Some of the data are presented in Figure 8 to show that the gas phase pressure drop depends highly on liquid physical properties, much more than could be accounted for by the liquid Reynolds number. As is evident from the figure, pressure drop in the gas phase when a falling film is present is up to five times higher than when gas flows alone. Our observations during experiments were that a high level of gas velocity (> 10 m/s) is accompanied by the formation of somewhat regular rolling waves over the full width and length of the plate. Interfacial shear produces higher waves than those that already exist on the liquid film surface, and waves enhance the pressure drop. This effect was more pronounced for the case of liquids with higher apparent viscosities because larger film thicknesses allowed easier deformation of the surface. This problem of a moving gas-liquid interface is discussed in detail by Dukler (1972).

As far as we know, these are the first available data on gas-pseudoplastic film flow. It was thought, however, that the amount of data is not large enough to construct an empirical correlation for the dependence of gas-phase pressure drop on liquid shear properties.

NOTATION

C = Carbopol concentration in water, $\%w$
g = gravity acceleration, cm/s^2
H^1 = distance between planes which form the channel for gas-liquid flow, cm
K = consistency factor, dyne s^n/cm^2
L = length of plate, cm
n = flow behavior index
Q = liquid volume flow rate per unit width of the plate, cm^3/cm s
u = velocity of the liquid film, cm/s
u^+ = dimensionless liquid velocity, see Equation (5)
u_* = friction velocity, cm/s
v_g = gas velocity, m/s
y = coordinate normal to the film flow
y^+ = dimensionless distance from the wall, see Equation (5)

Greek Letters

β = dimensionless interfacial shear
$\dot{\gamma}$ = rate of shear, s^{-1}
δ_0 = film thickness, cm
$\delta_0{}^+$ = value of y^+ at $y = \delta_0$
ρ = density, g/cm^3
σ = defined by Equation (9)
τ = shear stress, dyne/cm^2
τ_0 = wall shear stress, dyne/cm^2

Subscripts

L = liquid phase
G = gas phase

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Grouping of Many Species Each Consumed by Two Parallel First-Order Reactions

The behavioral features of a mixture containing many species each of which participates in two competing parallel first-order reactions may deviate significantly from those of the individual species. For example, the grouped selectivity may depend on the conversion and attain up to N-2 extremal values where N is the number of the reactants in the mixture. The kinetics of the grouped species depends on the composition of the feed and can be of an unconventional functional form. The use of empirical grouped kinetics may lead to unexpected pitfalls. For example, grouped rate expressions based on experiments carried out in one reactor may not be adequate for predicting the behavior in a reactor with a different residence time distribution.

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SCOPE

In many industrial processes the feed contains a mixture of many components which react simultaneously. Because of inherent experimental errors as well as analytical and computational difficulties, it is usually impossible to develop process models which describe the exact kinetics of each of the participating species. These difficulties are usually overcome by grouping together various species and treating them as pseudo components. The key to successful aggregation is the decision as to which species should be grouped together in order to attain a suitable balance between the predictive capabilities of the model and the experimental and computational efforts needed to determine the parameters in the model. Moreover, it is desirable to group the species so that the parameters in the model will be rather insensitive to changes in the composition of the feed (Weekman, 1974). Very little information is available at present concerning the sensitivity and pitfalls involved in a grouping procedure. A very elegant analysis by Wei and Kuo (1969), which was extended by Ozawa (1973), indicates that it is usually impossible to obtain an exact description of many monomolecular reactions by a lumped linear reaction network. Studies of the pitfalls and magnitude of errors involved in the use of empirical rate expressions for grouping many independent single or consecutive reactions were presented by Hutchinson and Luss (1970, 1971) and Golikeri and Luss (1972, 1974).

Our aim here is to examine the special behavioral features of a mixture containing many species each of which participates in two competing parallel first-order reactions. This information is used to point out some of the pitfalls of empirical grouped rate expressions, which can have important implications on the design, optimization, and control of chemical reactors. In addition, we analyze the types of rate expressions which are suitable for describing the conversion and selectivity of the grouped species and determine their dependence on the composition of the mixture.

CONCLUSION AND SIGNIFICANCE

Significant differences may exist between the behavior of the individual reacting species and that of the grouped species. For example, when the kinetics of each species is of first order, the exact rate expression describing the behavior of the mixture depends on its initial composition and is often of an unconventional form. The kinetics of the system can be described exactly by first-order rate expressions only when the reactivity of all the components is equal [Equation (30) is satisfied]. Similarly, the selectivity of the products obtained from any single component is an intrinsic constant which is independent of the conversion level. However, the selectivity of the grouped species may be a rather complicated function of the conversion. Numerical calculations indicate that the selectivity vs. conversion graph may attain up to N-2 extremal values for a mixture containing N species. It is proven that when the rate constants are subject to certain constraints [Equation (38) and (39)] the selectivity is a monotonic increasing function of conversion, while if (38) and (41) are satisfied the selectivity is a monotonic decreasing function of conversion.

