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Collective Behavior of Many Langmuir–Hinshelwood Reactions

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An approximate expression for the collective behavior of many Langmuir–Hinshelwood reactions is derived. The derivation is based on the assumption that all the reactants not only have comparable reactivities but also comparable adsorptivities. Comparison with exact results shows excellent agreement over a reasonably broad range of kinetic parameters. The expression can be used for data analysis and correlation. © 1991 Academic Press, Inc.

Recently, there has been considerable interest in the problem of predicting the collective behavior of many *nonlinear* reactions (*1–10*). This was motivated mainly by two factors. One is that in many practical situations it is the collective behavior, not the individual behavior, that matters (*11*). For example, in industrial hydrodesulfurization process, one cares only about the reduction of total sulfur, not of the individual sulfur-containing species. The other factor is that while the problem of finding the collective behavior of linear kinetics (first order) had already been solved many years ago (*12–15*), the more general case where the underlying kinetics are nonlinear have presented some mathematical difficulties (*1*).

The purpose of this work was to derive an approximate, closed-form expression for the collective behavior of many Langmuir–Hinshelwood (LH) kinetics. This problem has been treated for situations where the number of reactants is so large that the system can be approximated by a continuum (*2, 4–6, 10*). We do not invoke this assumption here. Rather, we assume that all the reactants have comparable reactivities and also comparable adsorptivities. With this assumption the problem becomes amenable to a perturbative analysis. The result may be used for data analysis and/or correlation, Li and Ho (*9*) used a similar approach to lump bimolecular reactions of comparable rates.

PROBLEM STATEMENT

Consider the following class of LH kinetics in an isothermal system (batch or plug-flow reactors) having N different reactants. The mass balance equations are

$$\frac{d\tilde{c}_i}{dt} = -\frac{k_i'\tilde{K}_i\tilde{c}_i}{1+\sum_{i=1}^{N}\tilde{K}_i\tilde{c}_i}$$

$$i = 1, 2, \cdots, N; \quad t = 0, \quad \tilde{c}_i = \tilde{c}_{if}, \qquad (1)$$

where k_i' and $\tilde{K}_i$ are the surface rate constant and adsorption equilibrium constant, respectively.

The concentrations of the total reactant *lump* at time t and zero are, respectively,

$$\tilde{C} = \sum_{i=1}^{N}\tilde{c}_i \quad \tilde{C}_f = \sum_{i=1}^{N}\tilde{c}_{if}, \qquad (2)$$

where $\tilde{C}_f$ is a finite, measurable quantity. Our task is to find $\tilde{C}$, the lump, as a function of t. Upon summing over i and letting $\tilde{k}_i = k_i'\tilde{K}_i$, Eq. (1) becomes

$$\frac{d\tilde{C}}{dt} = -\frac{\sum_{i=1}^{N}\tilde{k}_i\tilde{c}_i}{1+\sum_{i=1}^{N}\tilde{K}_i\tilde{c}_i}. \qquad (3)$$

It should be pointed out that the present problem may be discussed in a different context: $d\tilde{C}/dt$ may be thought of as the total

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reaction rate over an ensemble of energetically heterogenous catalytic sites. The coupled differential equations represented by Eqs. (1) and (3) are intractable analytically. In what follows we seek an approximate solution based on the observation that the lumped species are in general chemically similar.

PERTURBATIVE ANALYSIS

In practice, it is at the discretion of the kineticist as to how the various species should be lumped. One way to render the problem perturbative is to select a lump whose constituents have comparable rate constants and, *in addition,* comparable adsorpton coefficients. In so doing, we can decompose $\tilde{k}_i$ and $\tilde{K}_i$ into "base" and "deviatoric" components, that is

$$\tilde{k}_i = \bar{k} + k_i, \quad |k_i| \ll \bar{k}, \tag{4}$$

$$\tilde{K}_i = \bar{K} + K_i, \quad |K_i| \ll \bar{K}, \tag{5}$$

where the base components are average values defined as

$$\bar{k} = \frac{\sum \tilde{k}_i}{N}, \quad \bar{K} = \frac{\sum \tilde{K}_i}{N}. \tag{6}$$

To proceed further, we define the following nondimensional quantities:

$$\begin{array}{lll} c_i = \dfrac{\tilde{c}_i}{\tilde{C}_\mathrm{f}} & c_{i\mathrm{f}} = \dfrac{\tilde{c}_{i\mathrm{f}}}{\tilde{C}_\mathrm{f}} & \tau = \bar{k}t \\ C = \dfrac{\tilde{C}}{\tilde{C}_\mathrm{f}} & \mu = \bar{K}\tilde{C}_\mathrm{f} & \alpha_i = \dfrac{k_i}{\bar{k}} \\ \beta_i = \dfrac{K_i}{\bar{K}} & \alpha = \max\limits_i |\alpha_i| & \beta = \max\limits_i |\beta_i| \\ & \lambda_i = \dfrac{\alpha_i}{\alpha} & \nu_i = \dfrac{\beta_i}{\beta}. \end{array} \tag{7}$$

