Continuous-Mixture Kinetics and Equilibrium for Reversible Oligomerization Reactions

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Reversible oligomerization of distributions of molecules yields distributions of monomers, dimers, trimers, tetramers and higher-order oligomers. The distributions can be functions of molecular weight, carbon number, or other variables that may be considered continuous. Rate expressions are formulated for the rates of generation of oligomers and loss of reactants due to combination (fusion) reactions and for the generation of fragments and loss of oligomers due to cracking (fission) reactions. Two types of cracking reactions are proposed: proportioned fission where products are precisely proportioned to yield monomers, dimers or trimers of given molecular weight; random fission where the fission products are distributed over all molecular weights up to that of the reactant. The zero moment of a distribution is the species concentration, which satisfies molar equilibrium and kinetics relationships. The temporal evolution of molecular-weight moments is expressed in terms of differential equations for continuous-flow and batch stirred reactors. By setting forward and reverse rates equal, equilibrium relations are developed for zero- and higher-order moments, thus generalizing the mass-action equilibrium concept. Equilibrium states for proportioned and random fission manifest infinitesimally narrow and infinitely broad distributions.

Introduction

Aris and Gavalas (1966) outlined the general concepts and principles of the theory of reactions in continuous mixtures. Such mixtures are treated as though an infinite number of species in the mixture allows the mixture properties to be expressed as continuous functions. These functions depend on a property, for example, the molecular weight of the species, which is also considered continuous. Aris and Gavalas developed the basic ideas of chemical reaction kinetics and thermodynamics for continuous mixtures, including fundamental stoichiometric relations for *irreversible* monomolecular and cracking reactions. They considered applications to chemical reactors and discussed how experimental data might be analyzed. Recently, Cicarelli et al. (1992) further developed concepts of cracking kinetics.

Continuous-mixture studies have increased lately, and two collections of discussions have been published (Astarita and Sandler, 1991; Sapre and Krambeck, 1991). The surge in activity is motivated by the belief that continuous-mixture theories provide an approach to understanding thermodynamics and kinetics at a deeper level. Advances have been notable in the thermodynamics of phase equilibrium and the kinetics of irreversible chemical reactions. The continuous-mixture kinetics and thermodynamics of *reversible* chemical reactions have not been developed.

Oligomerization is an example of a process that involves reversible reactions of complex multicomponent mixtures. The conversion of light olefins to higher molecular-weight olefins is commercially important for the production of gasoline and distillate fuels (Quann and Krambeck, 1991; Quann et al., 1988; Tabak et al., 1986). With the synthetic zeolite ZSM-5 catalyst, the dominant reaction is the oligomerization of two olefins of molecular weight x and y to form an oligomer of molecular weight $x+y$. The oligomer in turn may serve as a reactant for further oligomerizations. When propylene (C_3) is the feed, the product sequence is C_3, C_6, C_9, C_{12}, and so on; if 1-hexene is the feed the products are C_6, C_{12}, C_{18}, C_{24}, and so on. Quann and Krambeck (1991) and Quann et al. (1988) point out that interfering reactions, such as disproportionation, cracking, and conjunct polymerization, can complicate the reaction pathways and yield intermediate products. Rather than being a molecule of a single molecular weight (MW), each oligomer consequently spans a range of MWs as a molecular-weight distribution (MWD).

Krambeck (1991) and Quann and Krambeck (1991) proposed a kinetic model for the oligomerization process consisting of a finite sequence of reversible reactions between discrete olefins. To allow a reduction in the reaction rate with increasing carbon number, the rate coefficients were considered to have the form $k j^{-w}$, where j is the carbon number. The equilibrium coefficient for the reversible reaction was determined by a thermodynamic lumping procedure. Disproportionation was included as being proportional to the oligomerization rate through a relative rate parameter, α. For 1-hexene fed to a plug-flow reactor, the C_6 peak nearly vanishes as the C_{12} and, to a lesser extent, the C_{18} and C_{24} peaks grow. By means of the three adjustable parameters, k, α, and w, the product distributions for 1-hexene feed and 1-hexadecene feed were satisfactorily described. The distribution of each oligomer can be represented with either carbon number or MW as the independent variable.

The experimental data reported by Ginosar et al. (1992) for the cis-trans isomerization of 1-hexene on an α-Al_2O_3/Al catalyst showed the presence of oligomers in the reactor. Gas chromatography of the effluent from the reactor showed peaks corresponding to C_{12}, C_{18}, C_{24}, and C_{30} isomers. Oligomer formation (up to C_{30}) occurs in the bulk fluid phase, even in the absence of the catalyst. The rate of this oligomer formation is enhanced with isothermal increases in pressure: more oligomers are formed at supercritical, as compared to subcritical, conditions. The oligomers are converted to aromatic compounds that deposit as coke on the catalyst. At supercritical conditions the activity of the catalyst can be maintained at a steady-state value, whereas total deactivation occurs at subcritical conditions. This indicates the greater desorption of the higher molecular-weight aromatic compounds under supercritical conditions. The experiments showed that the coke compounds and intermediates are mixtures of many chemical species. These mixtures are made up of oligomers formed by reaction of species that differ only slightly in MW.