It is shown that grouped kinetic rate expressions obtained in one reactor may not be applicable to another reactor with a different residence time distribution. For example, while a second-order rate expression may describe exactly the conversion of the grouped species in a plug flow reactor, a different rate expression may be needed for describing the conversion in an ideally mixed continuous stirred-tank reactor. Moreover, the dependence of the grouped selectivity on conversion is also sensitive to the residence time distribution of the reactor (Figure 4) even though the selectivity of the products obtained from a single component is independent of conversion and of the type of reactor used for carrying out the reaction.

The grouping procedure may lead to pitfalls especially when the aggregates contain species with rather different kinetic behavior. Consequently, in order to enhance the reliability of the kinetic model, it is desirable to form pseudo components which contain only species with similar kinetic behavior.

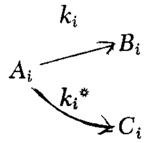
In recent years significant progress in the area of model discrimination and parameter estimation of simple kinetic networks has been made. However, the analysis and understanding of grouped complex reaction networks is still at its infancy despite its importance in the development of process models. Aris and Gavalas (1966) and Aris (1968) were among the first to analyze the behavior of grouped reaction networks. Wei and Kuo (1969) derived criteria for exact lumping of monomolecular reacting systems and their work was extended by Ozawa (1973), Bailey (1972), and Liu and Lapidus (1973). Unfortunately, this analysis is applicable only to systems in which the kinetics of both the individual and grouped species is of first order and requires kinetic information which is usually unavailable.

In industrial applications it is common to use empirical lumped rate expressions which often differ in their functional form from that applicable to the individual species. These models are most useful for design and control applications. A comprehensive review of grouped process models has been presented by Weekman (1974). The major deficiency of these empirical models is that their functional form as well as the associated parameters may be sensitive to changes in the composition of the feed and may fail to predict some behavioral features of the system.

A proper grouped model has to accomplish an adequate balance between the required predictive capabilities and the experimental and computational effort required to determine the corresponding kinetic parameters. The composition of the grouped species is often subject to analytical and economical constraints, which may require grouping species with rather different activities and selectivities. A rational development and use of a grouped process model requires information about the special behavioral features of reacting mixture and the factors which affect it. The aim of this work is to obtain such information for a specific reaction network.

EXACT GROUPED KINETICS

Consider a reaction mixture containing N species each of which participates in two competing parallel irreversible first-order reactions



$i = 1, 2, \ldots, N$

Assuming that the feed does not contain any products, the concentrations of the grouped species are

$$\overline{A}(t) = \sum_{i=1}^{N} A_i(t) = \sum_{i=1}^{N} A_i(0)\, e^{-(k_i+k_i^*)t} \qquad (1)$$

$$\overline{B}(t) = \sum_{i=1}^{N} B_i(t)$$

$$= \sum_{i=1}^{N} \frac{k_i}{k_i + k_i^*} A_i(0)\,(1 - e^{-(k_i+k_i^*)t}) \qquad (2)$$

$$\overline{C}(t) = \sum_{i=1}^{N} C_i(t)$$

$$= \sum_{i=1}^{N} \frac{k_i^*}{k_i + k_i^*} A_i(0)\,(1 - e^{-(k_i+k_i^*)t}) \qquad (3)$$

For this reaction network, the conversion of $\overline{A}$ as well as the yields of $\overline{B}$ and $\overline{C}$ are independent of the initial concentration of $\overline{A}(0)$. The concentration of $\overline{A}(t)$ is a unique monotonic decreasing function of time. Consequently, the exact rate of conversion can be expressed as

$$\frac{dx}{dt} = k_1 f_1(x) \qquad (4)$$

where

$$x = 1 - \overline{A}(t)/\overline{A}(0) \qquad (5)$$

The functional form of f_1 and the associated parameters depends on the spectrum of the rate constants $k_i + k_i^*$ (Aris, 1968; Hutchinson and Luss, 1970). Similarly, the yields of $\overline{B}(t)$ and $\overline{C}(t)$ are monotonic increasing functions of time and their exact rate can be expressed as

$$\frac{dy}{dt} = k_2 f_2(x) \qquad (6)$$

$$\frac{dz}{dt} = k_3 f_3(x) \qquad (7)$$

where y and z are the yields of B and C, respectively.

$$y = \overline{B}(t)/\overline{A}(0); \quad z = \overline{C}(t)/\overline{A}(0) \qquad (8)$$

Conservation of species requires that

$$k_1 f_1(x) = k_2 f_2(x) + k_3 f_3(x) \qquad (9)$$

When a single species is consumed by two parallel first-order reactions

$$f_1 = f_2 = f_3 \qquad (10)$$

In special cases (10) is still valid for reaction mixtures and the exact kinetics of the three grouped species can be represented by the same kinetic expression (not necessarily of first order). Under these conditions (9) and (10) imply that

$$k_1 = k_2 + k_3 \qquad (11)$$

and that the selectivity

$$S(t) = \frac{\overline{B}(t)}{\overline{C}(t)} = \frac{k_2}{k_3} \qquad (12)$$

is independent of the conversion level. When (12) is not valid for all conversion levels, (10) can not be valid and different rate expressions are needed to describe the exact behavior of the three grouped species. We conclude that when the selectivity depends on the conversion, use of (10) yields at best an approximation of the exact kinetics of $\overline{A}$, $\overline{B}$, and $\overline{C}$.

