

QUICK AND EASY RATE EQUATIONS FOR MULTISTEP REACTIONS

PHILLIP E. SAVAGE

University of Michigan • Ann Arbor, MI 48109-2136

In many different aspects of chemical engineering education, we teach students first to analyze a general system and then to simplify that general analysis as allowed by the specific system being examined. For example, we show students the general energy balance and then subsequently show how it can be simplified when applied to special cases (e.g., adiabatic systems, steady state systems, systems with negligible changes in kinetic or potential energy). We show students the equations of motion in fluid mechanics and then subsequently show how they can be simplified for special cases (e.g., steady flow, incompressible fluids, Newtonian fluids). In the field of chemical kinetics, an opportunity exists to apply this same educational approach when teaching students how to develop reaction rate equations based upon application of the quasi-stationary-state approximation (QSSA) to the governing chemical mechanism. The purpose of this article is to make this opportunity more widely known.

Chemical kinetics and reaction engineering textbooks^[1-5] discuss techniques for deriving closed-form analytical rate equations from sets of elementary reaction steps. Types of reaction systems covered include chain reactions, catalysis, and chemical vapor deposition. The QSSA is one of the tools discussed in texts. This approximation, which in many texts gets the confusing and potentially misleading label of “steady-state”^{*} attached to it, allows one to neglect the comparatively small net reaction rate for a reactive intermediate (RI) relative to its very fast formation and disappearance rates. The result is that one can take the formation and disappearance rates to be approximately equal, and then solve algebraically for the concentration of the reactive intermediate.

$$\underbrace{r_{\text{net,RI}}}_{\text{very small}} = \underbrace{r_{\text{formation,RI}}}_{\text{large}} - \underbrace{r_{\text{disappearance,RI}}}_{\text{large}} \approx 0 \quad (1)$$

Oftentimes, this result contains the concentration(s) of other

reactive intermediates, so the QSSA must be applied next to those reactive intermediates. This procedure is repeated to get explicit expressions for each reactive intermediate.

The application of the QSSA in textbooks almost always involves only one or two reactive intermediates, because the number of simultaneous equations and tediousness of the algebra, if done manually, grow as the number of reactive intermediates increases. Most texts, when covering multistep reactions with two or more intermediates, teach students to make restrictive assumptions (e.g., rate determining steps), which simplify the algebra. The price paid for the simplified mathematics, though, is a less general rate equation. If there is a shift in the rate-determining step with temperature or conversion, for example, the rate equation will no longer apply.

The lack of coverage of QSSA applications to larger multistep reaction systems in chemical engineering education need not persist. Easy-to-use general methods exist to develop analytical rate equations for arbitrarily large multistep reactions without making assumptions about the existence or identities of rate-determining steps. This article describes these general methods. One method, developed by Helfferich,^[6-8] applies to

Phillip Savage is a professor of chemical engineering at the University of Michigan. He received his B.S. from Penn State in 1982 and his M.Ch.E. (1983) and Ph.D. (1986) degrees from the University of Delaware, all in chemical engineering. His research and teaching interests focus on the rates, mechanisms, and engineering of organic chemical reactions. Current research projects deal with renewable energy from biomass and environmentally benign chemical synthesis.



* The QSSA has nothing to do with steady states, either mathematically or conceptually. The QSSA deals with process rates (rates of chemical reactions), and not rates of change (dC/dt). This approximation does not require or imply that dC_{RI}/dt = 0 nor does it require or imply that C_{RI} is constant. That using the term “steady state” creates confusion is evident in textbooks and educational articles where authors erroneously state that this approximation means the concentration of the reactive intermediate (RI) is constant!

reactions wherein all reactant, final product, and free catalyst concentrations are much greater than the concentrations of the intermediates. A second method, based upon work published by Christiansen,^[9,11] relaxes the requirement that the catalyst concentration exceed that of the reactive intermediates.

APPLICABILITY

The formulas given in this article provide the rate equation for any multistep chemical reaction mechanism that meets the following criteria.

- The steps in the mechanism are all sequential (no branches).
- None of the steps involve more than one molecule of reactive intermediate as reactant or more than one molecule of reactive intermediate as product (so the set of algebraic equations from application of the QSSA can be solved using linear algebra).
- All of the intermediates are present only in trace-level quantities (so the QSSA can be applied to each).

Networks that meet these three criteria are said to be “simple.”

Many reactions catalyzed by acid, base, organometallic complexes, or solid surfaces meet these criteria. The catalytic cycle in Figure 1,^[12] which accounts for the synthesis of bisphenol A from acetone and phenol, is one example.

NOTATION

We adopt the notation used in the original literature. X_i designates reactive intermediates, which by definition are present in trace level. The reaction steps are written with the reactive intermediates (X_i) appearing as the explicit reactant and product in a step. Any co-reactant (or co-product) molecules in a step appear either above (or below) the arrow for that reaction step. We use a double subscript notation for the rate coefficients. The first subscript identifies the reactive intermediate involved as a reactant in that step and the second subscript identifies the reactive intermediate that is formed.