To explain the activity maintenance or decay of the catalyst, Subramaniam and McCoy (1993) developed a lumped chemical kinetics model for the formation, adsorption, and desorption of coking compounds. The irreversible production of 1-hexene oligomers, C_6, C_{12}, C_{18}, and C_{24} in the bulk fluid phase is followed by their transformation to polynuclear aromatics (coke) of the same carbon number. In a continuous-flow, stirred-tank (CSTR) reactor, the catalyst gradually decays to total deactivation by coke adsorption when the rate of production of coke exceeds the net rate of desorption at subcritical conditions. At supercritical conditions the desorption rate is large enough to balance the rates of coke production and adsorption, resulting in a steady-state maintenance of catalyst activity.

The aim of the present work is to apply a continuous-mixture model to describe the chemical kinetics and equilibrium behavior of *reversible* oligomerization reactions. The combination (fusion) and cracking (fission) reaction rate expressions for the MWDs assume distinctive forms for so-called proportioned and random fission reactions. Although forms of the expressions have been used previously for particulate agglomeration and microbial fission (Hulbert and Katz, 1964; Himmelblau and Bischoff, 1968), the application to chemical reactions is apparently new. Moments based on MW allow information to be extracted from the mass balance equations. The zero moments are simply the concentrations of the oligomers and satisfy the lumped reaction-kinetics equations. For the reversible reactions at equilibrium, the zero moments yield mass-action expressions defining the equilibrium constant. The normalized and central moments of oligomers and reactants are also interrelated at each other. The moments satisfy hierarchical sets of differential equations for the batch or well-mixed flow reactor. At each order the moments depend upon lower-order moments, thus furnishing a generalization of the discrete-mixture theories. The differential equations become algebraic equations at equilibrium.

Continuous-Mixture Model

The approach to model the continuous-mixture kinetics of reversible oligomerization is illustrated for an example: the formation of oligomers up through tetramers. Extending the process to higher MW oligomers requires handling more terms, but is conceptually straightforward. The isomers of component P_1 combine to form the oligomers P_2, which further react to form P_3 and P_4. The reverse reaction occurs as well, and oligomers P_2, P_3 and P_4 can each decompose, or crack, into two fragments by binary fission to form P_1, P_2 and P_3 and their isomers. These processes can be written in terms of rate constants that have double subscripts for fusion reactions and single subscripts for reverse reactions:

$$\begin{aligned} &P_1 + P_1 \underset{k_2}{\overset{k_{11}}{\Longleftrightarrow}} P_2 \\ &P_1 + P_2 \underset{k_3}{\overset{k_{12}}{\Longleftrightarrow}} P_3 \\ &P_2 + P_2 \underset{k_4}{\overset{k_{22}}{\Longleftrightarrow}} P_4 \\ &P_1 + P_3 \underset{k'_4}{\overset{k_{13}}{\Longleftrightarrow}} P_4 \end{aligned} \tag{1}$$

Each chemical species is considered to comprise a continuous mixture spanning a molecular-weight range. If x is the MW, then for a CSTR, the MWD for each component is a function of both x and t, that is, $P_j(x, t)$ for $j = 1, 2, 3, 4$. At time t, $P_j(x, t)dx$ is the molar concentration of the oligomer having a MW in the range $(x, x+dx)$. The integral over all x for each of these MWDs is the lumped molar concentration, that is, the zero-order moment.

The mass balance equations for a CSTR fed with a MWD for each oligomer can be written with reaction-rate terms for the generation or loss of each oligomer:

$$\begin{aligned} dP_1/dt &= [P_{1f} - P_1]/\tau + \Sigma r_1^{\text{gen}} - \Sigma r_1^{\text{loss}} \\ dP_2/dt &= [P_{2f} - P_2]/\tau + \Sigma r_2^{\text{gen}} - \Sigma r_2^{\text{loss}} \\ dP_3/dt &= [P_{3f} - P_3]/\tau + \Sigma r_3^{\text{gen}} - \Sigma r_3^{\text{loss}} \\ dP_4/dt &= [P_{4f} - P_4]/\tau + \Sigma r_4^{\text{gen}} - \Sigma r_4^{\text{loss}} \end{aligned} \tag{2}$$

Here the average residence time for the reactor is τ. Units of time are supposed to be scaled so as to be dimensionless. The initial conditions allow for an initial charge of any of the oligomers P_j:

$$P_j(x, t=0) = P_{jo}(x) \qquad j=1, 2, 3, 4 \tag{3}$$

Likewise, the oligomers fed to the CSTR can span a range of MW, that is, $P_{jf}(x)$.