The above conclusions will be illustrated by two examples of mixtures containing very many species so that a continuous representation of the grouped species can be used and instead of (1) we can write

$$\overline{A}(t) = \int_0^\infty \int_0^\infty A(k, k^*)\, e^{-(k+k^*)t}\, dk\, dk^* \qquad (13)$$

where $A(k, k^*)$ is the initial concentration of A with rate constants k and k^* bounded in $(k, k + dk)$ and $(k^*, k^* + dk^*)$, respectively.

We consider first a case for which $A(k, k^*)$ is the product of two Gamma distributions

$$\frac{A(k, k^*)}{\overline{A}(0)} = \left(\frac{k^{\alpha_1} \exp(-k\beta)\beta^{\alpha_1+1}}{\Gamma(\alpha_1 + 1)}\right) \left(\frac{k^{*\alpha_2} \exp(-k^*\beta)\beta^{\alpha_2+1}}{\Gamma(\alpha_2 + 1)}\right) \qquad (14)$$

Substitution of (14) into (13) yields

$$x = \frac{\overline{A}(t)}{\overline{A}(0)} = \left(1 + \frac{t}{\beta}\right)^{-(\alpha_1+\alpha_2+2)} \qquad (15)$$

Differentiation of (15) yields

$$\frac{dx}{dt} = (\hat{k}_1 + \hat{k}_2)(1 - x)^n \qquad (16)$$

where

$$\hat{k}_1 = \frac{\alpha_1 + 1}{\beta} \quad \hat{k}_2 = \frac{\alpha_2 + 1}{\beta} \qquad (17)$$

$$n = 1 + \frac{1}{\alpha_1 + \alpha_2 + 2}$$

Similarly, we can show that in this case

$$\frac{dy}{dt} = \hat{k}_1 (1 - x)^n \qquad (18)$$

$$\frac{dz}{dt} = \hat{k}_2 (1 - x)^n \qquad (19)$$

Here (10) is satisfied and the selectivity

$$S(t) = \frac{\overline{B}(t)}{\overline{C}(t)} = \frac{\hat{k}_1}{\hat{k}_2} = \frac{\alpha_1 + 1}{\alpha_2 + 1} \qquad (20)$$

is independent of the conversion but depends on the distribution of the various species in the feed. It should be noted that when the exact kinetics is of nth order, n is usually larger than unity as both α_1 and α_2 are non-negative constants.

We will now consider a mixture for which

$$\frac{A(k, k^*)}{\overline{A}(0)} = \frac{k^{\alpha} \exp(-k\beta)\beta^{\alpha+1}}{\Gamma(\alpha + 1)}\, \delta(k^* - M) \qquad (21)$$

Substitution of (21) into (13) yields

$$1 - x(t) = e^{-Mt}\left(1 + \frac{t}{\beta}\right)^{-(\alpha+1)} = g(t) \qquad (22)$$

Differentiation of (22) yields

$$\frac{dx}{dt} = \left(M + \frac{\alpha + 1}{t + \beta}\right)(1 - x) \qquad (23)$$

The conversion $x(t)$ is a unique monotonic decreasing function of the time. Thus, we can in principle invert (22) to obtain

$$t = g^{-1}(x) \qquad (24)$$

Substitution of (24) into (23) enables us to express the exact conversion rate as an autonomous function of the conversion. The resulting kinetic expression however, will, be of an unconventional form. The rate of formation of $\overline{B}$ and $\overline{C}$ can be computed from

$$\frac{dy}{dt} = \int_0^\infty \frac{k^{\alpha+1}\exp[-k\beta - (M+k)t]\beta^{\alpha+1}}{\Gamma(\alpha+1)}\,dk = \frac{(\alpha+1)(1-x)}{\beta + t} \qquad (25)$$

$$\frac{dz}{dt} = \int_0^\infty \frac{Mk^{\alpha}\exp[-k\beta - (M+k)t]\beta^{\alpha+1}}{\Gamma(\alpha+1)}\,dk = M(1-x) \qquad (26)$$

Here (10) is not satisfied and the exact rate expression of each of the species is of a different functional form. According to (25) and (26),

$$\frac{dy}{dz} = \frac{d\overline{B}}{dC} = \frac{\alpha + 1}{M(t + \beta)} \qquad (27)$$

and the selectivity depends on the time, or equivalently on the conversion.

