the mixture still remaining to be sufficiently dense.[15] So the key issue is the determination of the condition under which the continuum formulation and its long-time limit are *both* valid. For irreversible first-order reactions, the validity condition can be written as[15]

$$\frac{1}{\hat{k}} \ll t \ll \frac{1}{\Delta} \qquad (1)$$

Here $\hat{k}$ is a characteristic rate constant for a moderately refractory species, and Δ the difference between the rate constants for two species whose reactivity's are adjacent to each other, for instance, $\Delta \equiv \max_i\{k_{i+1} - k_i\} > 0$ without loss of generality. Here, for convenience, we assume that the reactivity granularity Δ is a constant. The condition $t\Delta \ll 1$ signifies that time cannot be too long without the discrete nature of the mixture manifesting itself. Mathematically, this obliges Δ to be sufficiently small so that $t\Delta \to 0$ even as $t \to \infty$. As a corollary, the larger the ratio $\hat{k}/\Delta$, the wider the range of validity.

Currently, the sulfur (S) content of diesel fuel produced in the USA and some other countries cannot be greater than 10 wppm. Many refinery process feedstocks prior to HDS typically contain 1 wt% S (taking a round number). Meeting the diesel S specification means an ultra-deep HDS level of 99.9%. For low-S (or prehydrotreated) feedstocks, a reduction of from, say, 500 wppm feed S to 10 wppm product S means a deep HDS level of 98%. Thus, here one deals with a super high-conversion situation. As such, it is essential to know the reaction kinetics because process economics in general is very sensitive to the overall HDS reaction order. To achieve deep HDS, refiners need to remove S from highly refractory S species in which the S atoms are sterically hindered. Let us consider the HDS of dibenzothiophenes (DBTs). The HDS kinetics for such S heterocycles is usually first-order.[16] Referring to Figure 1, the reactivity of DBTs is determined by the steric hindrance around the sulfur atom. So the reactivity ranking is DBT > 4-methyl-DBT > 4,6-dimethyl-DBT. Based on the model-compound HDS data obtained at 300°C and 10.5 MPa over a sulfided Co-Mo/Al_2O_3 catalyst,[17] we estimate that $\hat{k}/\Delta \approx 40 \gg 1$, where $\hat{k}$ is the rate constant for the HDS of DBT and Δ is the rate constant difference between 1,4,7-trimethyl-DBT and 1,4,6-trimethyl-DBT. Another example can be taken from the HDS of light catalytic cycle oil for which the HDS rates of 14 dibenzothiophenic compounds were measured.[18] Taking $\hat{k}$ as the rate constant for 4-methyl-DBT HDS and Δ as the rate constant difference between 1,4,7-trimethyl-DBT and 1,4,6-trimethyl-DBT, we find a far more favorable situation $\hat{k}/\Delta \approx 163 \gg 1$. The reason is that in the HDS of a petroleum fraction, the presence of a vast number of competing reactions would compress the disparities among the HDS reactivities of S species. The upshot here is that Eq. 1 is hard to violate in most practical situations.

This work aims to seek a better understanding of the aforementioned paradox and the adequacy of the continuum approximation. To set the stage for subsequent developments, we first recapitulate some relevant background information.

Continuum Approximation and Asymptotic Kinetics

When N is very large, we may replace the sum $C(t) = \Sigma_i c_i$ with the following lumping integral[19]

$$C(t) = \int_0^\infty c(k,t)D(k)dk \qquad (2)$$

Here each reactant is labeled by the continuous variable k. The concentration of reactant k is $c(k,\ t)$. The slice $D(k)dk$ is the total number of reactant types with rate constant between k and $k + dk$, so D is a reactant-type distribution function. $D(k)$ ties the continuous mixture $c(k, t)$ to its discrete counterpart $c_i(t)$, for it simply acts as the Jacobian of the discrete-to-continuous (i-to-k) coordinate transformation. For any given finite volume of the mixture, it is the number of reactant types, not the concentration of each reactant type that justifies the continuum hypothesis. A power-law expression for $D(k)$ has been used for developing refining process models.[6–8] The overall behavior of a continuous mixture should degenerate to that of a single component of reactivity k^* if all components happen to have the same reactivity k^*.[14] This single-component-identity is automatically satisfied by Eq. 2. To see this, consider the PFR mass-balance equation $dc(k, t)/dt = r(k, c)$ with $c(k, 0) = c_f(k)$. Let the solution of this equation be represented by $\bar{c}(k,\ t;\ c_f)$. In the single-component case, D then becomes a delta function and

$$C(t) = \int_o^\infty \bar{c}[k, t; c_f(k)]\delta(k - k^*)dk = \bar{c}[k^*, t; c_f(k^*)] \tag{3}$$

A laudable outcome of the continuum approach is that for a variety of kinetics (nth order, Langmuir-Hinshelwood, bimolecular reactions, etc.) and regardless of reactor type (PFR or continuous stirred-tank reactor, CSTR), one can always find an asymptotic overall rate expression $R_a(C)$ for large t. Moreover, one can also say in advance that the leading-order behavior of $C(t)$ takes one of following power-law or modified power-law forms[3]

$$C(t) \propto \frac{1}{t^m}, \frac{lnt}{t^q}, \text{ or } \frac{e^{-\rho t}}{t^\varsigma} \text{ at large } t \tag{4}$$

The above scaling relations succinctly generalize a multitude of possible long-time behaviors. The most common behavior by far is the simple power law $C = O(1/t^m)$ for large t. In this case, the long-time behavior is governed either by highly refractory species or by all species. In the former case, m is determined by the most refractory fraction of the feed; in the latter case, m is independent of the feed properties. When $C(t) = O(lnt/t^q)$ at large t, q is determined by refractory species. The occurrence of $C(t) = O(e^{-pt}/t^\varsigma)$ corresponds to two special situations for first-order reversible reactions in a PFR (more on this later). The large-t behavior of C is dominated either by refractory species or species of intermediate reactivity.[20]

It is useful to scale the reaction systems at hand with the following dimensionless variables[21]

$$\begin{aligned} U = C(t)/C_o, x = k/\hat{k}, \tau = \hat{k}t \\ f(x) = c_f(x)/c_0, g(x) = D(x)/N \end{aligned} \tag{5}$$

where U and τ are the dimensionless total concentration and residence time, respectively. Also, $C_o = C(0) = Nc_0$. The characteristic rate constant $\hat{k}$, which can be viewed as an equivalent first-order rate constant, will be specified later. A reactant with a small x is refractory; the closer its x value is to zero, the more refractory is the reactant.

The foregoing scaling leads to the following normalization conditions

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

In many cases, the mixture's long-time (or high conversion) behavior is primarily dictated by the most refractory part of the feed (this is not always true; more on this later). We consider the case where the behaviors of $g(x)$ and $f(x)$ near $x = 0$ are expressible as

$$f(x) = x^v(f_0 + f_1x + \cdots) \sim f_0x^v \tag{7}$$

$$g(x) = x^\mu(g_0 + g_1x + \cdots) \sim g_0x^\mu \tag{8}$$

in which $v \geq 0$ and $1 + \mu > 0$. If the feed has a finite amount of unconvertible species, $\mu = v = 0$. When $\mu \leq 0$, the mixture has a finite number of reactant types that are virtually unreactive. A characteristic common to first-order reactions (reversible or irreversible) is that $c(x, t)$ is linear in its feed concentration $c_f(x)$. As such, $f(x)$ and $g(x)$ always appear as the product $f(x)g(x)$ in Eq. 2. We thus let $h(x) = f(x)g(x)$ and $\gamma \equiv 1 + \mu + v$. The latter is an overall feed parameter: a small γ implies a refractory feed. Also, $h(k) \sim h_0x^{\gamma-1}$ near $x = 0$ with $h_0 = f_0g_0$.

For irreversible first-order reactions in an isothermal PFR, we have

$$U_c(\tau) = \int_0^\infty h(x)\mathrm{e}^{-x\tau}dx \tag{9}$$

where the subscript c signifies a continuous mixture. At large τ, the integrand is appreciable only in a thin boundary-layer region near $x = 0$. Retaining only the leading-order term yields the asymptotic power laws at high conversions[13,14]

$$U_c(\tau) \sim \frac{h_0\Gamma(\gamma)}{\tau^\gamma} \tag{10}$$

$$\frac{dU_c}{d\tau} \sim R_a(U_c) = -\frac{\gamma}{[h_0\Gamma(\gamma)]^{1/\gamma}}U_c^{1+1/\gamma} \tag{11}$$

Referring to the right-hand side of Eq. 11, let n_a be the overall asymptotic reaction order for the mixture, then $n_a = (1 + 1/\gamma) > 1$. It should be noted that if $h(x)$ follows the gamma distribution[2] as many hydrocarbon mixtures do,[3] then $R(C)$ obeys a higher-than-first-order power-law for all t. Here we see an increase in the reaction order in going from individual species to the mixture. However, this is not necessarily true in all situations, as will be discussed later.