Thus, α and β are measures of the maximum spreads of $\tilde{k}_i$ and $\tilde{K}_i$, respectively. By means of Eq. (6), we have

$$\sum_i \alpha_i = \sum_i \beta_i = 0. \tag{8}$$

And we can recast Eqs. (1) and (3) as

$$\frac{dc_i}{d\tau} = -\frac{(1 + \alpha\lambda_i)\, c_i}{1 + \mu(C + \beta \sum_i \nu_i c_i)} \tag{9}$$

$$\frac{dC}{d\tau} = -\frac{C + \alpha \sum_i \lambda_i c_i}{1 + \mu(C + \beta \sum_i \nu_i c_i)} \tag{10}$$

with the initial conditions

$$\tau = 0, \quad c_i = c_{if}, \quad C = 1. \tag{11}$$

The parameters α and β are both small and of comparable magnitudes. Our task now is to find an approximate expression for C as a function of τ.

The solutions to Eqs. (9) and (10) for small α and β can be sought in terms of the expansions

$$c_i = c_{io} + \alpha u_{i1} + \beta u'_{i1} + \text{hot} \tag{12}$$

$$C = C_0 + \alpha U_1 + \beta U'_1 + \text{hot}, \tag{13}$$

where hot stands for higher-order terms and

$$C_0 = \sum_{i=1}^{N} c_{i0}, \quad U_m = \sum_{i=1}^{N} u_{im},$$

$$U'_m = \sum_{i=1}^{N} u'_{im}; \quad m = 1, 2, \cdots, N. \tag{14}$$

Substituting Eqs. (12) and (13) into Eqs. (9) and (10) and equating coefficients of like powers of α and β, we obtain a set of perturbation equations, the first six of which are

$$\frac{dc_{i0}}{d\tau} = -\frac{c_{i0}}{1 + \mu C_0} \tag{15}$$

$$\frac{du_{i1}}{d\tau} = -\frac{u_{i1} + \lambda_i c_{i0}}{1 + \mu C_0} + \frac{\mu c_{i0} U_1}{(1 + \mu C_0)^2} \tag{16}$$

$$\frac{du'_{i1}}{d\tau} = -\frac{u'_{i1}}{1 + \mu C_0} + \frac{\mu c_{i0}(U'_1 + \sum \nu_i c_{i0})}{(1 + \mu C_0)^2} \tag{17}$$

$$\frac{dC_0}{d\tau} = -\frac{C_0}{1 + \mu C_0} \tag{18}$$

$$\frac{dU_1}{d\tau} = -\frac{U_1 + \sum \lambda_i c_{i0}}{1 + \mu C_0} + \frac{\mu U_1 C_0}{(1 + \mu C_0)^2} \tag{19}$$

$$\frac{dU'_1}{d\tau} = -\frac{U'_1}{1 + \mu C_0} +$$

$$\frac{\mu U_1' C_0 + \mu C_0 \sum \nu_i c_{i0}}{(1 + \mu C_0)^2} \qquad (20)$$

The corresponding initial conditions are

$$\tau = 0, \quad c_{i0} = c_{if}, \quad u_{im} = u_{im}' = 0 \qquad (21)$$

$$C_0 = 1, \quad U_m = U_m' = 0. \qquad (22)$$

Observe that Eqs. (15) and (18) represent the limiting case $\alpha = \beta = 0$ where all the reactants are kinetically indistinguishable. Hence, the mixture behaves like a single component, and Eqs. (15) and (18) of course have the same form.

Equations (15) and (18) can be combined to give

$$\frac{dc_{i0}}{dC_0} = \frac{c_{i0}}{C_0}, \qquad (23)$$

which upon integration yields

$$c_{i0} = c_{if} C_0. \qquad (24)$$

With Eqs. (21) and (24), one can solve Eq. (15) to obtain c_{i0} (so C_0) as an implicit function of τ; namely,

$$\tau = \mu\left(1 - \frac{c_{i0}}{c_{if}}\right) - \ln\frac{c_{i0}}{c_{if}} \qquad (25)$$

$$\tau = \mu(1 - C_0) - \ln C_0. \qquad (26)$$

Equation (26) says that in terms of reaction time for a given conversion, the Langmuir–Hinshelwood kinetics represented by Eq. (18) is a sum of zeroth-order and first-order kinetics.