SELECTIVITY OF THE GROUPED SPECIES

When a single species is consumed by two parallel first-order reactions, the selectivity is an intrinsic constant. This is no more true in general for a reacting mixture containing many species. Here

$$\frac{\overline{B}}{C} = \frac{\displaystyle\sum_{i=1}^{N} \frac{k_i A_i(0)}{k_i + k_i^*}\,(1 - \exp[-(k_i + k_i^*)t])}{\displaystyle\sum_{i=1}^{N} \frac{k_i^* A_i(0)}{k_i + k_i^*}\,(1 - \exp[-(k_i + k_i^*)t])} \qquad (28)$$

and the selectivity is a constant only in special cases. One of these occurs when

$$\frac{k_i}{k_i^*} = r \quad \text{for all} \quad i = 1, 2, \ldots, N \qquad (29)$$

This is the only case for which the selectivity is independent of both the conversion and the distribution of the components in the feed. Another interesting case occurs when

$$k_i + k_i^* = K \quad \text{for all} \quad i = 1, 2, \ldots, N \qquad (30)$$

Here the aggregated system can be represented exactly as a pseudo ternary system with first-order kinetics

$$\frac{dx}{dt} = (I_B + I_C)(1 - x) \qquad (31)$$

$$\frac{dy}{dt} = I_B(1 - x) \qquad (32)$$

$$\frac{dz}{dt} = I_C(1 - x) \qquad (33)$$

where I_B and I_C are the normalized initial rate of formation of $\overline{B}$ and $\overline{C}$, namely,

$$I_B = \sum_{i=1}^{N} k_i A_i(0)/\overline{A}(0) \qquad (34)$$

$$I_C = \sum_{i=1}^{N} k_i^* A_i(0)/\overline{A}(0) \qquad (35)$$

The corresponding selectivity

$$S(t) = \frac{\overline{B}(t)}{C(t)} = \frac{I_B}{I_C} \qquad (36)$$

is independent of the conversion level but depends on the composition of the feed. It should be noted that the invariance of the selectivity with conversion does not imply, in general, that the kinetics of the grouped species can be described by a first-order expression.

Equation (28) implies that

$$\operatorname*{Min}_i\left(\frac{k_i}{k_i^*}\right) < S(t) < \operatorname*{Max}_i\left(\frac{k_i}{k_i^*}\right) \qquad (37)$$

When the mixture contains species with rather different intrinsic selectivities (k_i/k_i^*), the above bounds are very conservative. Unfortunately, due to the large number of parameters which affect $\overline{S}(t)$, it is not possible to derive general rules about the magnitude or even the sign of the changes in $\overline{S}(t)$ except for special cases. For example, we prove in Appendix A that if we arrange the reactants in the order of increasing activities, namely,

$$k_i + k_i^* \leqq k_{i+1} + k^*_{i+1} \quad i = 1, 2, \ldots, N - 1 \qquad (38)$$

and if the intrinsic selectivities are a monotonic decreasing function of the index, that is,

$$\frac{k_i}{k_i^*} \geqq \frac{k_{i+1}}{k^*_{i+1}} \quad i = 1, 2, \ldots, N - 1 \qquad (39)$$

then

$$\frac{dS}{dt} \geqq 0 \qquad (40)$$

for $t \geqq 0$. On the other hand, if

$$\frac{k_i}{k_i^*} \leqq \frac{k_{i+1}}{k^*_{i+1}} \quad i = 1, 2, \ldots, N - 1 \qquad (41)$$

then

$$\frac{dS}{dt} \leqq 0 \qquad (42)$$

Consequently, when the mixture contains only two species either (39) or (41) must be satisfied and $S(t)$ is a monotonic function of time or conversion. When the mixture contains N species, the intrinsic selectivities of the various species may be arranged in $N!$ different ways according to their magnitude and it is not possible to predict the behavior of $S(t)$ in general. Our calculations indicate that $S(t)$ may have at most $N - 2$ extremum points, but we have not been able to prove this result.

In order to illustrate some of the above points, consider again the mixture for which the initial composition is described by (21). Here (38) is satisfied and conse-

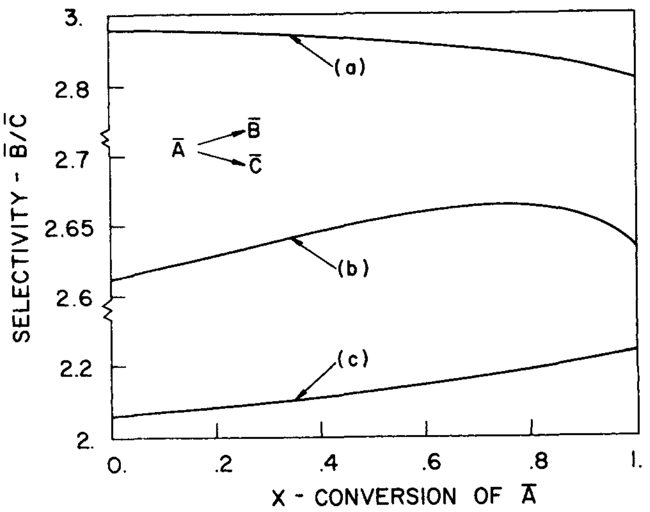


Fig. 1. The dependence of the grouped selectivity on conversion for a mixture containing three reactants. Feed composition reported in Table 1.

quently the selectivity must be a monotonic decreasing function of time. By substitution of (22) into (25) and (26) and integration, we obtain

$$S(t) = \frac{\bar{B}(t)}{\bar{C}(t)} = \frac{(\alpha + 1)}{M\beta} \, \frac{\displaystyle\int_0^t e^{-Mt'}\left(1 + \frac{t'}{\beta}\right)^{-(\alpha+2)} dt'}{\displaystyle\int_0^t e^{-Mt'}\left(1 + \frac{t'}{\beta}\right)^{-(\alpha+1)} dt'} \qquad (43)$$