Now consider the underlying discrete mixture denoted by the subscript d. For simplicity all the rate constants are equally spaced, so $x_i = i\delta$ and $\Delta = \hat{k}\delta$. Then

$$U_d(\tau; \delta) = \sum_{i=1}^\infty h(i\delta)e^{-i\delta\tau}\delta \tag{12}$$

For fixed τ, as $\delta \to 0$, U_c is a satisfactory approximation to U_d since Eqs. 9 and 12 are the definition of the Riemann integral in elementary calculus. For fixed δ and $\tau \to \infty$, U_d decays exponentially as it is governed by a single, most refractory species. Yet Eq. 10 shows the power-law behavior $U_c = O(1/\tau^\gamma)$ at large τ, indicating the inadequacy of the continuum description as alluded to earlier. An *ad hoc* fix is to impose a sufficiently fine granularity so that δ goes to zero a bit faster than τ goes to infinity. The validity condition then constitutes the following

$$\tau\delta \rightarrow 0 \text{ as } \delta \rightarrow 0 \text{ and } \tau \rightarrow \infty \tag{13}$$

which leads to Eq. 1. Equation 13 can be rigorously derived.[15]

Reversible First-Order Reactions

Here we examine the effect of reversibility on the validity condition for first-order reactions. The reactions are represented by $A_i \rightleftharpoons \tilde{A}_i$, with k_i and $\tilde{k}_i$ being the forward and reverse rate constants, respectively. Let $c_i(t)$ and $\tilde{c}_i(t)$ be the concentrations of A_i and $\tilde{A}_i$, respectively, then the net reaction rate is $r_i = k_i c_i - \tilde{k}_i \tilde{c}_i$. The mass-balance equations for a PFR or batch reactor are

$$\frac{dc_i}{dt} = -(k_i + \tilde{k}_i)c_i(t) + \tilde{k}_i[c_i(0) + \tilde{c}_i(0)] \tag{14}$$

The corresponding equilibrium constant is $K_i = k_i/\tilde{k}_i$. The overall kinetics and collective behavior of these reactions had been examined.[19–20]

The corresponding continuous mixture is characterized by the forward rate constant k and the equilibrium constant K. Without loss of generality, we assign $\hat{k}$ to be a characteristic rate constant for the forward reactions and let $\tilde{c}_f(x) = c_o\tilde{f}(x)$, $\tilde{h}(x) = \tilde{f}(x)g(x)$, $\tilde{\gamma} = \mu + \tilde{v} + 1$, and, $\tilde{f}(x) \sim x^{\tilde{v}}(\tilde{f}_0 + \tilde{f}_1 x + \cdots)$ for small x. The function $\tilde{f}(x)$ is scaled as $\int \tilde{f}(x)g(x)dx = \tilde{U}(0)/U(0)$. The distribution of K is describable by the Polyanyi relation[22]

$$K(x) = \frac{x^{-\lambda}}{\alpha}, \quad \alpha > 0 \tag{15}$$

where α and λ are constants. For the hydrogenation of mononuclear aromatics on metal sulfides, x and K change in the opposite directions ($\lambda > 0$). The opposite is true ($\lambda < 0$) for noble metal catalysts.[23]

The dimensionless total concentration of A_i in the continuous mixture can be evaluated from the following integral[20]

$$\begin{aligned} U_c(\tau) - U_e &= \int_0^\infty \frac{K(x)h(x) - \tilde{h}(x)}{1 + K(x)} e^{-\kappa(x)\tau} dx \\ &= \int_0^\infty \phi(x) e^{-\kappa(x)\tau} dx \equiv I_c \end{aligned} \tag{16}$$

where $\phi \equiv (Kh - \tilde{h})/(1 + K)$ and U_e is the equilibrium concentration that can be calculated by

$$U_e = \int_0^\infty \frac{h(x) + \tilde{h}(x)}{1 + x^{-\lambda}/\alpha} dx \tag{17}$$

and

$$\kappa(x) = x(1 + \alpha x^{\lambda}) \geq 0 \tag{18}$$

The dimensionless $\kappa(x)$ is essentially an effective rate constant.

Here the effect of lumping manifests itself through interactions among the distributions $h(k)$, $\tilde{h}(x)$, and $K(x)$. As a result, the mixture's behavior is far richer than in the irreversible case.[20] For the PFR, there exist 13 possibilities for the long-time behavior of U_c. In the CSTR case, there are 21 possibilities. In what follows we focus on the PFR case.

The key to the asymptotic evaluation of the integral in Eq. 16 is that the overwhelming contribution to I_c comes from a thin region near $x = \hat{x}$ where $\hat{x}$ is the point at which $\kappa(x)$ assumes its minimum value. As long as $\lambda \geq -1$, $\kappa(x)$ increases monotonically, so the boundary layer lies near $\hat{x} = 0$. For $\lambda < -1$, then $\hat{x} > 0$, $\dot{\kappa}(\hat{x}) = (d\kappa/dx)_{x=\hat{x}} = 0$, and $\ddot{\kappa}(\hat{x}) = (d^2\kappa/dx^2)_{x=\hat{x}} > 0$.

When $\lambda \geq 0$, $(U_c - U_e)$ is governed by the most refractory species and obeys the asymptotic power-law: $(U_c - U_e) = O(1/\tau^m)$ $(m > 0)$ at large τ (Eqs. 118–121 in Ref. 20). Here the asymptotic behavior is similar to that of irreversible first-order reactions. So Eq. 13 as a validity condition applies to this case as well.

For $-1 < \lambda < 0$, the mixture after a sufficiently long-time approaches equilibrium in a power-law fashion dictated by refractory species. An inspection of Eqs. 122 and 124 in Ref. 20 indicates that the validity condition is

$$\tau(\delta)^{1+\lambda} \rightarrow 0 \quad \text{as} \quad \delta \rightarrow 0 \quad \text{and} \quad \tau \rightarrow \infty \tag{19}$$

which is more stringent than Eq. 13.

For $\lambda = -1$, $K(x) = x/\alpha$ and the long-time behavior is governed by refractory species because $\hat{x} = 0$. Equation 16 becomes[20]

$$\begin{aligned} U_c(\tau) - U_e &= e^{-\alpha\tau} \int_0^\infty \phi(x) e^{-x\tau} dx \\ &\sim \left[\frac{h_0 \Gamma(\gamma + 1)}{\alpha \tau^{\gamma+1}} - \frac{\tilde{h}_0 \Gamma(\tilde{\gamma})}{\tau^{\tilde{\gamma}}} \right] e^{-\alpha\tau} \end{aligned} \tag{20}$$

which is a power-law decay modified by the term $\exp(-\alpha\tau)$. Since the integrand in Eq. 20 is similar to that for irreversible first-order reactions (Eq. 9), the validity condition remains the same, that is, $\tau\delta \rightarrow 0$ as $\delta \rightarrow 0$ and $\tau \rightarrow \infty$.

The $\lambda < -1$ case requires some special attention because κ has a minimum within the interval $(0, \infty)$, revealing an interior-layer effect. Specifically

$$\hat{x} = [\alpha(|\lambda| - 1)]^{1/|\lambda|} > 0 \tag{21}$$

At this point

$$\kappa(\hat{x}) = |\lambda| \alpha^{1/|\lambda|} (|\lambda| - 1)^{-1+1/|\lambda|} > 0 \tag{22}$$

Here K is such a strong increasing function of x that neither the refractory nor the reactive species win. Instead, species with intermediate reactivity reign. Note that $\lambda = -1$ signifies the transition of dominant species. It pays to approximate $\kappa(x)$ by its Taylor series about $x = \hat{x}$, that is

$$\kappa(x) \approx \kappa(\hat{x}) + \frac{1}{2}\ddot{\kappa}(\hat{x})(x - \hat{x})^2 \tag{23}$$

As $\tau \to \infty$ it can be shown by Laplace's method for integrals[24] that[20]

$$I_c(\tau) \sim \phi(\hat{x})\sqrt{\frac{2\pi}{\ddot{\kappa}(\hat{x})\tau}}e^{-\kappa(\hat{x})\tau} \equiv p(\hat{x};\,\tau) \quad as \quad \tau \to \infty \tag{24}$$

where $\phi(\hat{x}) = [(|\lambda| - 1)h(\hat{x}) - \tilde{h}(\hat{x})]/|\lambda| \neq 0$, and $\ddot{\kappa}(\hat{x}) = \alpha|\lambda|(|\lambda| - 1)\hat{x}^{-(|\lambda|+1)}$.