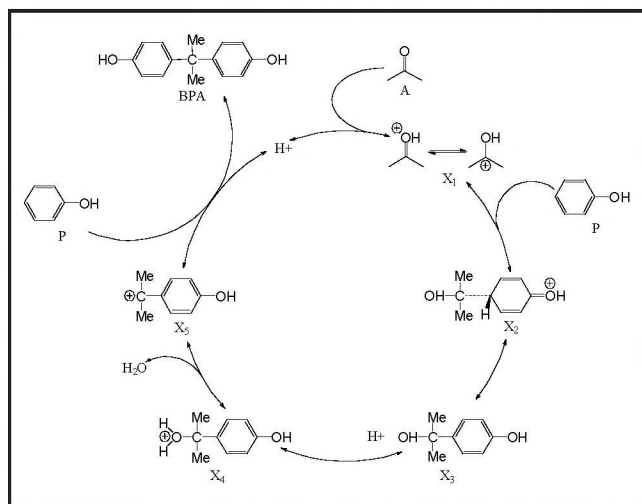


Figure 1. Catalytic cycle for BPA synthesis from phenol and acetone (adapted from Ref [12]).

To illustrate this notation, consider the reaction $X_i + B \rightleftharpoons X_j$. The forward rate constant is k_{ij} and the reverse rate constant is k_{ji} . We rewrite this step as $X_i \xrightleftharpoons{B} X_j$, with B appearing above the arrow because it is a co-reactant. The pseudo-first-order forward rate coefficient for this step is λ_{ij} , where $\lambda_{ij} = k_{ij}C_B$. The pseudo-first-order reverse rate coefficient is λ_{ji} , where $\lambda_{ji} = k_{ji}$. The net rate of this reversible reaction step would be written as

$$-r_B = k_{ij}C_{X_i}C_B - k_{ji}C_{X_j} = \lambda_{ij}C_{X_i} - \lambda_{ji}C_{X_j} \quad (2)$$

Using pseudo-first-order rate coefficients (λ_{ij}) allows all rates to be written explicitly in terms of the concentrations of the reactive intermediates and the reactant and product.

RATE EQUATION – HELFFERICH METHOD (BULK CATALYSIS)

Helfferich developed this first method while doing process development work for Shell Chemical. It was homogeneous reactions of commercial significance catalyzed by transition metals that provided motivation. In these systems, the free catalyst concentration was large relative to the concentrations of the catalyst-containing reactive intermediates. The rate equation for such a simple multistep network, which converts reactant A into end product P, is^[6-8]

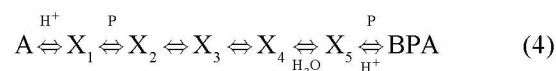
$$r_p = \frac{\prod_{i=0}^{k-1} \lambda_{i,i+1} C_A - \prod_{i=0}^{k-1} \lambda_{i+1,i} C_P}{\sum_{i=1}^k \left(\prod_{l=1}^{i-1} \lambda_{l,l-1} \prod_{l=i}^{k-1} \lambda_{l,l+1} \right)} \quad (3)$$

where r_p is the rate of forming product P, $\prod_{i=0}^{k-1} \lambda_{i,i+1}$ is the product of all of the forward pseudo-first-order rate coefficients, $\prod_{i=0}^{k-1} \lambda_{i+1,i}$

is the product of all of the reverse pseudo-first-order rate coefficients in the multistep reaction, and the index k is the number of steps in the sequence. If the lower limit in the product exceeds the upper, the product is taken to be equal to unity. The denominator in the rate equation involves a summation over a double product. Refer to Helfferich^[6,7] for a simple, easy-to-remember way to perform these operations and generate the denominator without going through the formalism of evaluating each term in the summation.

Application

Figure 1 shows the multistep reaction for the acid-catalyzed synthesis of bisphenol A from acetone (A) and phenol (P). This six-step mechanism can be written as



Acetone is species number zero and BPA is species number six. For this network the relationships between the pseudo-first-order rate coefficients and the true rate constants are

$$\begin{aligned}
\lambda_{01} &= k_{01} C_{H^+} & \lambda_{10} &= k_{10} \\
\lambda_{12} &= k_{12} C_P & \lambda_{21} &= k_{21} \\
\lambda_{23} &= k_{23} & \lambda_{32} &= k_{32} \\
\lambda_{34} &= k_{34} & \lambda_{43} &= k_{43} \\
\lambda_{45} &= k_{45} & \lambda_{54} &= k_{54} C_{H_2O} \\
\lambda_{56} &= k_{56} C_P & \lambda_{65} &= k_{65} C_{H^+} \quad (5)
\end{aligned}$$