Assuming α to be an integer, the two limiting selectivities for short and long residence times are

$$S(0) = \frac{\alpha + 1}{M\beta} \qquad (44)$$

$$S(\infty) = \frac{(\alpha + 1)}{M\beta} \, \frac{E_{\alpha+2}(M\beta)}{E_{\alpha+1}(M\beta)} \qquad (45)$$

where $E_n(x)$ denotes the exponential integral (Abramowitz and Stegun, 1964, p. 228)

$$E_n(x) = \int_1^\infty \frac{e^{-xt}}{t^n} dt \qquad (46)$$

Figures 1 and 2 illustrate the influence of changes in the initial composition of a mixture containing three species on the dependence of the selectivity on the conversion. The three different initial compositions which are described in Table 1 yield three different patterns of dependence. It is seen that the selectivity can be either a monotonic increasing or decreasing function of the conversion, or may attain an extremal value. The extremal selectivity may be either a maximal or minimal value and need not be bounded by the two limiting selectivities for low and high conversion.

Table 1. Distribution of the Rate Constants and Feed Composition for the Examples Shown in Figures 1 to 3

Figure	i	k_i	k_i^*	$A_i(0)$ case a	case b	case c
	1	.9	.6	.028	.1	.4
1	2	.8	.2	.3	.3	.3
	3	.35	.15	.4	.4	.4
	1	1.6	.4	1.4	.1	.03
2	2	0.7	.5	0.4	.4	.4
	3	0.6	.2	0.3	.3	.3
	1	1.6	.4	.1		
3	2	0.7	.5	.4		
	3	0.6	.2	.3		
	4	0.05	.25	.01		

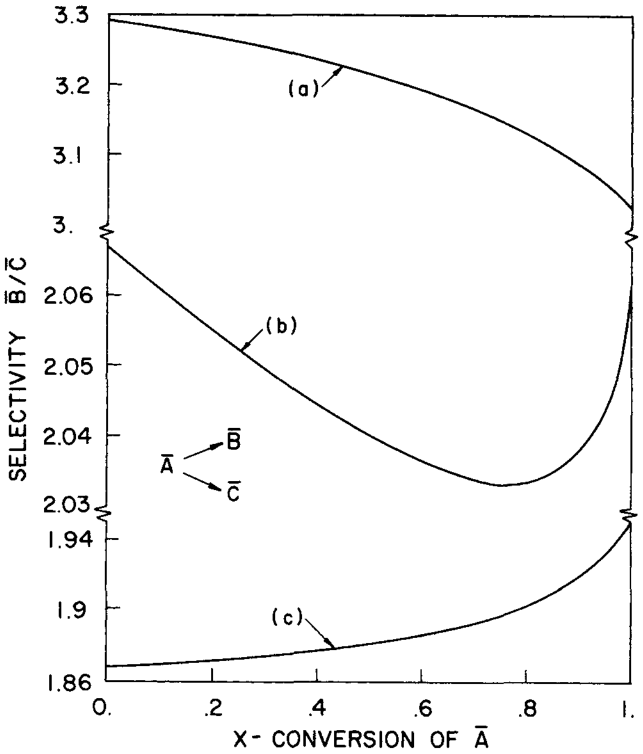


Fig. 2. The dependence of the grouped selectivity on conversion for a mixture containing three reactants. Feed composition reported in Table 1.

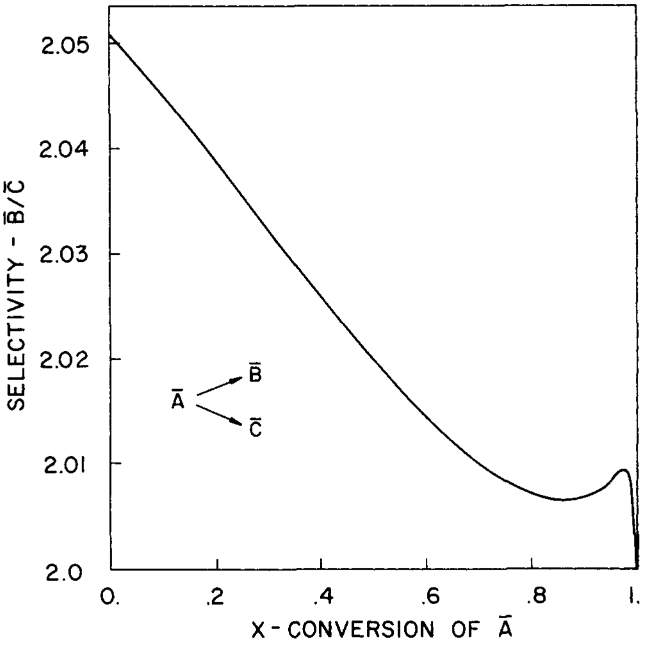


Fig. 3. The dependence of the grouped selectivity on conversion for a mixture containing four species. Feed composition reported in Table 1.