Now we turn to the underlying discrete mixture. From Eq. 16, one can write the counterpart of I_c as a Riemann sum approximation, that is

$$I_d(\tau) = \sum_{i=0}^{\infty} \phi(i\delta)e^{-\kappa(i\delta)\tau}\delta \tag{25}$$

Note that δ acts as a scale factor in Eq. 25.[15] The question now is, under what conditions do we have $I_d \sim p(\hat{x};\tau)$ as $\tau \to \infty$? To examine this, we use Laplace's method for sums[24] and break I_d into three parts: $I_d = I_\delta^- + I_\delta + I_\delta^+$, where

$$I_\delta^- = \sum_{i:0\le i\delta \le \hat{x}-\varepsilon} \phi(i\delta)e^{-\kappa(i\delta)\tau}\delta \tag{26}$$

$$I_\delta = \sum_{i:\hat{x}-\varepsilon<i\delta<\hat{x}+\varepsilon} \phi(i\delta)e^{-\kappa(i\delta)\tau}\delta \tag{27}$$

$$I_\delta^+ = \sum_{i:i\delta \ge \hat{x}+\varepsilon} \phi(i\delta)e^{-\kappa(i\delta)\tau}\delta \tag{28}$$

Here $0 < \varepsilon \ll 1$ is chosen such that for $\hat{x} - \varepsilon < x < \hat{x} + \varepsilon$, we have $\phi(x) = \phi(\hat{x}) + O(\varepsilon)$ and $\kappa(x) = \kappa(\hat{x}) + O(\varepsilon)$.

It follows from Eq. 26 that

$$|I_\delta^-| \le \left[\sum_{i:0\le i\delta\le\hat{x}-\varepsilon} |\phi(i\delta)|\delta\right] e^{-\kappa(\hat{x}-\varepsilon)\tau} \tag{29}$$

so

$$|I_\delta^-| \le \left[\int_0^\infty |\phi(x)|dx + O(\delta)\right] e^{-\kappa(\hat{x}-\varepsilon)\tau} \tag{30}$$

Similarly,

$$|I_\delta^+| \le \left[\int_0^\infty |\phi(x)|dx + O(\delta)\right] e^{-\kappa(\hat{x}+\varepsilon)\tau} \tag{31}$$

Now, examining the interior layer near $\hat{x}$, we note

$$|I_\delta| = \delta \sum_{i:\hat{x}-\varepsilon<i\delta<\hat{x}+\varepsilon} [\phi(\hat{x}) + O(\varepsilon)]e^{-\tau\{\kappa(\hat{x})+[\ddot{\kappa}(\hat{x})+O(\varepsilon)](i\delta-\hat{x})^2/2\}} \tag{32}$$

Let $\hat{x} = j\delta + \xi$ where $0 \le \xi < \delta$ and j is the greatest integer in $(\hat{x}/\delta)$. Equation 32 can be rewritten as

$$I_\delta = \delta e^{-\kappa(\hat{x})\tau} \sum_{i:\xi-\varepsilon<(i-j)\delta<\xi+\varepsilon} [\phi(\hat{x}) + O(\varepsilon)]e^{-\tau[\ddot{\kappa}(\hat{x})+O(\varepsilon)][(i-j)\delta-\xi]^2/2} \tag{33}$$

Setting $\delta' = \delta\sqrt{\tau}$, $\xi' = \xi\sqrt{\tau}$ $(\xi' < \delta')$, and $i' = i - j$, we get the following expression

$$\sqrt{\tau}e^{\kappa(\hat{x})\tau}I_\delta = \sum_{i':\,\xi'-\varepsilon\sqrt{\tau}<i'\delta'<\xi'+\varepsilon\sqrt{\tau}} [\phi(\hat{x}) + O(\varepsilon)]\delta' e^{-[\ddot{\kappa}(\hat{x})+O(\varepsilon)](i'\delta'-\xi')^2/2} \tag{34}$$

Since $\kappa(\hat{x} - \varepsilon) > \kappa(\hat{x})$, we can see from Eqs. 30, 31 and 34 that for finite δ', as $\tau \to \infty$, $\left|I_\delta^-/I_\delta\right| \le$ constant $\cdot \sqrt{\tau}e^{-\tau[\kappa(\hat{x}-\varepsilon)-\kappa(\hat{x})]} \to 0$. Similarly, $\left|I_\delta^+/I_\delta\right| \to 0$ as $\tau \to \infty$.

Next, letting $\tau \to \infty$, $\delta' \to 0$, and then $\varepsilon \to 0$, Eq. 34 becomes

$$\sqrt{\tau}e^{\kappa(\hat{x})\tau}I_\delta \to \int_{-\infty}^{\infty} \phi(\hat{x})e^{-[\ddot{\kappa}(\hat{x})]x^2/2}dx = \phi(\hat{x})\sqrt{\frac{2\pi}{\ddot{\kappa}(\hat{x})}} \tag{35}$$

Thus, $I_d \approx I_\delta \approx I_c$ as $\tau \to \infty$. The validity condition for $\lambda < -1$ takes the form

$$\delta \to 0, \tau \to \infty \quad \text{and} \quad \delta' = \sqrt{\tau}\delta \to 0 \tag{36}$$

That is, the continuum description is valid only if Eq. 36 is satisfied, which is less stringent than Eq. 13.

Uniformly Coupled Reactions

By uniformly coupled reactions it is meant that $r_i = -k_i c_i F(\Sigma_j w_j c_j)$.[25–26] Since the function F depends only on $\Sigma_j w_j c_j$, its influence on the disappearance of all reactants is uniform. When $F = 1/(1 + \Sigma_j w_j c_j)^n$, w_j play the role of the adsorption constants in a Langmuir-Hinshelwood mechanism. The mass-balance equation for a PFR reads

$$\frac{dc_i}{dt} = -\frac{k_i c_i}{(1 + \sum_{j=1}^{N} w_j c_j)^n} \tag{37}$$

If $F = (\Sigma_j w_j c_j)^{n-1}$, one speaks of bimolecular power-law kinetics

$$\frac{dc_i}{dt} = -k_i c_i \left(\sum\nolimits_{j=1}^{N} w_j c_j\right)^{n-1} \tag{38}$$

In particular, the $n = 2$ and $w_j = k_j$ case corresponds to a class of mass-action bimolecular kinetics with separable rate constants: $r_i = k_{ij} c_i c_j = k_i k_j c_i c_j$. The mass-balance equation becomes

$$\frac{dc_i}{dt} = -k_i c_i \left(\sum\nolimits_{j=1}^{N} k_j c_j\right) \tag{39}$$

In the analysis to follow, we replace w_j in Eq. 38 with k_j.

Now consider the long-time behavior of the corresponding continuous mixture.[11] For the Langmuir-Hinshelwood mechanism, the long-time behavior degenerates to that for irreversible first-order reactions because competitive adsorption becomes insignificant at large t. Then the validity condition is nothing but Eq. 13. The analysis that follows focuses on bimolecular power-law reactions with separable rate constants. We let $\tau = (\bar{\boldsymbol{k}}\boldsymbol{c_o})^{\boldsymbol{n-1}}\boldsymbol{t}$ where $\bar{k}$ is a characteristic rate constant for the separable bimolecular system. So $\hat{\boldsymbol{k}} = \bar{\boldsymbol{k}}\boldsymbol{c}_{\boldsymbol{0}}^{\boldsymbol{n-1}}$ is the equivalent first-order rate constant.