The molecular-weight moments of the MWDs are defined as:

$$P_j^{(n)}(t) = \int_0^\infty x^n P_j(x, t)dx \tag{4}$$

The zero-order moments ($n=0$) are simply the time-dependent molar concentrations of the different species. The first moments, $P_j^{(1)}(t)$, are the mass concentrations (mass/volume). The normalized first moment (average MW) and the second central moment (variance of the MWD) are given by, respectively:

$$P_j^{\text{avg}} = P_j^{(1)}/P_j^{(0)} \tag{5}$$

and

$$P_j^{\text{var}} = P_j^{(2)}/P_j^{(0)} - [P_j^{\text{avg}}]^2 \tag{6}$$

If a gamma distribution function in terms of $y_j = x/\beta_j$ is chosen to represent the MWDs:

$$P_j(x) = P_j^{(0)} y_j^{\alpha_j - 1} e^{-y_j}/\beta_j \Gamma(\alpha_j) \tag{7}$$

then the mean and variance are given by (Abramowitz and Stegun, 1968):

$$P_j^{\text{avg}} = \alpha_j \beta_j \text{ and } P_j^{\text{var}} = \alpha_j \beta_j^2. \tag{8}$$

The Gaussian representation is:

$$P_j(x, t) = [P_j^{(0)}/(2\pi P_j^{\text{var}})^{1/2}]\exp[-(x-P_j^{\text{avg}})^2/2P_j^{\text{var}}] \tag{9}$$

which approximates the gamma distribution for large α_j (that is, a narrow MWD).

Rate Expressions

The explicit expressions for generation and loss terms are provided in Table 1. The forward (oligomerization) reaction terms are based on concepts developed by Hulburt and Katz (1964) [see also Himmelblau and Bischoff (1968)] for agglomeration kinetics. When two molecules react by combining together, we assume that the rate is proportional to the product of the MWDs, and hence two MWDs appear in each such term for loss or generation. For example, when P_1 and P_2 combine to form P_3 the loss of $P_1(x)$ is proportional to the product of $P_1(x)$ and the integral over all MWs of $P_2(x)$. The stoichiometric coefficient 2 appears when the combining molecules are identical. The generation of $P_3(x)$ occurs by the fusion of $P_1(x-x')$ and $P_2(x')$, and the generation term is proportional to the integral over all x'.

Table 1. Loss and Generation Terms for Reversible Oligomerization Reactions*

$P_1 + P_1 \underset{k_2}{\overset{k_{11}}{\Longleftrightarrow}} P_2$	(A)
$r_1^{\text{loss}}(x, t) = 2k_{11}P_1(x, t)\int_0^\infty P_1(x', t)dx'$	(1T)
$r_1^{\text{gen}}(x, t) = 2k_2\int_x^\infty P_2(x', t)\delta(x-x'/2)dx'$	(2T)
$r_2^{\text{gen}}(x, t) = k_{11}\int_0^x P_1(x-x', t)P_1(x', t)dx'$	(3T)
$r_2^{\text{loss}}(x, t) = k_2P_2(x, t)$	(4T)
$P_1 + P_2 \underset{k_3}{\overset{k_{12}}{\Longleftrightarrow}} P_3$	(B)
$r_1^{\text{loss}}(x, t) = k_{12}P_1(x, t)\int_0^\infty P_2(x', t)dx'$	(5T)
$r_1^{\text{gen}}(x, t) = k_3\int_x^\infty P_3(x', t)\delta(x-x'/3)dx'$	(6T)
$r_2^{\text{loss}}(x, t) = k_{12}P_2(x, t)\int_0^\infty P_1(x', t)dx'$	(7T)
$r_2^{\text{gen}}(x, t) = k_3\int_x^\infty P_3(x', t)\delta(x-2x'/3)dx'$	(8T)
$r_3^{\text{gen}}(x, t) = k_{12}\int_0^x P_1(x-x', t)P_2(x', t)dx'$	(9T)
$r_3^{\text{loss}}(x, t) = k_3P_3(x, t)$	(10T)
$P_2 + P_2 \underset{k_4}{\overset{k_{22}}{\Longleftrightarrow}} P_4$	(C)
$r_2^{\text{loss}}(x, t) = 2k_{22}P_2(x, t)\int_0^\infty P_2(x', t)dx'$	(11T)
$r_2^{\text{gen}}(x, t) = 2k_4\int_x^\infty P_4(x', t)\delta(x-x'/2)dx'$	(12T)
$r_4^{\text{gen}}(x, t) = k_{22}\int_0^x P_2(x-x', t)P_2(x', t)dx'$	(13T)
$r_4^{\text{loss}}(x, t) = k_4P_4(x, t)$	(14T)
$P_1 + P_3 \underset{k_4'}{\overset{k_{13}}{\Longleftrightarrow}} P_4$	(D)
$r_1^{\text{loss}}(x, t) = k_{13}P_1(x, t)\int_0^\infty P_3(x', t)dx'$	(15T)
$r_1^{\text{gen}}(x, t) = k_4'\int_x^\infty P_4(x', t)\delta(x-x'/4)dx'$	(16T)
$r_3^{\text{loss}}(x, t) = k_{13}P_3(x, t)\int_0^\infty P_1(x', t)dx'$	(17T)
$r_3^{\text{gen}}(x, t) = k_4'\int_x^\infty P_4(x', t)\delta(x-3x'/4)dx'$	(18T)
$r_4^{\text{gen}}(x, t) = k_{13}\int_0^x P_3(x-x', t)P_1(x', t)dx'$	(19T)
$r_4^{\text{loss}}(x, t) = k_4'P_4(x, t)$	(20T)