It follows from Eq. (26) that

$$d\tau = -\left(\mu + \frac{1}{C_0}\right) dC_0. \qquad (27)$$

Substituting Eqs.(27) and (24) into Eq. (19), one can relate C_0 to U_1 by the differential equation

$$\frac{dU_1}{dC_0} = \sigma + \frac{U_1}{C_0} - \frac{\mu U_1}{1 + \mu C_0}, \qquad (28)$$

which is subject to the initial condition

$$C_0 = 1, \quad U_1 = 0. \qquad (29)$$

In Eq. (28) σ is defined as

$$\sigma \equiv \sum_{i=1}^{N} \lambda_i c_{if}. \qquad (30)$$

In the same vein, one can relate C_0 to U_1' as

$$\frac{dU_1'}{dC_0} = \frac{U_1'}{C_0} - \frac{\mu U_1' + \mu\delta C_0}{1 + \mu C_0} \qquad (31)$$

$$C_0 = 1, \quad U_1' = 0 \qquad (32)$$

$$\delta \equiv \sum_{i=1}^{N} \nu_i c_{if}. \qquad (33)$$

The solutions to Eqs. (28) and (31) are, respectively,

$$U_1 = \frac{\sigma C_0}{1 + \mu C_0}[\mu(C_0 - 1) + \ln C_0] \qquad (34)$$

$$U_1' = \frac{\delta\mu C_0(1 - C_0)}{1 + \mu C_0}. \qquad (35)$$

It now follows that the total concentration C at any time can be approximately calculated by the following pair of expressions

$$C \sim C_1 = C_0 + \alpha U_1 + \beta U_1' = C_0 + \frac{C_0}{1 + \mu C_0}[\mu(1 - C_0)(\beta\delta - \sigma\alpha) + \alpha\sigma \ln C_0] \qquad (36)$$

$$\tau = \mu(1 - C_0) - \ln C_0. \qquad (26)$$

Here C_0 and C_1 are zeroth- and first-order approximations to $C(\tau)$, respectively. While $dC_0/d\tau$ can be expressed as a function of C_0 [Eq. (18)], this is not the case for $dC_1/d\tau$. If this were the case, then $dC_1/d\tau = f(C_1)$ can be viewed as an approximate overall kinetic constitutive expression for the mixture as a whole. By contrast, for continuous mixtures, one can derive exact overall kinetics for certain types of LH reactions (*4–6*).

Equation (36) provides a functional form for data correlation, which is independent of the size (the N value) of the mixture. To a first approximation, the overall behavior of the mixture depends parametrically on K, $\sum K_i c_{if}/K$, and $\sum k_i c_{if}/k$. In the absence of such functional form, it is common in practice to empirically fit the C vs τ data by a power-law equation. The problem with this approach is that the power-law parameters depend on the conversion level.

SPECIAL CASES

Explicit expressions for C as a function of τ can be obtained for some limiting cases. For example, when all species are strongly adsorbed, $\mu \gg 1$, we then can simplify Eq. (36) to

$$C \sim 1 - \frac{\tau}{\mu}(1 - \beta\delta + \sigma\alpha). \qquad (37)$$

That is, to a first approximation, C decays linearly as zero-order kinetics. The exhaustion time occurs when $\tau = \tau^* \sim \mu/(1 - \beta\delta + \sigma\alpha) \sim \mu$.

On the other hand, when all the species are weakly adsorbed, $\mu \ll 1$, then

$$C \sim e^{-\tau}(1 - \alpha\sigma\tau), \qquad (38)$$

which departs slightly from first-order behavior over a relatively wide range of conversion ($\alpha\sigma$ is small). Unlike C_0, C_1 is *not* a composite of first- and zero-order kinetics. Note that the exhaustion time in this case occurs at $\tau = \tau^* \sim 1/\alpha\sigma$.

NUMERICAL RESULTS

To assess the accuracy of the perturbation solution, we computed the exact solution by numerically integrating Eqs. (9) and (10) using a fourth-order Runge–Kutta method. It is to this that the perturbation solution is compared. For simplicity, all the calculations were made for $N = 3$ and the following ν_i and λ_i values: $(\nu_1, \nu_2, \nu_3) = (0.34, -0.19, -0.15)$; $(\lambda_1, \lambda_2, \lambda_3) = (0.28, 0.16, -0.44)$.