A warped time $u(\tau)$ is introduced to decouple the reactions: $du = Fd\tau$ with $u(0) = 0$. On this time scale, each individual species disappears independently at a pseudo-first-order rate, with $c(x, \tau) = c_f(x)\exp[-xu(\tau)]$. So $f(x)$ and $g(x)$ appear as the product $f(x)g(x) = h(x)$, as was the case with Eq. 9. The total concentration in a PFR is[11,25]

$$U_c(\tau) = \int_0^\infty h(x)e^{-u(\tau)x}dx \tag{40}$$

The problem becomes one of finding $u(\tau)$ by solving the following integro-differential equation

$$\frac{du}{d\tau} = F(\tau) = \left[\int_0^\infty xh(x)e^{-u(\tau)x}dx\right]^{n-1} \quad u(0) = 0 \tag{41}$$

Note that u is monotone increasing and u = constant cannot satisfy Eq. 41. So $u(\tau) \to \infty$ as $\tau \to \infty$. The large-τ asymptote for $U_c(\tau)$ takes the form[11]

$$U_c(\tau) \sim \frac{\sigma}{\tau^m} \tag{42}$$

where

$$\sigma = \frac{h_0\Gamma(\gamma)}{\left\{\psi^{n-1}[(n-1)(\gamma+1)+1]\right\}^{\gamma/[1+(n-1)(\gamma+1)]}} \tag{43}$$

with $\psi = f_0g_0\Gamma(\gamma + 1)$. Also

$$m = \frac{\gamma}{1+(n-1)(\gamma+1)} \tag{44}$$

The corresponding asymptotic reaction order is $n_a = (m + 1)/m$, that is

$$\frac{dU_c}{d\tau} \sim -m\sigma^{-1/m}U_c^{n_a} = R_a(U_c) \tag{45}$$

Moreover, $\gamma = 1$ if the mixture has a finite amount of unconvertibles. Then $U_c(\tau) \sim 1/\sqrt{\tau}$ and $dU_c/d\tau \propto -U_c^3/2$ as $\tau \to \infty$, a result obtained previously.[27]

Next, the discrete counterpart of Eq. 41 is

$$\frac{du_d}{d\tau} = F_d(\tau) = \left[\sum_{j=1}^{\infty}(j\delta)h(j\delta)e^{-u_dj\delta}\delta\right]^{n-1} \tag{46}$$

It can be shown that[15] if $u_d \to \infty$ and $u_d\delta \ll 1$, then

$$\sum_{j=1}^{\infty}(j\delta)h(j\delta)e^{-u_dj\delta}\delta \sim \int_0^\infty f_0g_0x^\gamma e^{-u(\tau)x}dx \sim \frac{f_0g_0\Gamma(\gamma+1)}{u_d(\tau)^{\gamma+1}} \tag{47}$$

This expression allows u_d to be solved via solving the following differential equation

$$\frac{du_d}{d\tau} \sim \left[\frac{f_0g_0\Gamma(\gamma+1)}{u_d(\tau)^{\gamma+1}}\right]^{n-1} \quad \text{for large } \tau \tag{48}$$

we thus have

$$u_d(\tau) \sim \left\{\theta\,[f_0g_0\Gamma(\gamma+1)]^{n-1}\tau\right\}^{1/\theta} \tag{49}$$

where $\theta = (\gamma + 1)(n - 1) + 1$.

Thus, the condition $u_d\delta \ll 1$ means that

$$\left|\tau\delta^\theta\right| \ll 1 \tag{50}$$

As an example, for $n = 2$ and $\gamma = 1$, then the condition becomes $\left|\tau^{1/3}\delta\right| \ll 1$, which is less stringent than Eq. 13.

Power-Law Kinetics

The problem addressed here is the collective behavior of a vast number of parallel nth-order reactions of the form

$$\frac{dc_i}{dt} = -k_ic_i^n \tag{51}$$

Note that n is assumed to be constant. Referring to Eq. 5, the scaling is done by letting $\hat{k} = k^*c_0^{n-1}$ so $\tau = k^*c_0^{n-1}t$, where k^* is a characteristic rate constant for the system $dc_i/dt = -k_ic_i^n$.

Let $\beta = 1/(n - 1)$. For $\beta > 0$, corresponding to high-order kinetics ($n > 1$), the total concentrations in the continuous mixture reads[21]

$$U_c(\tau) = \int_0^\infty \frac{f(x)g(x)dx}{\left[1 + \frac{f(x)^{1/\beta}\tau x}{\beta}\right]^\beta} \quad \beta > 0 \tag{52}$$

It bears emphasizing that Eq. 52 is structurally similar to those for first-order reactions, irreversible or reversible, in isothermal CSTRs.[20] For instance, in the case of irreversible reactions in a series of ℓ CSTRs, U_{CSTR} is of the form

$$U_{CTSR}(\tau) = \int_0^\infty \frac{f(x)g(x)dx}{\left[1+\frac{\tau x}{\ell}\right]^\ell} \tag{53}$$

Thus, the results obtained for nth-order reactions in the PFR have a significant bearing on first-order reactions in CSTRs. We will return to this point later.

Returning to the nth-order discrete mixture, we have

$$U_d(\tau) = \sum_{i=1}^{\infty} \frac{f(i\delta)g(i\delta)\delta}{\left[1 + \frac{f(i\delta)^{1/\beta}\tau i\delta}{\beta}\right]^{\beta}} \tag{54}$$

For any fixed τ, $U_d \to U_c$ as $\delta \to 0$. What we need to investigate is the behavior of U_d as $\delta \to 0$ and $\tau \to \infty$. There are four possibilities to consider.[21]

Case A: $0 < \beta < 1 + \mu$

This is a high reaction-order case in that $n > 1 + 1/(1 + \mu)$. As shown previously,[21] U_c follows the asymptotic power-law

$$U_c \sim \frac{\bar{I}_c}{\tau^{\beta}}; \quad \bar{I}_c \equiv \beta^{\beta} \int_0^{\infty} \frac{g(x)dx}{x^{\beta}} \quad \text{as } \tau \to \infty \tag{55}$$

This behavior, which depends on $g(x)$ not on $f(x)$, is very different from that of first-order reaction mixtures in that U_c is governed by all species rather than by the refractory ones. There is no boundary-layer effect; even the most reactive species remain influential after a long time. The overall, asymptotic order for the mixture is the same as that for individual species.[21]

In view of Eq. 55, we factor out τ^{β} in Eq. 54, and find by monotone convergence that

$$\tau^{\beta} U_d(\tau) = \sum_{i=1}^{\infty} \frac{f(i\delta)g(i\delta)\delta}{\left[\frac{1}{\tau} + f(i\delta)^{1/\beta} i\delta/\beta\right]^{\beta}} \to \sum_{n=1}^{\infty} \frac{\beta^{\beta} g(i\delta)\delta}{(i\delta)^{\beta}} \equiv \bar{I}_d \quad \text{as} \quad \tau \to \infty \tag{56}$$

Given that $\bar{I}_d \to \bar{I}_c$ as $\delta \to 0$, so $U_d \sim U_c$ as $\tau \to \infty$ and $\delta \to 0$.

It transpires from the foregoing that the apparent paradox discussed in the Introduction does not exist in this case. That is, the long-time asymptotic kinetics derived from the continuum approximation is valid for arbitrarily large times.

Case B: $\beta > 1 + \mu > 0$

This is an intermediate reaction-order case: $1 < n < 1 + 1/(1 + \mu)$. The large-τ behavior of U_c is dominated by refractory species and obeys the power-law[21]

$$U_c(\tau) \sim \frac{g_0 f_0^{\eta} \beta^{z+1}}{\beta + v} B(z, w) \frac{1}{\tau^{z}} \tag{57}$$

where $z = \beta\gamma/(\beta + v)$, $\eta = 1 - z/\beta$, and $w = \beta - z = \beta\eta > 0$. $B(z, w)$ is the beta function, defined as $(z, w > 0)$

$$B(z,w) \equiv \int_0^{\infty} \frac{\xi^{z-1} d\xi}{(1+\xi)^{z+w}} = \int_0^1 \xi^{z-1}(1-\xi)^{w-1} d\xi \tag{58}$$

The total concentration in the corresponding discrete mixture U_d is calculated as a sum of two parts: $U_d = U_d^- + U_d^+$ where

$$U_d^- = \sum_{i:i\delta<\varepsilon} \frac{f(i\delta)g(i\delta)\delta}{\left[1 + \frac{f(i\delta)^{1/\beta}\tau i\delta}{\beta}\right]^{\beta}} \tag{59}$$

$$U_d^+ = \sum_{i:i\delta\geq\varepsilon} \frac{f(i\delta)g(i\delta)\delta}{\left[1 + \frac{f(i\delta)^{1/\beta}\tau i\delta}{\beta}\right]^{\beta}} \tag{60}$$

in which ε is a small positive number. U_d^- and U_d^+ are the contributions from the refractory and reactive species, respectively.