* The generation terms for cracking reactions are shown for proportioned fission; for random fission the delta functions are replaced with $6x(x'-x)/x'^3$.

The rate expression proposed by Aris and Gavalas (1966) for cracking of coal components allows a molecule to break into two product molecules whose MWs, x' and $x-x'$, sum to the MW of the reactant, x. The rate expression for the generation of a distribution of product molecules $P_i(x)$ from the cracking of reactant molecules $P_j(x)$ is represented in general by:

$$r_i^{\text{gen}}(x) = k_j\int_x^\infty P_j(x', t)\Omega_j(x, x')dx' \tag{10}$$

The stoichiometric coefficient $\Omega_j(x, x')$ must satisfy normalization and symmetry conditions (Aris and Gavalas, 1966):

$$\int_0^x \Omega_j(x, x')dx' = 1 \qquad (11)$$

and

$$\Omega_j(x, x') = \Omega_j(x' - x, x') \qquad (12)$$

Equivalent to a disproportionation process, two molecules of MW x and y that combine can subsequently crack to yield a pair of molecules of MW x' and y'. Two types of cracking terms are considered here: proportioned fission and random fission. In some applications, a combination of these two forms may be useful.

Proportioned Fission. For this case, the form of the reverse (cracking) terms describes fission processes yielding fragments that are precisely proportioned, for example, for microorganisms that produce equal-sized daughter cells (Himmelblau and Bischoff, 1968). A delta function for $\Omega_j(x, x')$ in each fission generation term ensures that the fission generates only the selected MW molecules. For the equal-size daughter cells in the treatment of Himmelblau and Bischoff (1968), this function is $\delta(x - x'/2)$. If the oligomer $P_4(x')$ cracks to $P_1(x)$ and $P_3(x)$ the delta functions are $\delta(x - x'/4)$ and $\delta(x - 3x'/4)$, respectively. The integration over x' obeys the condition that $x \le x'$. The moments of this generation term are obtained by integrating in either order over x and x', thus,

$$k_j \int_0^\infty dx\, x^n \int_x^\infty dx'\, P_j(x', t)\delta(x - x'b) = k_j P_j^{(n)} b^n \qquad (13)$$

For proportioned fission if the initial condition consists of delta-function MWDs, then the distributions must remain delta functions for all time, since only specified oligomers are allowed by the reactions.

Random Fission. The expression proposed by Prasad et al. (1986) is:

$$\Omega(x, x') = 6x(x' - x)/x'^3 \qquad (14)$$

which provides a continuous distribution of product fragments, and satisfies the symmetry and normalization conditions. Unlike the case of proportioned fission, x' is allowed to have *any* random value within the interval $(0, x)$. The moments of this generation term are obtained after interchanging the order of integration of x and x'. The result is:

$$\int_x^\infty r_i^{\text{gen}}(x)x^n dx = 6k_j P_j^{(n)}/(n+2)(n+3) \qquad (15)$$

The different factors in the moments of the proportioned and random fission generation terms are b^n and $6/(n+2)(n+3)$, respectively. If the initial condition for random fission is a delta function, the result is a MWD that broadens due to the cracking reaction.

Moment Equations

The chemical reaction thermodynamics of *discrete* mixtures is based on stoichiometric coefficients σ_i that relate the differential change in moles of the different species to the differential extent of reaction, $d\epsilon$, that is, $dN_i = \sigma_i d\epsilon$. Since the stoichiometric functions for MWDs in the continuous-mixture oligomerization reactions cannot be expressed in such a simple form, the usual thermodynamic approach to minimizing free energy is not immediately applicable (Astarita, 1989). Instead, we will develop moment relations that can be utilized to determine the equilibrium conditions, as well as the system dynamics.

We have assumed that all the rate coefficients k_i and k_{ij} are independent of MW. If one assumes that these coefficients are polynomials in x, higher-order moments appear in the reaction rate terms.