When the reaction mixture contains more than three species, dependence of the selectivity on the conversion may become more intricate. We have already mentioned that according to our numerical calculations the selectivity of a mixture containing N species may attain up to $N - 2$ extremal values. Figure 3 describes an example for which two extremal values are attained for a mixture containing four species.

PITFALLS OF LUMPING

The design and control of chemical reactors requires use of process models which are usually based on kinetic information obtained in a laboratory or pilot plant reactor. The configuration and residence time distribution (RTD) of this reactor may be different from that of the industrial reactor. For example, a kinetic model based on a spinning basket reactor may be used to design a packed bed reactor. The above procedure may lead to pitfalls when applied to mixtures containing many reactants with a wide distribution of rate constants. In order to illustrate this point consider first a reaction mixture for which

$$k_i^* = rk_i \quad \text{for all} \quad i = 1, 2, \ldots, N \tag{47}$$

and

$$\frac{A(k_i + k_i^*)}{\bar{A}(0)} = \beta e^{-\beta(k_i + k_i^*)} = \beta e^{-\beta K} \tag{48}$$

where

$$K = k_i + k_i^* = k_i(1 + r) \tag{49}$$

When this mixture reacts in a plug flow tubular reactor

$$1 - x = \int_0^\infty \beta e^{-K(\beta + t)}\, dK = \frac{1}{1 + t/\beta} \tag{50}$$

and differentiation of (50) yields

$$\frac{dx}{dt} = \int_0^\infty K\beta e^{-K(\beta + t)}\, dK = \frac{1}{\beta}(1 - x)^2 \tag{51}$$

Hence, a second-order rate expression describes exactly the conversion in a batch or plug flow tubular reactor. When the same reaction is carried out in an ideally mixed continuously stirred-tank reactor (CSTR) with a residence time τ,

$$\frac{A_i(\tau)}{A_i(0)} = \frac{1}{1 + K_i\tau} \quad i = 1, 2, \ldots, N \tag{52}$$

and the grouped conversion is

$$1 - x = \frac{\bar{A}(\tau)}{\bar{A}(0)} = \int_0^\infty \frac{\beta e^{-\beta K}}{1 + K\tau}\, dK = \frac{\beta}{\tau} e^{\frac{\beta}{\tau}} E_1\left(\frac{\beta}{\tau}\right) \tag{53}$$

When a single second-order reaction is carried out in an ideally mixed CSTR,

$$k_2 = \frac{x}{\tau(1 - x)^2} \tag{54}$$

where k_2 is the corresponding rate constant. Substitution of (53) into (54) yields

$$k_2 = \frac{1 - \frac{\beta}{\tau} e^{\frac{\beta}{\tau}} E_1\left(\frac{\beta}{\tau}\right)}{\tau\left[\frac{\beta}{\tau} e^{\frac{\beta}{\tau}} E_1\left(\frac{\beta}{\tau}\right)\right]^2} \tag{55}$$

indicating that k_2 is no more a constant but is a monotonic increasing function of the residence time, or equivalently of the conversion. When the conversion is very low, k_2 is equal to $1/\beta$ in exact agreement with the results obtained for the plug reactor (51). However, at conversion levels of 0.1, 0.5, 0.9, and 0.95, $k_2\beta$ is equal to 1.009, 1.22, 3.065, and 4.96, respectively. Thus, the rate constant determined in a plug flow reactor can not be used to predict the conversion in a CSTR.

It is of interest to note that if we make the wrong assumption that the CSTR is completely segregated, then by the use of the grouped kinetic expression (51) we obtain

$$1 - x = \frac{1}{\tau}\int_0^\infty \frac{e^{-t/\tau}}{1 + t/\beta}\, dt = \frac{\beta}{\tau} e^{\frac{\beta}{\tau}} E_1\left(\frac{\beta}{\tau}\right) \tag{56}$$

which agrees exactly with (53). This is a fortuitous agreement which would not hold for reaction mixtures with different initial compositions.

We conclude that use of empirical grouped rate expressions may lead to unexpected pitfalls in predicting the performance of a reactor from kinetic information obtained from one with a different RTD. For a mixture in which many first-order reactions occur, the above pitfalls may be obviated by use of the RTD to predict conversion. Specifically, x_r, the grouped conversion in a reactor with a residence distribution function $E_r(\theta)$, can be computed directly from x_p, the grouped conversion attained in a plug flow or batch reactor using the relation

$$x_r = \int_0^\infty x_p(\theta)\, E_r(\theta)\, d\theta \tag{57}$$

The use of reactors with different RTD may affect also the selectivity. For example, consider the reaction mixture defined by (21) with $\alpha = 0$. The values of x, y, and z for a plug flow reactor can be computed from (22) and (25) and (26). When the same mixture reacts in a CSTR,

$$\begin{aligned} 1 - x &= \int_0^\infty \frac{\beta e^{-\beta k} dk}{1 + (k + M)\tau} \\ &= \frac{\beta}{\tau} e^{\beta\left(\frac{1}{\tau} + M\right)} E_1\left[\beta\left(\frac{1}{\tau} + M\right)\right] \end{aligned} \tag{58}$$

Similarly

$$z = \tau \int_0^\infty \frac{M\beta e^{-k\beta} dk}{1 + (k + M)\tau} = M\tau(1 - x) \tag{59}$$

and

$$y = x - z \tag{60}$$

A comparison of the dependence of the selectivity (y/z) for this reaction mixture on the conversion in a CSTR and plug flow reactor is presented in Figure 4. It is seen that at the same conversion level the selectivity in the plug flow reactor exceeds that attained in the CSTR. Thus, prediction of the grouped selectivity in any reactor from experiments performed in a reactor with a different RTD may lead to unexpected pitfalls.