Consider the reactive fraction, we have as $\tau \to \infty$

$$\left|\tau^{\beta} U_d^+\right| = \sum_{i:i\delta\geq\varepsilon} \frac{f(i\delta)g(i\delta)\delta}{\left[\frac{1}{\tau} + \frac{f(i\delta)^{1/\beta} i\delta}{\beta}\right]^{\beta}}$$

$$\to \beta^{\beta} \sum_{i:i\delta\geq\varepsilon} \frac{g(i\delta)\delta}{(i\delta)^{\beta}} = \beta^{\beta} \int_{\varepsilon}^{\infty} \frac{g(x)dx}{x^{\beta}} + O(\delta) \tag{61}$$

Since $\beta > 1 + \mu$ implies that $\beta > z$, we obtain

$$\frac{U_d^+}{U_c} \sim \text{const.}[1 + O(\delta)] \frac{1}{\tau^{\beta-z}} \to 0 \quad \text{as} \quad \tau \quad \to \infty \tag{62}$$

Thus, the reactive fraction does not play a role in our attempt to match U_c and U_d. We next examine the refractory fraction to seek the condition under which U_c and U_d can be matched.

Let $f(x) = f_0 x^{v}[1 + O(x)]$ and $g(x) = g_0 x^{\mu}[1 + O(x)]$. Equation 59 becomes

$$U_d^- = \sum_{i:i\delta<\varepsilon} \frac{f_0 g_0 (i\delta)^{\mu+v} \delta[1 + O(\varepsilon)]}{\left[1 + \frac{f_0^{1/\beta}(i\delta)^{1+v/\beta}\tau}{\beta}\right]^{\beta}} \tag{63}$$

Substituting $\tau\delta^{1+v/\beta} \equiv (\delta')^{1+v/\beta}$ yields

$$\tau^{z} U_d^- = \sum_{i:i\delta'<\varepsilon\tau^{\beta/(v+\beta)}} \frac{f_0 g_0 (i\delta')^{\mu+v} \delta'[1 + O(\varepsilon)]}{\left[1 + \frac{f_0^{1/\beta}(i\delta')^{1+v/\beta}}{\beta}\right]^{\beta}} \tag{64}$$

For convergence of the sum to an integral, we need to impose $0 < \delta' \ll 1$. This leads to the following validity condition as $\tau \to \infty$

$$\delta' = \tau^{\frac{\beta}{\beta+v}} \delta = \tau^{\frac{1}{1+v(n-1)}} \delta \to 0 \tag{65}$$

Taking the limit $\tau \to \infty$ and $\delta' \to 0$ in Eq. 64, we obtain

$$\tau^{z} U_d^- \sim \int_0^{\infty} \frac{f_0 g_0 x^{\mu+v} dx}{\left[1 + \frac{f_0^{1/\beta} x^{1+v/\beta}}{\beta}\right]^{\beta}} [1 + O(\varepsilon)] \tag{66}$$

Changing variable with $\xi = f_0^{1/\beta} x^{1+v/\beta}/\beta$ and letting $\varepsilon \to 0$ gives Eq. 57.

Case C: $\beta = 1 + \mu$

This is also an intermediate reaction-order case, with $n = 1 + 1/(1 + \mu)$. We have[21]

$$U_c(\tau) \sim \frac{g_0 \beta^{z+1}}{\beta + v} \left(\frac{ln\tau}{\tau^z} \right) \quad \tau \to \infty \tag{67}$$

Similar to Case B, here the mixture's long-time behavior is also governed by refractory species. However, the logarithmic term signifies that the singular $\beta = 1 + \mu$ case marks the transition from all-species-dominated mixture (Case A) to refractory-species-dominated mixture (Case B). This transition presents some subtleties, as discussed below.

It can be shown that $\left| U_d^{+} / U_c \right| \sim$ constant$/ln\tau \to 0$ as $\tau \to \infty$, so U_d^{+} does not contribute. To show $U_d^{-} \sim U_c$ as $\tau \to \infty$, it is necessary to divide the refractory species into two subfractions: one is very refractory classified by $i\delta' < a$ ($U_d^{=}$); the other is moderately refractory classified by $i\delta' \geq a$ ($U_d^{\mp}$). Note that $a \gg 1$; as such, Eq. 64 is rewritten as

$$\begin{aligned} \tau^z U_d^{=} &= \sum\nolimits_{i\delta' < a} \frac{f_0 g_0 (i\delta')^{\mu+v} \delta' [1 + O(\varepsilon)]}{\left[1 + \frac{f_0^{1/\beta} (i\delta')^{1+v/\beta}}{\beta} \right]^{\beta}} \\ &= \left\{ f_0 g_0 \int_0^a \frac{x^{\mu+v} dx}{\left[1 + \frac{f_0^{1/\beta} x^{1+v/\beta}}{\beta} \right]^{\beta}} + O(\delta') \right\} [1 + O(\varepsilon)] \end{aligned} \tag{68}$$

Since $z = \beta$, $\left| U_d^{=} / U_c \right| \sim$ constant$/ln\tau \to 0$ as $\tau \to \infty$. So the very refractory fraction does not contribute either.

On the other hand, for the moderately refractory fraction, Eq. 64 becomes

$$\begin{aligned} \tau^z U_d^{\mp} &= \sum\nolimits_{a \leq i\delta' < \varepsilon\tau^{\beta/(v+\beta)}} \frac{f_0 g_0 (i\delta')^{\mu+v} \delta' [1 + O(\varepsilon)]}{\left[1 + \frac{f_0^{1/\beta} (i\delta')^{1+v/\beta}}{\beta} \right]^{\beta}} \\ &= \beta^{\beta} g_0 \sum\nolimits_{a \leq i\delta' < \varepsilon\tau^{\beta/(v+\beta)}} \frac{1}{i} [1 + O(\varepsilon)] \left[1 + O\left(\frac{1}{a^{1+v/\beta}} \right) \right] \end{aligned} \tag{69}$$

Since

$$\sum\nolimits_{i=1}^{N} \frac{1}{i} \sim lnN \tag{70}$$

Equation 69 can be rewritten for $a \gg 1$ and $\tau \gg 1$ as

$$\tau^z U_d^{\mp} \sim \frac{\beta^{\beta} g_0}{(v + \beta)} \ln\tau \quad \text{as } \tau \to \infty \tag{71}$$

That is, $U_d^{+} \sim U_c$ as $\tau \to \infty$.

The resulting validity condition is that as $\tau \to \infty$

$$\delta' = \tau^{\beta/(\beta+v)} \delta = \tau^{(1+\mu)/(1+\mu+v)} \delta \to \text{finite} \tag{72}$$

which is less restrictive than Eq. 65 and depends on both μ and v. As long as δ' remains finite, the asymptotic equivalence of the continuum and discrete descriptions is guaranteed. Here δ approaches zero as fast as $\tau^{\beta/(\beta+v)} \to \infty$. In Case B, δ needs to go to zero a bit faster than $\tau^{\beta/(\beta+v)} \to \infty$. The subtlety here is that it is the moderately refractory fraction that governs the long-time asymptotic behavior of the mixture. In going from Case A to Case B, the dominating fraction changes gradually from the whole feed to the refractory fraction. Case C marks the transition: that the dominating fraction comprises moderately refractory species.

Case D: $\beta < 0$ and $| \beta | > v > 0$

In this case, U_c takes the form[21]

$$U_c = \int_0^{\chi(\tau)} f(x) g(x) \left[1 - \frac{\tau}{\tau^*(x)} \right]^{|\beta|} dx \quad \{x\colon \tau < \tau^*\} \tag{73}$$

The function $\tau^*(x)$ is the exhaustion time at which reactant x is completely consumed. Thus, the foregoing integral is only over reactants that have not depleted by time $\tau < \tau^*$. Unless all the reactants happen to have the same exhaustion time, the behavior of the reactant lump will not be that of a zeroth-order reaction. Finding the root(s) of the denominator in Eq. 52 gives $\tau^*(x)$ as

$$\tau^*(x) = |\beta| f(x)^{1/|\beta|} (1/x) \tag{74}$$

We are only interested in the situation where τ^* remains unbounded, which is ensured by $|\beta| > v$. The case where τ^* is bounded means that U_c is identically zero when $\tau > \max \tau^*$. This occurs with very low-order reaction mixtures, $n \leq (1 - 1/v)$. In this case, the continuum approach does not apply.