To obtain differential equations for the moments, multiply the CSTR mass balance equations by $x^n dx$ and integrate. The binomial coefficient, $({}^n r) = n!/(n-r)!r!$, arises (Himmelblau and Bischoff, 1968) due to the substitution of an integration variable, $y = x - x'$, in the expressions for r^{gen} and the subsequent expansion of $(y + x')^n$. The general, nth-order moment equations take the form,

$$\begin{aligned}
dP_1^{(n)}/dt = {} & [P_{1f}^{(n)} - P_1^{(n)}]/\tau - 2k_{11}P_1^{(n)}P_1^{(0)} - k_{12}P_1^{(n)}P_2^{(0)} \\
& - k_{13}P_1^{(n)}P_3^{(0)} + 2k_2P_2^{(n)}\{-2^{-n}\} + k_3P_3^{(n)}\{3^{-n}\} + k_4'P_4^{(n)}\{4^{-n}\} \\
dP_2^{(n)}/dt = {} & [P_{2f}^{(n)} - P_2^{(n)}]/\tau - k_{12}P_2^{(n)}P_1^{(0)} - 2k_{22}P_2^{(n)}P_2^{(0)} \\
& + k_{11}\Sigma({}^n j)P_1^{(n-j)}P_1^{(j)} - k_2P_2^{(n)} + k_3P_3^{(n)}\{2^n/3^n\} \\
& + 2k_4P_4^{(n)}\{2^{-n}\} \\
dP_3^{(n)}/dt = {} & [P_{3f}^{(n)} - P_3^{(n)}]/\tau - k_{13}P_3^{(n)}P_1^{(0)} \\
& + k_{12}\Sigma({}^n j)P_1^{(n-j)}P_2^{(j)} - k_3P_3^{(n)} + k_4'P_4^{(n)}\{3^n/4^n\} \\
dP_4^{(n)}/dt = {} & [P_{4f}^{(n)} - P_4^{(n)}]/\tau + k_{22}\Sigma({}^n j)P_2^{(n-j)}P_2^{(j)} \\
& + k_{13}\Sigma({}^n j)P_1^{(n-j)}P_3^{(j)} - (k_4 + k_4')P_4^{(n)} \qquad (16)
\end{aligned}$$

The initial conditions for the moments are:

$$P_j^{(n)}(t=0) = P_{jo}^{(n)} \quad \text{for } j = 1, 2, 3, 4. \qquad (17)$$

The case of proportioned fission is shown above. For random fission the coefficients in brackets { } are all replaced by $6/(n+2)(n+3)$. The evolution of the MWDs for either case is thus governed by a hierarchy of ordinary differential equations. The zero-moment case, $n = 0$, returns the lumped kinetics equations in terms of molar concentrations. When $k_{ij} = 0$ we have only the fission (cracking) reaction with no oligomerization, and all molecules are cracked to the minimum MW. When $k_i = 0$ we have oligomerization with no reverse reaction, and only $P_4(x)$ exists (is nonzero) in the final state. Another useful special case is when only one reversible reaction takes place, for instance, when only rate constants k_{12} and k_3 are nonzero.

Equilibrium State

To understand the equilibrium state for the moments, we focus on the batch reactor ($\tau \rightarrow \infty$). As mentioned, the first moment is the mass concentration. Thus for the batch, a condition of conservation of total mass is that the first moments sum to a constant for either proportioned or random fission, that is, for summations over $j=1, 2, 3, 4$:

$$\Sigma P_j^{(1)}(t) = \Sigma P_j^{(1)}(t=0) \tag{18}$$

Therefore, for the differential equations governing the batch-reactor moments,

$$\Sigma dP_j^{(1)}/dt = 0 \tag{19}$$

and the first moment equations sum to zero.

Equilibrium for Zero Moments. The rate coefficients are related by equilibrium constants that are determined by equating the zero moments of loss terms for each of the oligomerization reactions,

$$\begin{aligned} P_2^{(0)}/P_1^{(0)}P_1^{(0)} &= k_{11}/k_2 = K_{11} \\ P_3^{(0)}/P_1^{(0)}P_2^{(0)} &= k_{12}/k_3 = K_{12} \\ P_4^{(0)}/P_2^{(0)}P_2^{(0)} &= k_{22}/k_4 = K_{22} \\ P_4^{(0)}/P_1^{(0)}P_3^{(0)} &= k_{13}/k_4' = K_{13} \end{aligned} \tag{20}$$

The results are identical for proportioned and random fission. These equilibrium conditions satisfy the moment equations for $n=0$ when $dP_j^{(n)}/dt=0$ and $\tau \rightarrow \infty$. The lumped concentrations (zero moments) thus satisfy the expected mass-action equilibrium relations.