Example 1

Here we let $\alpha = 0.2$, $\beta = 0.15$, and $\mu = 1$. The feed composition is $(c_{if}) = (0.17, 0.42, 0.41)$. Table 1 compares the results. The second column lists the exact solution calculated numerically. The third and fourth columns list the corresponding values of C_1 and C_0, respectively. One sees that the approximate expression, Eq. (36), gives almost the exact results. Even the zeroth-order approximation is quite accurate.

TABLE 1

Comparison of Numerical and Perturbaton Solutions
($\alpha = 0.2$, $\beta = 0.15$)

τ	C_{exact}	C_1	C_0
0	1.000000	1.000000	1.000000
0.3	0.856790	0.856744	0.855763
0.6	0.725575	0.725416	0.723565
0.9	0.606970	0.606647	0.604068
1.2	0.501378	0.500861	0.497719
1.5	0.408916	0.408195	0.404674
1.8	0.329365	0.328454	0.324738
2.1	0.262149	0.261079	0.257344
2.4	0.206368	0.205183	0.201578
2.7	0.160866	0.159616	0.156257
3.0	0.124330	0.123065	0.120028
3.3	0.094052	0.094168	0.091493
3.6	0.072780	0.071606	0.069301
4.2	0.041805	0.040820	0.039195
4.8	0.023743	0.022973	0.021886
5.4	0.013401	0.012830	0.012129
6.0	0.007541	0.007134	0.006693

Example 2

Having gained some confidence in the perturbation solution, we now try larger values of α and β: $\alpha = 0.55$ and $\beta = 0.6$. The feed composition and μ remain the same as those in Example 1. Table 2 shows that C_1 is again good enough for most practical purposes and represents an improvement over C_0. Note that even in this case the exact and

TABLE 2

Comparison of Numerical and Perturbaton Solutions
($\alpha = 0.55$, $\beta = 0.6$)

τ	C_{exact}	C_1	C_0
0	1.000000	1.000000	1.000000
0.3	0.857755	0.857422	0.855763
0.6	0.728022	0.726839	0.723565
0.9	0.611252	0.608827	0.604068
1.2	0.507658	0.503745	0.497719
1.5	0.417156	0.411673	0.404674
1.8	0.339339	0.332365	0.324738
2.1	0.273487	0.265236	0.257344
2.4	0.218610	0.209394	0.201578
2.7	0.173524	0.163709	0.156257
3.0	0.136950	0.126903	0.120028
3.3	0.107605	0.097658	0.091493
3.6	0.084269	0.074697	0.069301
4.2	0.051377	0.043095	0.039195
4.8	0.031232	0.024546	0.021886
5.4	0.019007	0.013871	0.012129
6.0	0.016039	0.007801	0.006930

TABLE 3

Comparison of Numerical and Perturbaton Solutions ($\alpha = 0.55$, $\beta = 0.6$)

τ	C_{exact}	C_1	C_0
0	1.000000	1.000000	1.000000
0.3	0.849084	0.848760	0.855763
0.6	0.711324	0.710491	0.723565
0.9	0.587533	0.586025	0.604068
1.2	0.478256	0.475944	0.497719
1.5	0.383665	0.380478	0.404674
1.8	0.303474	0.299418	0.324738
2.1	0.236925	0.232088	0.257344
2.4	0.182834	0.177379	0.201578
2.7	0.139714	0.133855	0.156257
3.0	0.105924	0.099896	0.120028
3.3	0.079829	0.073852	0.091493
3.6	0.059911	0.054171	0.069301
3.9	0.044844	0.039479	0.052223
4.2	0.033522	0.028621	0.039195
4.8	0.018732	0.014859	0.021886
5.4	0.010517	0.007620	0.012129
6.0	0.005954	0.003869	0.006693

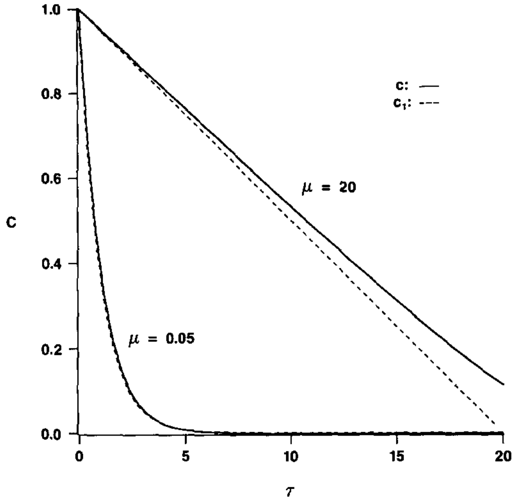

FIG. 1. Comparison of $C(\tau)$ and $C_1(\tau)$ for the asymptotic cases of $\mu \gg 1$ and $\mu \ll 1$.

approximate solutions are so close to each other that they cannot be distinguished by a figure.