Set $\omega \equiv 1 - v/|\beta| > 0$ and let $\chi(\tau)$ be the inverse function of τ^*, that is, $\tau^*[\chi(\tau)] = \tau$. We can calculate the following asymptotics

$$\tau^* \sim \bar{\tau} = |\beta| f_0^{1/|\beta|} x^{-\omega} \quad \text{as } x \to 0 \tag{75}$$

$$\chi \sim \bar{\chi}(\tau) = \left(\frac{\left| \beta f_0^{1/|\beta|} \right|}{\tau} \right)^{1/\omega} \quad \text{as } \tau \to \infty \tag{76}$$

As previously shown,[21] U_c is of the form

$$U_c(\tau) \sim \frac{g_0 f_0^{\eta} |\beta|^{z+1}}{|\beta| - v} B(z, 1 + |\beta|) \frac{1}{\tau^z} \tag{77}$$

For the discrete counterpart, we have

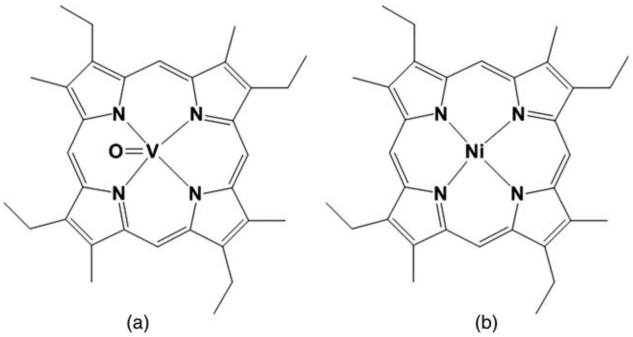

(a) (b)

Figure 2. Vanadyl and nickel etioporphyrins.

$$U_d(\tau) = \sum_{0<i\delta<\chi} f(i\delta)g(i\delta)\left[1 - \frac{\tau}{\tau^*(i\delta)}\right]^{|\beta|}\delta$$
$$\sim \sum_{0<i\delta<\chi} f_0 g_0 (i\delta)^{\mu+v}\left[1 - \frac{\tau(i\delta)^{\omega}}{|\beta| f_0^{1/|\beta|}}\right]^{|\beta|}\delta \qquad (78)$$

Let $\bar{\delta}^{\omega} \equiv \tau\delta^{\omega}$, then

$$U_d(\tau) \sim \tau^{-(\mu+v+1)/\omega} f_0 g_0 \sum_{i\bar{\delta}<\tau^{1/\omega}\chi} (i\bar{\delta})^{\mu+v}\left[1 - \frac{(i\bar{\delta})^{\omega}}{|\beta| f_0^{1/|\beta|}}\right]^{|\beta|}\bar{\delta} \qquad (79)$$

The upper limit on i can be estimated from Eq. 76

$$\tau^{1/\omega}\chi(\tau) \sim \left(|\beta| f_0^{1/|\beta|}\right)^{1/\omega} \equiv \varpi \qquad (80)$$

It follows that

$$\tau^z U_d(\tau) \sim f_0 g_0 \sum_{i\bar{\delta}<\varpi} (i\bar{\delta})^{\mu+v}\left[1 - \left(\frac{i\bar{\delta}}{\varpi}\right)^{\omega}\right]^{|\beta|}\bar{\delta} \qquad (81)$$

Now letting $\bar{\delta} \to 0$, we obtain the corresponding integral

$$\tau^z U_d(\tau) \sim f_0 g_0 \int_0^{\varpi} x^{\mu+v}\left[1 - \left(\frac{x}{\varpi}\right)^{\omega}\right]^{|\beta|} dx \qquad (82)$$

Let $\xi \equiv (x/\varpi)^{\omega}$, Eq. 82 gives

$$\tau^z U_d(\tau) \sim \frac{g_0 f_0^{\eta}|\beta|^{z+1}}{|\beta| - v} B(z, 1 + |\beta|) \sim \tau^z U_c(\tau) \qquad (83)$$

That is, $U_d/U_c \sim 1$ as $\tau \to \infty$ and $\bar{\delta} \to 0$, the latter implying that

$$\bar{\delta} = \tau^{|\beta|/(|\beta|-v)}\delta = \tau^{1/(1-v+nv)}\delta \to 0 \qquad (84)$$

with $(1 - v + nv) > 0$. Note that the condition depends on v not on μ.

A significant consequence is that when $(1 - v + nv)$ is small (e.g., $|\beta| \to v$), the validity condition can be far more stringent than that for irreversible first-order reactions. Here we are dealing with low-order reactions, commonly encountered in catalytic processing of highly adsorptive hydrocarbons. Hung and Wei[28–29] found that the kinetics of the removal of vanadium and nickel from porphyrins are usually fractional order. As an example, Figure 2 shows the structures of vanadyl and nickel etioporphyrins. The HDN of organonitrogen species is often observed to be fractional order. The data of Miller and Hineman[30] for the HDN of quinoline are plotted in Figure 3 as $ln(N_p/N_f)$ vs. 1/LHSV, where N_p, N_f, and LHSV are total nitrogen in the liquid effluent, total nitrogen in the feed, and liquid hourly space velocity, respectively. The data can be fitted by an HDN order of 0.5 for two different catalysts.

We note in passing that highly adsorptive species do not come off catalyst surface easily. As such, they linger on the catalyst surface and polymerize to form coke, thus, deactivating the catalyst. Coke formation has been modeled using the continuum approach.[31]

Discussions

Range of validity

Table 1 lists several selected validity conditions for different reactions taking place in an isothermal PFR or batch reactor. In situations where the continuum approximation is conditionally valid, the validity condition takes the power-law form

$$\delta^y \tau \ll 1 \qquad (85)$$

For practical applications, it is useful to cast Eq. 85 in terms of the equivalent first-order rate constant $\hat{k}$

$$\frac{1}{\hat{k}} \ll t \ll \left(\frac{\hat{k}}{\Delta}\right)^y \frac{1}{\hat{k}} \qquad (86)$$

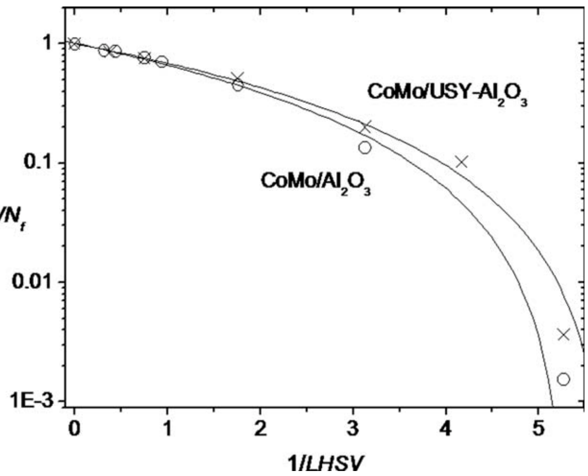


Figure 3. ln(N_p/N_f) vs. 1/LHSV for the HDN of quinoline over sulfided CoMo/Al$_2$O$_3$ and CoMo/Al$_2$O$_3$-USY catalysts at 375°C and 6.89·10^3 kPa hydrogen pressure.

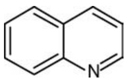
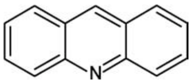
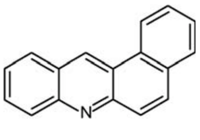
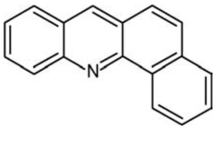
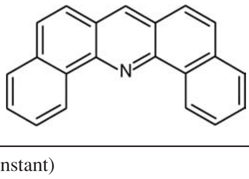
Table 1. Validity Conditions for Various Large-τ Asymptotic Kinetics

Reaction Kinetics	Governing Species	Validity Condition
Irreversible nth-order, $1 - 1/v < n < 1 + 1/(1 + \mu)$	Refractory	$\tau^{1/(1-v+nv)}\delta \ll 1$
Irreversible first-order, $n = 1$	Refractory	$\tau\delta \ll 1$
Irreversible nth-order, $n = 1 + 1/(1 + \mu)$	Moderately refractory	$\tau^{(1+\mu)/(1+\mu+v)}\delta \rightarrow$ finite
Irreversible nth-order, $n > 1 + 1/(1 + \mu)$	All species	All τ
Reversible first-order, $\lambda \geq 0$	Refractory	$\tau\delta \ll 1$
Reversible first-order, $-1 < \lambda < 0$	Refractory	$\tau^{1/(1+\lambda)}\delta \ll 1$
Reversible first-order, $\lambda = -1$	Refractory	$\tau\delta \ll 1$
Reversible first-order, $\lambda < -1$	Intermediate reactivity	$\sqrt{\tau}\delta \ll 1$
Bimolecular power−law	Refractory	$\tau\delta^{(\gamma+1)(n-1)+1} \ll 1$
Bimolecular mass action, $n = 2$, $\gamma = 1$	Refractory	$\tau^{1/3}\delta \ll 1$

This is a generalization of Eq. 1; for irreversible first-order, $y = 1$. For the special reversible first-order reactions with $\lambda < -1$, $y = 2$. In the case of coupled bimolecular second-order reactions, $y = 3$, which says that $t \ll [(\bar{k}c_o)^2/\Delta^3]$. Here, the validity condition has a concentration term due to the kinetic nonlinearity. For nth-order reactions with $(1 - 1/v) < n < 1$, $y = 1 - v + nv$. As mentioned earlier, the $n \leq (1 - 1/v)$ case is not compatible with the continuum description. For $n > 1 + 1/(1 + \mu)$, the continuum approximation is valid for arbitrarily long time.