The four equations for the zero moments are not independent, since dividing the third by the fourth equation, and substituting for $P_3^{(0)}$ from the second equation yields the first equation. The equilibrium and rate constants therefore satisfy:

$$K_{12}K_{13}/K_{11}K_{22} = 1 \quad \text{and} \quad k_{12}k_{13}/k_{11}k_{22} = k_3k_4'/k_2k_4 \tag{21}$$

Equilibrium for Proportioned Fission. It is convenient to define reduced MWDs as follows:

$$p_j(x) = P_j(x)/P_j^{(0)} \quad \text{with} \quad p_j^{\text{avg}} = P_j^{\text{avg}} \quad \text{and} \quad p_j^{\text{var}} = P_j^{\text{var}} \tag{22}$$

The system of integral equations that satisfies the equilibrium conditions, $dP_j(x)/dt=0$, can be grouped into pairs of equations balancing the gain and loss terms in the four reactions. When the integrals over δ-functions are evaluated, and the zero-moment equilibrium relations used to eliminate the rate constants, one obtains:

$$p_1(x) = p_2(2x) = p_3(3x) = p_4(4x) \tag{23}$$

The other terms yield integral equations of the form:

$$\int_0^\infty p_i(x-x', t)p_j(x', t)dx' = p_{i+j}(x) \tag{24}$$

These equations are satisfied by the delta functions:

$$p_j(x) = \delta(x - jP_1^{\text{avg}}) \tag{25}$$

Therefore, the equilibrium MWDs for the proportioned fission case are delta functions positioned at $j\,P_1^{\text{avg}}$, where $j=1, 2, 3, 4$.

These results are consistent with the moment equation solutions at equilibrium. The higher moments provide more detailed information about the structure of the MWDs than the zero moments. Even though proportioned and random fission cases yield identical equilibrium results for the zero moments, the higher moments are different for the two cases. It can be proved, by substitution in the moment equations for proportioned fission, that at equilibrium:

$$p_1^{(n)} = p_2^{(n)}/2^n = p_3^{(n)}/3^n = p_4^{(n)}/4^n \tag{26}$$

This is most easily demonstrated by considering the system of moment algebraic equations as linear combinations of the moment equations for the separate reactions. It follows directly that:

$$P_1^{\text{avg}} = P_2^{\text{avg}}/2 = P_3^{\text{avg}}/3 = P_4^{\text{avg}}/4 \tag{27}$$

and

$$P_1^{\text{var}} = P_2^{\text{var}}/2^2 = P_3^{\text{var}}/3^2 = P_4^{\text{var}}/4^2 \tag{28}$$

and so on for higher central moments:

$$P_1^{\text{cen}} = P_2^{\text{cen}}/2^n = P_3^{\text{cen}}/3^n = P_4^{\text{cen}}/4^n \tag{29}$$

where

$$P_j^{\text{cen}} = \int_0^\infty (x - P_j^{\text{avg}})^n P_j(x)dx/P_j^{(0)} \tag{30}$$

These equalities are manifestations of the allowed combination of every molecule in a MWD with every molecule in a reacting-partner MWD. While the zero moments yield the lumped mass-action relations for equilibrium constants, the higher-order moments are needed to provide information about the structure of the MWDs.

The equilibrium values of the moments can be numerically calculated by setting $dP_j^{(n)}/dt=0$ in Eqs. 16 and solving the resulting simultaneous nonlinear algebraic equations. Since these zero and first moment equations are not independent, additional equations are required. From Eq. 18,

$$\Sigma P_j^{(1)} = \text{constant} \tag{31}$$

and by a mole balance based on the stoichiometry

$$\Sigma jP_j^{(0)} = \text{constant} \tag{32}$$

where the two different constants can be determined, for example, by the initial conditions and stoichiometry for the differential equations. Figure 1, discussed in detail below, shows the evolution of the MWDs for the rate constants given in Table 2.

Equilibrium for Random Fission. Chemical equilibrium is governed by equilibrium pairs of reactions representing the reversible (fission-fusion) processes. For the random fission case the product fragments span an increasing MW range as time evolves. Balancing generation and loss terms for the interaction between P_1, P_2, and P_3, yields the two equations:

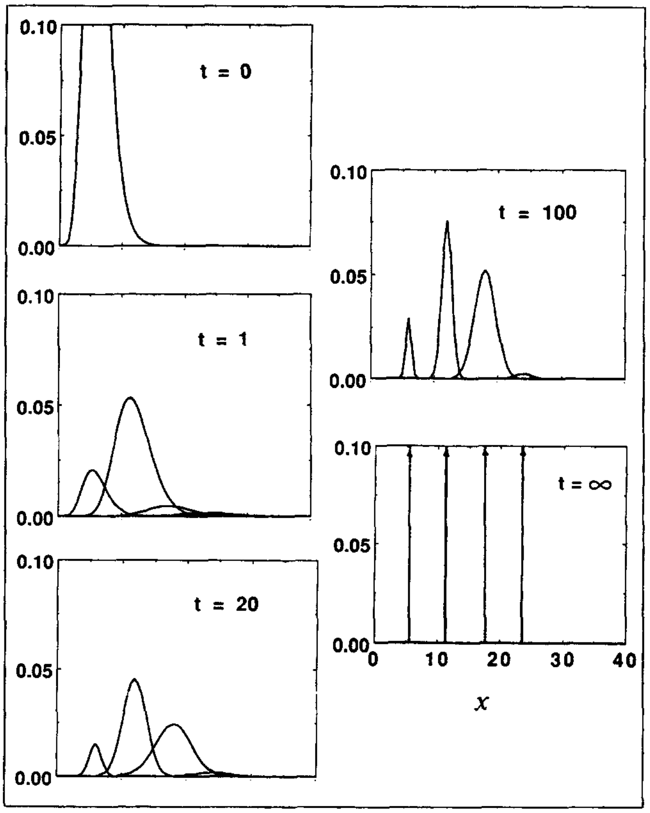

Figure 1. Evolution to equilibrium of the MWDs for a reversible oligomerization with proportioned fission in a batch reactor.

The initial condition is a gamma distribution at $x = 6$.

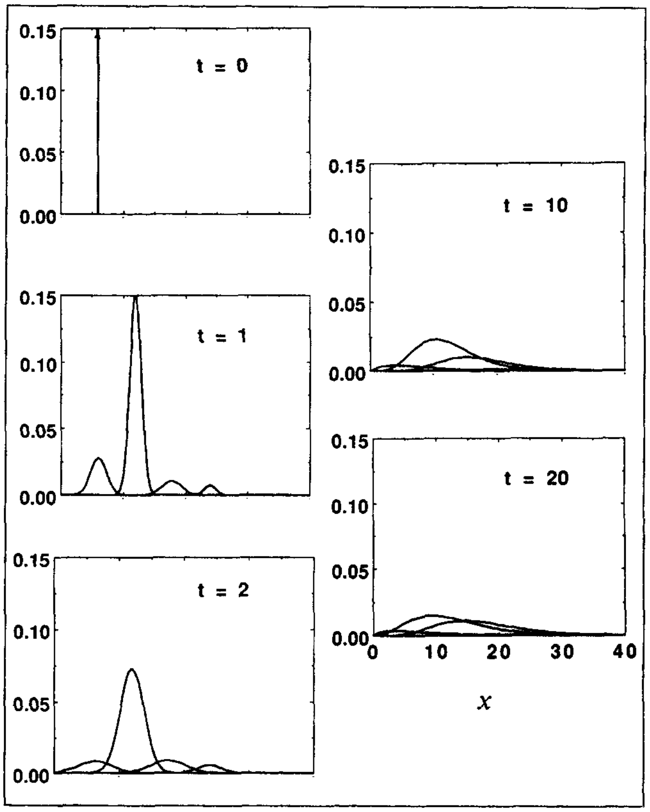

Figure 2. Evolution of the MWDs in a batch reactor for reversible oligomerization with random fission.

The initial condition is a delta function at $x = 6$.

$$k_{12}P_1(x,\ t)P_2^{(0)} = k_3\int_x^{\infty} P_3(x',\ t)\Omega(x,\ x')dx' \qquad (33)$$

$$k_{12}P_2(x,\ t)P_1^{(0)} = k_3\int_x^{\infty} P_3(x',\ t)\Omega(x,\ x')dx' \qquad (34)$$

from which we obtain:

$$P_1(x,\ t)/P_1^{(0)} = P_2(x,\ t)/P_2^{(0)} \text{ or } p_1(x,\ t) = p_2(x,\ t) \qquad (35)$$

Similar arguments with the other reactions show that:

$$p_1(x,\ t) = p_2(x,\ t) = p_3(x,\ t) = p_4(x,\ t) \qquad (36)$$

that is, when generation and loss terms for the four separate reactions of Table 1 are balanced, we find that $P_j(x)/P_j^{(0)}$ is a constant for $j = 1, 2, 3, 4$. Therefore, at equilibrium all four of the MWDs coincide as an infinitely broad and infinitesimally high distribution. The overlapping of the MWDs indicates that the distribution between species in different MWDs is lost. Such overlapping and indistinguishable MWDs lead to ill-defined moments at very large times (Figure 2).

Table 2. Values of Rate Constants Used for Computations

k_{11}	k_{12}	k_{13}	k_{22}
4.63	0.579	0.171	0.171
k_2	k_3	k_4	k_4'
0.0300	0.0125	0.500	0.150

Evidently, reacting continuous mixtures with different fission mechanisms can evolve to different equilibrium states for the MWDs. The different equilibrium MWDs are, however, consistent with the traditional thermodynamic mass-action relations for concentration (zero moments).