The results of this example are quite encouraging. A $\beta = 0.6$ means that the three species can have the following adsorptivity spectrum: $1.6\bar{K}$, $\bar{K}$, and $0.4\bar{K}$. *So the values of* $\bar{K}_i$ *span a factor of as high as four.*

In the above examples, C_1 and C_0 are both lower than the exact result. The following example shows that this is not always true.

Example 3

We again let $\alpha = 0.55$, $\beta = 0.6$, and $\mu = 1$. The initial composition is $(c_{if}) = (0.55, 0.32, 0.13)$. As Table 3 shows, C_1 again gives a very good estimate of $C(\tau)$, whereas C_0 gives too high an estimate.

Example 4

Here we test Eqs. (37) and (38) using the same values of α, β, and (c_{if}) as those in Example 1. The results are shown in Fig. 1. For $\mu = 0.05$, $C(\tau)$ calculated by Eq. (38) is almost indistinguishable from that by numerical integration (solid lines). For $\mu = 20$, Eq. (37) gives a $C(\tau)$ profile reasonably close to the exact result.

CLOSING REMARKS

Usually, the lumped species are chemically similar, so the assumptions used in the perturbative analysis are reasonable. For illustrative purposes, we have considered only three-species systems in the numerical examples. The present perturbative scheme should be particularly useful for large multicomponent mixtures as long as the individual rate constants and adsorptivities do not span significant ranges. To obtain more accurate results, higher-order terms can be easily constructed.

APPENDIX

Notation

$C(\tau)$ = total dimensionless concentration of reactants at time τ
$\tilde{C}_f$ = total concentration of reactants in feed.
$\tilde{C}(t)$ = total concentration of reactants at time t
C_1 = first-order approximation to $C(\tau)$, Eq. (36)
$\tilde{c}_i$ = concentration of ith species at time t
$\tilde{c}_{if}$ = concentration of ith species in feed

c_i = dimensionless concentration of ith species at time t
c_{if} = dimensionless concentration of ith species in feed
k_i' = reaction rate constant, Eq. (1)
$\tilde{k}_i$ = defined as product of k_i' and $\tilde{K}_i$
K_i = adsorption equilibrium constant
$\bar{K}$ = average adsorption constant, Eq. (6)
k_i = deviatoric rate constant, Eq. (4)
K_i = deviatoric adsorption constant, Eq. (5)
N = total number of reactants
t = time
u_{im} = functions defined in Eq. (13), $m = 1, 2 \ldots$
U_m = functions defined in Eq. (14), $m = 1, 2 \ldots.$
U_m' = functions defined in Eq. (14), $m = 1, 2 \ldots.$

Greek Letters

α = parameter defined in Eq. (7)
β = parameter defined in Eq. (7)
δ = parameter defined in Eq. (33)
τ = dimensionless time, Eq. (7)
λ_i = parameter defined in Eq. (7)
μ = dimensionless adsorption constant, Eq. (7)
ν_i = parameter defined in Eq. (7)
σ = parameter defined in Eq. (30)

REFERENCES

1. Ho, T. C., and Aris, R., *AIChE J.* **33,** 1050 (1987).
2. Astarita, G., and Ocone, R., *AIChE J.* **34,** 1299 (1988).
3. Chou, M. Y., and Ho, T. C., *AIChE J.* **34,** 1519 (1988).
4. Astarita, G., *AIChE J.* **35,** 529 (1989).
5. Aris, R., *AIChE J.* **35,** 539 (1989).
6. Chou, M. Y., and Ho, T. C., *AIChE J.* **35,** 533 (1989).
7. Astarita, G., and Nigam, A., *AIChE J.* **35,** 1927 (1989).
8. Ho, T. C., White, B. S. and Hu, R., *AIChE J.* **36,** 685 (1990).
9. Li, B. Z., and Ho, T. C., *Chem. Eng. Sci.* **46,** 273 (1991).
10. Ho, T. C., *Chem. Eng. Sci.* **46,** 281 (1991).
11. Weekman, V. W., Jr., "Lumps, Models, and Kinetics in Practice," Vol. 75, No. 11, AIChE Monograph Series 1979.
12. Aris, R., *Arch. Rat. Mech. Anal.*, **27,** 35 (1968).
13. Hutchinson, P., and Luss, D., *Chem. Eng. J.*, **1,** 129 (1970).
14. Golikeri, S. V., and Luss, D., *Chem. Eng. Sci.*, **29,** 845 (1974).
15. Luss, D., and Golikeri, S. V., *ibid.*, **21,** 865 (1975).