Equation 86 also says that the validity of the continuum approximation requires that $(\hat{k}/\Delta)^y \gg 1$. For HDS reactions ($n = y = 1$), the examples given in the Introduction indicate that indeed $(\hat{k}/\Delta) \gg 1$. For perspective, let us look at the HDN reactions, for which we have found some literature data obtained from model-compound studies.[32–33] As Table 2 shows, due to the lack of a detailed kinetic analysis, the reactivity is represented by the pseudo-first-order rate constants k_p at a particular feed concentration. The k_p for quinoline is taken as the characteristic rate constant, so $\hat{k} = 9.38{\cdot}10^{-4}$ (l/g catalyst/s). We calculate Δ as the reactivity difference between acridine ($6.56{\cdot}10^{-4}$) and benz[c]acridine ($5.72{\cdot}10^{-4}$). Let $n = v = 0.5$, so $y = 0.25$. Then the relative size of the validity region is $(\hat{k}/\Delta)^{0.25} \sim 1.83$, which is an alarming result. Nonetheless, we point out that model-compound kinetic experiments tend to give a high Δ value. As illustrated earlier for HDS, real-feed hydroprocessing tends to suppress Δ due to fierce competitive adsorption among a vast number of species. It also bears emphasizing that the validity range depends on catalyst, reaction conditions, and reactor type.

Table 2. HDN Reactivities of Nitrogen Compounds

compound (wt% in feed)	structure	k_p, l/g cat. sec
quinoline (1.0)		$9.38{\cdot}10^{-4}$
acridine (0.54)		$6.56{\cdot}10^{-4}$
benz[c]acridine (0.47)		$5.72{\cdot}10^{-4}$
benz[a]acridine (0.42)		$4.03{\cdot}10^{-4}$
dibenz[c,h]acridine (0.41)		$1.41{\cdot}10^{-3}$

(k_p: pseudo-first-order rate constant)

High vs. low-order reactions

As alluded to earlier, for high-order reactions, $n > 1 + 1/(1 + \mu)$, the long-time asymptotic kinetics derived from the continuum approximation for PFRs are valid for arbitrarily large times. In this case, the mixture's behavior is governed by all species. The situation is very different for first-order reactions: the mixture's asymptotic behavior is governed only by refractory species and time cannot be unconditionally large.

The foregoing begs the question: why does the continuum-based asymptotic kinetics break down after a long time in one case but not in the other? To shed some light on this question, we consider a binary discrete mixture in a PFR. The concentrations of the refractory (hard) and reactive (easy) species are c_h and c_e, respectively. Two scenarios are considered. In scenario A, the reaction is first-order, so $c_h = c_{hf}\exp(-k_h t)$ and $c_e = c_{ef}\exp(-k_e t)$. Figure 4 shows the conversions of the constituent species and the mixture as functions of time (dimensionless) for $k_h = 0.1$, $k_e = 0.2$, $c_{hf} = 0.1$, and $c_{ef} = 0.9$ (all dimensionless). One sees that after an initial transient the conversion of the mixture is essentially dictated by the hard species. In scenario B, the reaction is second-order, hence, $c_h = c_{hf}/(1 + k_h c_{hf} t)$ and $c_e = c_{ef}/(1 + k_e c_{ef} t)$. As Figure 5 shows, the conversion of the mixture is governed by both species for all t. Even after a long time, the easy species can still influence the mixture's behavior.

The difference between the two scenarios can best be seen by looking at the concentration ratios c_h/c_e as a function of time. For scenario B, $c_h/c_e \rightarrow k_e/k_h = \text{constant} < \infty$ as $t \rightarrow \infty$. That is, the c_h/c_e ratio remains bounded throughout the whole time. In other words, the relative contributions of the hard and easy species to the mixture's behavior do not vary significantly. This is also the case for other nth-order reactions except for $n = 1$, as can be seen next.

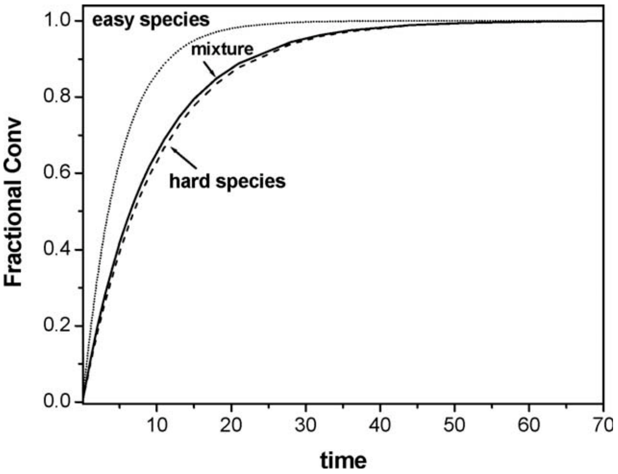


Figure 4. Fractional conversions vs. dimensionless time for a first-order reaction mixture: easy species (dotted curve), hard species (dashed curve), mixture (solid curve): dimensionless rate constants and initial concentrations are: $k_h = 0.1$, $k_e = 0.2$, $c_{hf} = 0.1$, and $c_{ef} = 0.9$.

For scenario A, $c_h/c_e \propto \exp[-(k_h - k_e)t] \to \infty$ as $t \to \infty$. So the ratio explodes exponentially after a short time. Thereafter, the "burden" of portraying the mixture's behavior is shifted to the hard species (the boundary-layer effect). This characteristic punctuates the continuum thesis: that the number of species is numerous and the difference between two adjacent species is vanishingly small. We may call the behaviors in scenarios A and B "nonuniform" and "uniform," respectively. In the uniform case, each and every reactant contributes something significant to the overall conversion of the mixture at all times (neither boundary nor interior layer would develop). In the nonuniform case, the mixture's behavior becomes dominated by an ever-shrinking subset of reacting species as time goes by. As a consequence, the underlying discrete mixture and its continuous approximant will diverge eventually.

It should be noted that an irreversible first-order reaction mixtures behaves as a nonuniform mixture in a PFR even though none of the constituent reactants is completely consumed in a finite time. For reaction mixtures with $n < 1$, the constituent reactants would exhaust in a finite time, which would make it even harder for the continuum description to remain valid at large times. This is why the validity condition for the $(1 - 1/v) < n < 1$ case is more stringent than that for $n = 1$, see Table 1. In short, the continuum thesis becomes increasingly untenable as reaction order decreases.

That the continuum representation can be valid for arbitrarily long times for high-order reactions is related to a homogenization effect. To elaborate, let us consider a high-order (say, $n \geq 2$) reaction mixture in a PFR. The decay rates of all species decelerate rapidly soon after the reaction commences. This tends to homogenize the constituents of the mixture. The result is that even the most reactive species remain influential after a long time. The overall asymptotic reaction order for the mixture is the same as that of the individual reactions. In contrast, for first-order reactions, there is an increase in reaction order in going from individual species to the mixture (Eq. 11). A point of note here is that the overall reaction order for a mixture as a whole is not necessarily higher than the underlying order for constituent reactants.

The results, when applied to those obtained previously,[20] provide additional insights into the homogenization effect, as discussed next.