It should be pointed out that changes in the configuration of a chemical reactor may lead to additional pitfalls when, as often is the case, the kinetic model does not account for all possible reaction paths. For example, when catalytic reactions are carried out in a fluidized bed or in a rotating basket reactor, homogeneous side reactions may have an important influence on the yield and conversion. On the other hand, these side reactions may be unimportant when the reaction is carried out in a packed-bed reactor. This discussion is not concerned with such pitfalls.

The empirical kinetics are often nonlinear. Hence, they predict that the conversion of the grouped species depends on the initial total concentration $\bar{A}(0)$. This is an erroneous result since the conversion of any of the species, which is consumed by parallel first-order reactions, is independent

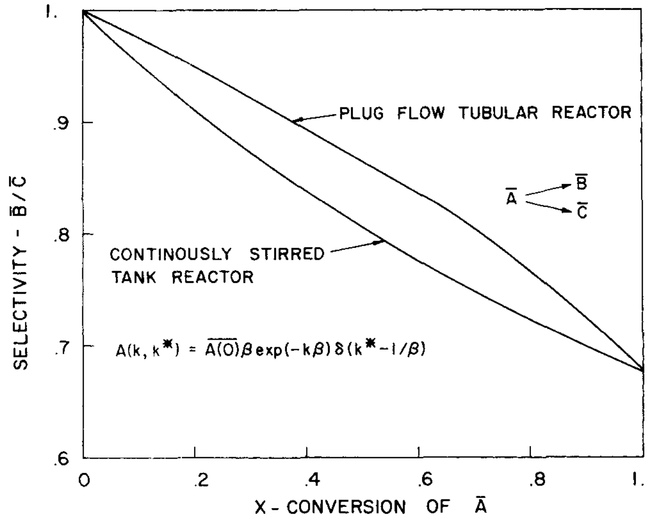


Fig. 4. The dependence of the grouped selectivity on the conversion in a tubular reactor and a CSTR. The graphs are independent of the value of β.

of initial concentration. Thus, it is necessary to adjust the rate constant of an empirical nonlinear kinetic expression when the concentration of the feed is changed. Similarly, the grouped selectivity of a reaction mixture, in which many first-order reactions occur, is independent of $\overline{A}(0)$ even though it may depend on the conversion. It is therefore important to select rate expressions which preserve this property. One way of avoiding these pitfalls is to describe the behavior of the grouped species by linear kinetics. We have already shown that linear kinetics describe exactly the grouped concentration when the reactivities of all the species are the same, that is, (10) is satisfied. Thus, it is desirable to group together species which have about the same reactivities.

CONCLUDING REMARKS

The specific examples presented here are somewhat extreme as we group together components with widely different rate constants into a pseudo ternary reaction network. In such cases the uncertainty and pitfalls involved in the application of the model can be diminished by splitting the pseudo components into subgroups containing species with similar kinetic behavior.

The individual rate constants of all the species are usually not known and the grouping into pseudo components is usually based on some other properties which can be determined more easily. So far the selection of the proper property for classifying the various aggregates is based on the experience and ingenuity of the experimentalist. When a certain property is used for grouping the species into pseudo components, the reliability of the derived kinetic model depends on the correlation between that property and the kinetics of the individual components. In certain cases, such as hydrodenitrogenation, a correlation exists between the boiling point of the components and their activity (Retallick, 1964). Consequently, grouping of species according to the boiling temperature range may be adequate. However, in many other reacting systems there exists a very weak, if any, correlation between the boiling point of a species and the kinetics. In these cases, it is of paramount importance to use another property for the grouping of the pseudo components in order to avoid aggregation of species with widely different kinetic behavior. An elegant application of this principle was presented by Jaffe (1974) who noted that the heat of hydrogenation of petroleum compounds depended mainly on the type of the reactive carbon-carbon bond. Assuming that the kinetics of species with the same reactive carbon bond are similar, he developed a successful hydrogenation model grouping species with similar heat of reaction.

We have seen that the behavior of the pseudo components may deviate significantly from that of a single reactant. Therefore, a kinetic model based on the behavior of a representative reactant may lead to unexpected pitfalls in the design. The examples presented here indicate that, when the pseudo component contains species with rather different kinetic behavior, the kinetic expression obtained in one reactor may not be suitable for predicting the conversion and or the selectivity in a reactor with a different residence time distribution. This unique feature of the grouped kinetics has important implications on the design and control of reactors and may be used as a test for the adequacy of the grouping procedure.

It is of practical importance to develop a better understanding of the special behavioral features of grouped species in order to avoid pitfalls during the applications of such models. Moreover, information about the pitfalls of these grouping schemes are useful for attaining a rational balance between the inherent uncertainty of any grouped model and the expense of developing a more detailed and accurate model.