Time Evolution of MWDs

The 12 ordinary differential equations for the zero, first, and second moments of P_1, P_2, P_3, and P_4, are solved by a variable-step Runge-Kutta routine. Table 2 shows values of parameters used for the calculations. The rate constants of Table 2 satisfy the conditions of Eq. 21, and are proportional to j^{-3}, where j is the carbon number (Quann and Krambeck, 1991). Figure 1 shows results for reversible oligomerization with proportioned fission in a batch reactor. The initial condition is a MWD with $P_1^{(0)} = 1$, $P_1^{\text{avg}} = 6$, and $P_1^{\text{var}} = 4$, represented in Figure 1 as a gamma distribution. As k_{11} is large compared to the other rate constants, the initial peak at $x = 6$ quickly declines as the other three peaks grow. The MWDs are approximated as gamma distributions, which become Gaussian peaks as the values of variance diminish. The total area under the peaks (total molar concentration) is not constant with time due to the fusion of molecules. The peaks slowly become narrower due to the focusing effect of the proportioned fission. As the central moments vanish, eventually all the MWDs become delta functions positioned at 6, 12, 18 and 24. This batch reactor case also represents a steady-state plug-flow reactor if t is replaced by the reactor distance coordinate divided by the fluid velocity.

For reversible oligomerization with proportioned fission in a CSTR, when the initial condition is equivalent to the feed condition, that is, $P_{jo}^{(n)} = P_{jf}^{(n)}$, the values of $P_j^{\text{avg}}(t)$ and $P_j^{\text{var}}(t)$ are constant with time. The feed and initial conditions chosen for sample calculations were $P_1^{\text{avg}}(t=0) = 6$ and $P_1^{\text{var}}(t=0) = 4$, which yielded $P_j^{\text{avg}}(t) = 6j$ and $P_j^{\text{var}}(t) = 4j$ for $j = 1, 2, 3, 4$. The zero moments of the four oligomers evolved from the initial condition, $P_1^{(0)}(t=0) = 1$, to steady-state (not equilibrium) values for the CSTR.

Figure 2 shows the evolution of the MWDs in a batch reactor for reversible oligomerization with random fission. The initial condition is a delta function at $x = 6$. The initial peak quickly declines as the C_{12} peak rapidly grows. Eventually all peaks are flattened as they broaden with the passage of time. In a CSTR, the MWDs reach a steady state determined by the feed condition.

Conclusion

According to the concepts of continuous-mixture kinetics, complex mixtures are treated as though molecular weight (or carbon number) is a continuous variable. The continuous-mixture mass balance equations reduce to the lumped (averaged) equations when integrated over the MW. In the present case, reversible oligomerization is modeled with fusion and fission rate expressions, the latter represented as either proportioned or random fission terms. The time evolution of MWDs for monomers, dimers, trimers, and tetramers is governed by integro-differential equations. At equilibrium, the time derivatives vanish and the resulting integral equations dictate the chemical reaction equilibrium state. The coupled nonlinear, ordinary differential equations for the MW moments (integrals over the MWD) are solved numerically to determine the time-dependent behavior of the system. The procedure is based on principles outlined by Hulburt and Katz (1964) (see also Himmelblau and Bischoff, 1968), but evidently never before applied to chemical reactions. The MWDs for reactants and products are approximated as gamma distributions constructed from the moments. For the CSTR fed with a narrow distribution of reactant olefins (for example, 1-hexene), these MWDs approach a steady state as time evolves. The batch reactor demonstrates the evolution to equilibrium. For proportioned and random fission, the equilibrium MWDs are infinitesimally narrow or infinitely broad distributions, respectively, although the lumped concentrations (zero moments) satisfy the same mass-action relation.

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Notation

b = factor appearing in the delta function, $\delta(x - bx')$
k_{ij} = forward (fusion) rate constants
k_j = reverse (fission) rate constants
K_{ij} = equilibrium constants
$p_j(x, t)$ = reduced MWD for jth oligomer
P_j = jth oligomer
$P_j(x, t)$ = MWD for jth oligomer
$P_{jf}(x)$ = inlet (feed) MWD for jth oligomer
$P_{jo}(x)$ = initial ($t = 0$) MWD for jth oligomer
$P_j^{(n)}(t)$ = nth MW moment of the MWD for the jth oligomer
$P_j^{\text{avg}}(t)$ = first (reduced) moment, or average MW of jth oligomer
$P_j^{\text{var}}(t)$ = second central (reduced) moment, or variance of the MWD for the jth oligomer
$P_j^{\text{cen}}(t)$ = nth central (reduced) moment of the MWD for the jth oligomer
r_j^{gen} = rate of generation of jth oligomer
r_j^{loss} = rate of loss of jth oligomer
t = time
x = MW or number of carbon atoms

Greek letters

α_j = parameter in the gamma distribution
β_j = parameter in the gamma distribution
$\delta(x)$ = Dirac delta function of MW
τ = average residence time for CSTR
$\Omega_j(x, x')$ = stoichiometry coefficient for continuous-mixture generation term

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