Effects of mixing and feed properties

While an irreversible first-order reaction mixture in a PFR is nonuniform, it becomes uniform in a CSTR for reactive feeds ($\gamma > 1$), due to the interplay of the wide spread of reactor residence time and feed properties (Eqs. 10–11 in Ref. 20). In the CSTR, the residence times of the molecules of each reactant are distributed exponentially. While all reactants are slowed down relative to those in the PFR, the fast-reacting ones are hindered more than the slow-reacting ones. This mixing-induced homogenization diminishes the disparities among the species, so refractory and reactive species are weighed more or less equally in determining the mixture's long-time behavior.[20] Consistent with this is the fact that the overall asymptotic reaction order for the mixture is the same as that for individual reactants.[20]

In the case of a series of ℓ CSTRs,[20] an irreversible first-order reaction mixture is uniform for $\gamma > \ell$. A similar conclusion can be reached for uniformly coupled reactions.[20] As shown earlier, a reversible first-order reaction mixture is nonuniform in the PFR. Based on previous results (Tables 2–6 in Ref. 20), one can see that the same mixture in a single CSTR becomes uniform when (1) $\lambda > 0$, $\gamma > 1$, and $\tilde{\gamma} > 1 - \lambda$, (2) $\lambda < 0$, $\gamma > 1 - |\lambda|$, and $\tilde{\gamma} > 1 - |\lambda|$, or (3) $\lambda = 0$, $\gamma > 1$, and $\tilde{\gamma} > 1$. The upshot here is that the validity conditions are less stringent for a CSTR than for a PFR.

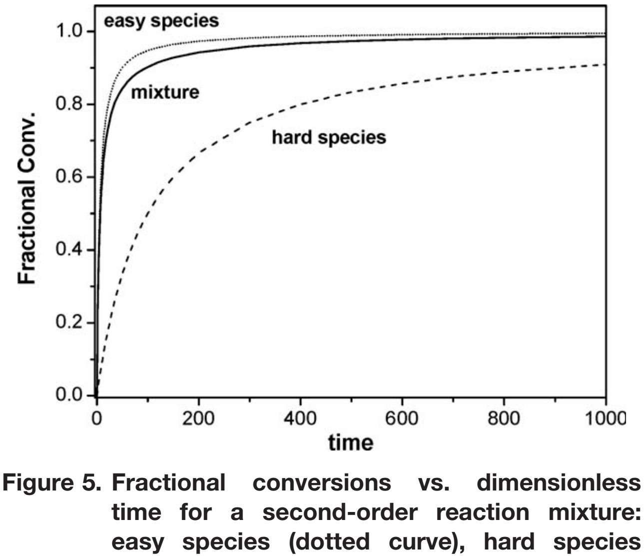


Figure 5. Fractional conversions vs. dimensionless time for a second-order reaction mixture: easy species (dotted curve), hard species (dashed curve), mixture (solid curve): dimensionless rate constants and initial concentrations are: $k_h = 0.1$, $k_e = 0.2$, $c_{hf} = 0.1$, and $c_{ef} = 0.9$.

Effects of diffusion and feed properties

We should point out that the homogenization can be enhanced by pore diffusion. The reason is that while the diffusion effect slows down all reactions, it debits the reactive species more than the refractory species. Thus, in the absence of diffusion limitation, an irreversible first-order reaction mixture in the CSTR is uniform only if $\gamma > 1$. The same mixture in the presence of diffusion resistance becomes uniform when $\gamma > 1/2$ (Eq. 51 in Ref. 20).

Dichotomies

The Introduction section introduces the concept of intermediate asymptotics[34] for irreversible first-order reactions in a PFR. This means that the so-called "long-time" asymptotic behavior obtained from the continuum approximation actually is valid only over an intermediate time regime. That is, time is long enough so U_c no longer depends on the details of $f(x)$ and $g(x)$, yet it is still far from the ultimate equilibrium state. The good news is that one can determine the mixture's behavior with a minimum amount of feed information. In many cases, only the most refractory fraction of the feed needs to be characterized (f_o, g_o, and γ). The unwelcome news is that the condition in Eq. 1 may be too stringent to be practically useful.

On the other hand, there are circumstances where the continuum-based asymptotic kinetics are valid for arbitrarily long times (e.g., high-order power-law kinetics). While this is a big plus, the accompanying disadvantage is that U_c has a long memory: it depends on the details of $g(x)$ (see Eq. 55). One may draw some comfort in knowing that U_c does not depend on $f(x)$ and $U_c \propto 1/\tau^{\beta}$, with β being independent of feed properties.

Concluding Remarks

Continuum approximation has long been used for analyzing thermodynamic and kinetic behaviors of large, complex mixtures. It is important to know the inherent limitation of the approximation. This is especially true for kinetic studies, which must be discussed in the context of the interactions among reaction kinetics, reactor mixing characteristics, and diffusion. Invoking the approximation is the only way to gain a predictive understanding of the qualitative behavior of large reaction mixtures at moderately large or arbitrarily large times. Such asymptotic behavior can depend on all species, species of intermediate reactivity, moderately refractory species, or refractory species. In situations where the asymptotic behavior depends on all species, the approximation is valid for arbitrarily large times and the mixture is called uniform. Otherwise, the mixture is called nonuniform.

The adequacy of the continuum description depends on kinetics, feed properties, reactor type, and pore diffusion. For many situations of practical interest, the validity conditions for the continuum approximation take the form of an inequality involving a product of powers of time and reactivity granularity. The approximation also brings about some dichotomies and subtleties. In general, the continuum description is more suitable for high-order reactions than for low-order ones in plug-flow reactors. In fact, when the order is sufficiently high, the approximation is valid for arbitrarily long times. Mixtures of very low-order reactions are actually not compatible with the continuum description. For a given reaction kinetics, either diffusion intrusion or increasing mixing would widen the range of validity of the approximation. Thus, a CSTR is more amenable than a PFR to the continuum representation. The application of the continuum approximation will continue to benefit from advances in analytical techniques for molecular characterization of complex mixtures. The results obtained from this study will help pinpoint where the emphasis should be in this endeavor.

Notation

c_i = concentration of ith species
c_{if} = concentration of ith species in the feed
$c_f(k)$ = feed concentration of k species in the continuous mixture
c_o = characteristic species concentration in feed
C = total concentration of all reactants
C_o = total concentration at time = 0
D = reactant type distribution function, Eq. 2
f = feed concentration distribution function, Eq. 5
f_o = constant in feed distribution function, Eq. 7
g = reactant type distribution function, Eq. 5
g_o = constant in reactant type distribution function, Eq. 7
h = function defined as $h \equiv fg$
k_i = rate constant associated with ith species
k = rate constant or label for continuous mixture
$\tilde{k}_i$ = reversible rate constant for ith species
$\hat{k}$ = equivalent first-order rate constant, Eq. 5
$\bar{k}$ = characteristic rate constant for separable bimolecular reactions
k^* = characteristic rate constant for power-law reactions
k_p = pseudo-first-order rate constant, Table 2
K = equilibrium constant, Eq. 15
m = constant defined in Eq. 4
n = reaction order
n_a = overall asymptotic reaction order for mixture at large times
N = total number of reactant types
p = function defined in Eq. 24
q = constant defined in Eq. 4
R = overall apparent kinetics for reaction mixtures as a whole
R_a = overall asymptotic kinetics at large times
r_i = reaction rate for the ith reactant
t = reaction time
u = warped time
U = dimensionless total concentration, Eq. 5
U_c = dimensionless total concentration in continuous mixture
U_d = dimensionless total concentration in discrete mixture
U_e = dimensionless equilibrium total concentration, Eq. 17
w_j = rate parameter in uniformly coupled kinetics
x = dimensionless rate constant, Eq. 5
$\hat{x}$ = value of x at which $\kappa(x)$ is minimum
y = constant defined in Eqs. 85–86 and Table 1
z = defined as $z = \beta\gamma/(\beta + \nu)$

Greek letters

α = constant defined in Eq. 15
β = constant defined as $\beta \equiv 1/(n - 1)$
γ = constant defined as $\gamma \equiv 1 + \mu + \nu$
δ = dimensionless reactivity granularity, $\delta \equiv x_i/i$
Δ = reactivity granularity defined as $\Delta \equiv \hat{k}\delta$
ε = a small positive constant, $0 < \varepsilon \ll 1$
ζ = constant defined in Eq. 4
η = constant defined as $\eta \equiv 1 - z/\beta$
θ = constant defined as $\theta \equiv (\gamma + 1)(n - 1) + 1$
κ = function defined in Eq. 18
λ = constant defined in Eq. 15
μ = constant defined in Eq. 8
ν = constant defined in Eq. 7

σ = constant defined in Eq. 42
ρ = constant defined in Eq. 4
τ = dimensionless time defined in Eq. 5
τ^* = reactant exhaustion time, see Eq. 74
ϕ = function defined in Eq. 16
χ = inverse function of τ^*
ψ = constant defined as $\psi \equiv f_0 g_0 \Gamma(\gamma + 1)$
ω = constant defined as $\omega \equiv 1 - v/|\beta|$
$\tilde{\omega}$ = constant defined in Eq. 80

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