NOTATION

$A(k, k^*)$ = concentration of A with rate constants in $(k, k + dk)$ and $(k^*, k^* + dk^*)$
$A_i(t)$ = concentration of A_i at time t
$\overline{A}(t)$ = concentration of all $A_i(t)$ species
$B_i(t)$ = concentration of B_i at time t
$\overline{B}(t)$ = concentration of all $B_i(t)$ species
$C_i(t)$ = concentration of C_i at time t
$\overline{C}(t)$ = concentration of all $C_i(t)$ species
$E_n(x)$ = exponential integral of order n
$E(\theta)$ = residence distribution function
$g(t)$ = the time dependence of the conversion
I_B = normalized initial rate of formation of B
I_C = normalized initial rate of formation of C
k_i = rate constant associated with the formation of $\overline{B}_i$
k_i^* = rate constant associated with the formation of $\overline{C}_i$
$\hat{k}$ = lumped rate constant
K = rate constant defined by (30)
N = number of reacting species
r = ratio of rate constants, defined by (29)
$S(t)$ = selectivity of time t
t = time
x = conversion of $\overline{A}$
y = yield of $\overline{B}$
z = yield of $\overline{C}$

Greek Letters

α = parameter characterizing Gamma distribution
β = parameter characterizing Gamma distribution
θ = variable in residence time distribution
τ = average residence time

Subscripts

i = in ith reaction
B = quantity corresponding to $\overline{B}$
C = quantity corresponding to $\overline{C}$

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APPENDIX A

Proof of (39) to (42)

The selectivity S is defined as

$$S(t) = \frac{\overline{B}(t)}{\overline{C}(t)} = \frac{\sum_{i=1}^{N} B_i(t)}{\sum_{i=1}^{N} C_i(t)} \tag{A1}$$

Differentiation of (A1) yields

$$\overline{C}^2 \frac{dS}{dt} = \sum_{i=1}^{N} C_i \sum_{i=1}^{N} \frac{dB_i}{dt} - \sum_{i=1}^{N} B_i \sum_{i=1}^{N} \frac{dC_i}{dt} \tag{A2}$$

Now

$$C_i \frac{dB_i}{dt} = B_i \frac{dC_i}{dt} = \frac{k_i k_i^* A_i^2(0)}{k_i + k_i^*} X_i(1 - X_i) \tag{A3}$$

where

$$X_i = \exp[-(k_i + k_i^*)t] \tag{A4}$$

Use of (A3) and simple algebraic manipulations enable transformation of (A3) into

$$\overline{C}^2 \frac{dS}{dt} = \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{(k_i k_j^* - k_i^* k_j) A_i(0) A_j(0)}{(k_i + k_i^*)(k_j + k_j^*)} F_{ij} \tag{A5}$$

where

$$F_{ij} = (k_i + k_i^*)X_i + (k_j + k_j^* - k_i - k_i^*)X_i X_j - (k_j + k_j^*)X_j \tag{A6}$$

Note that we order the species such that

$$k_i + k_i^* \leqq k_j + k_j^* \quad \text{for} \quad j > i \tag{A7}$$

and therefore

$$k_j + k_j^* - k_i - k_i^* \geqq 0 \tag{A8}$$

According to Hardy et al. (1934, p. 74), any convex function ψ satisfies the following inequality:

$$\frac{\sum_{i=1}^{N} p_i \psi(y_i)}{\sum_{i=1}^{N} p_i} \geqq \psi \left[\frac{\sum_{i=1}^{N} p_i y_i}{\sum_{i=1}^{N} p_i} \right] \tag{A9}$$

where p is a non-negative function. Substitution of

$$\begin{aligned} p_1 &= k_i + k_i^* \quad p_2 = k_j + k_j^* - k_i - k_i^* \\ y_1 &= k_i + k_i^* \quad y_2 = k_j + k_j^* + k_i + k_i^* \\ \psi(y) &= e^{-yt} \end{aligned} \tag{A10}$$

into (A9) yields

$$\frac{(k_i + k_i^*)X_i + (k_j + k_j^* - k_i - k_i^*)X_j X_i}{k_j + k_j^*} \geqq \exp\left[\frac{-(p_1 y_1 + p_2 y_2)t}{k_j + k_j^*} \right] = X_j \tag{A11}$$

(A11) implies that

$$F_{ij} \geqq 0 \quad \text{for} \quad j > i \tag{A12}$$

Hence, (A5) predicts that (39) implies (40), while (41) guarantees that (42) is valid.

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An Analogy for Heat Transfer with Wavy / Stratified Gas-Liquid Flow

The von Karman analogy between heat transfer and momentum transfer in turbulent fluids is shown to apply to heat transfer through wavy liquid films in horizontal, stratified, gas-liquid flow. Nusselt numbers predicted from the analogy are shown to be in good agreement with experimental data for air-water flows involving three-dimensional wavy films and large-amplitude roll waves. The Nusselt numbers encountered with these turbulent water films are found to be in the same range as those associated with condensation of organics in horizontal tubes under stratified flow conditions.

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