By applying the formula for the rate equation to this specific example

$$r_{BPA} = \frac{\prod_{i=0}^5 \lambda_{i,i+1} C_A - \prod_{i=0}^5 \lambda_{i+1,i} C_{BPA}}{\sum_{i=1}^6 \left(\prod_{l=1}^{i-1} \lambda_{l,l-1} \prod_{l=i}^5 \lambda_{l,l+1} \right)} \quad (6)$$

one can very quickly write the rate as

$$r_{BPA} = \frac{\lambda_{01} \lambda_{12} \lambda_{23} \lambda_{34} \lambda_{45} \lambda_{56} C_A - \lambda_{10} \lambda_{21} \lambda_{32} \lambda_{43} \lambda_{54} \lambda_{65} C_{BPA}}{\lambda_{12} \lambda_{23} \lambda_{34} \lambda_{45} \lambda_{56} + \lambda_{10} \lambda_{23} \lambda_{34} \lambda_{45} \lambda_{56} + \lambda_{10} \lambda_{21} \lambda_{34} \lambda_{45} \lambda_{56} + \lambda_{10} \lambda_{21} \lambda_{32} \lambda_{45} \lambda_{56} + \lambda_{10} \lambda_{21} \lambda_{32} \lambda_{43} \lambda_{56} + \lambda_{10} \lambda_{21} \lambda_{32} \lambda_{43} \lambda_{54}} \quad (7)$$

Replacing the λ_{ij} in the rate equation with the corresponding k_{ij} and any co-reactant concentration for that step, and then simplifying leads to the general form of this rate equation as

$$r_{BPA} = \frac{k_a C_{H^+} C_P C_A - k_b C_{H^+} C_W C_{BPA}}{k_c C_P^2 + k_d C_P + k_e C_W} \quad (8)$$

where the k_i parameters are collections of rate constants for individual steps. This final form of the general rate equation is not very complicated even though no assumptions were made about any step being rate determining.

Rate equations for this system have been reported^[12] to be irreversible and both first-order in phenol ($r_{BPA} = k C_{H^+} C_A C_P$) and second-order in phenol ($r_{BPA} = k C_{H^+} C_A C_P^2$). These experimental rate equations are simply special cases of the general rate equation above. First-order kinetics arise when the second step is rate-determining and irreversible. Second-order kinetics arise when the final step is rate determining and irreversible. If a step is rate-determining, the pseudo-first-order rate coefficients for that step must be very much smaller than the rate coefficients for all other steps in the sequence. That is $\lambda_{ij, rds} \ll$ all other λ_{ij} . Moreover, if a step is irreversible, $\lambda_{ji} = 0$ for that step.

When the second step, $X_1 \overset{P}{\rightleftharpoons} X_2$, is rate-determining, λ_{12} and λ_{21} are much smaller than all other λ_{ij} , so denominator terms containing either λ_{12} or λ_{21} will be much smaller than denominator terms that do not contain these terms. Therefore, only the denominator terms that omit λ_{12} and λ_{21} need to be retained in the rate equation. It is only the second term in the denominator that survives. Moreover, if any step is irreversible, the second term in the numerator vanishes. The rate equation for this scenario then becomes

$$r_{BPA} = \frac{\lambda_{01} \lambda_{12} \lambda_{23} \lambda_{34} \lambda_{45} \lambda_{56} C_A}{\lambda_{10} \lambda_{23} \lambda_{34} \lambda_{45} \lambda_{56}} = \frac{\lambda_{01} \lambda_{12} C_A}{\lambda_{10}} = \frac{k_{01} k_{12}}{k_{10}} C_{H^+} C_P C_A = k_{12} K_{01} C_{H^+} C_P C_A \quad (9)$$

which is precisely a first-order rate equation, as seen experimentally. K_{01} is the equilibrium constant for the first reaction step.

When the final step, $X_5 \overset{P}{\rightleftharpoons} BPA$, is rate determining, only the denominator terms that omit λ_{56} and λ_{65} need to be retained in the rate equation. Also, as before, the contribution for the reverse reaction in the numerator vanishes when any step is irreversible. The rate equation for this scenario is

$$r_{BPA} = \frac{\lambda_{01} \lambda_{12} \lambda_{23} \lambda_{34} \lambda_{45} \lambda_{56} C_A}{\lambda_{10} \lambda_{21} \lambda_{32} \lambda_{43} \lambda_{54}} = \frac{k_{01} k_{12} k_{23} k_{34} k_{45} k_{56} C_{H^+} C_P C_A}{k_{10} k_{21} k_{32} k_{43} k_{54} C_{H_2O}} = k_{56} K_{01} K_{12} K_{23} K_{34} K_{45} \frac{C_{H^+} C_P C_A}{C_{H_2O}} \quad (10)$$

Here we obtain the rate equation that is second order in phenol, as was seen experimentally.

TABLE 1 Form of QSSA Rate Equation for Specific Three-Step Catalyzed Reactions	
Reaction System	General Rate Equation
Heterogeneous Isomerization	$r = \frac{(k_a C_A - k_b C_B) C_T}{1 + k_c C_A + k_d C_B}$
Enzyme Catalysis	$r = \frac{(k_a C_S - k_b C_P) C_E^O}{1 + k_c C_S + k_d C_P}$
Ozone Decomposition	$r = \frac{(k_a C_{O_3}^2 - k_b C_{O_2}^3) C_T}{k_c C_{O_3} + k_d C_{O_3}^2 + k_e C_{O_2} + k_f C_{O_2}^2 + k_g C_{O_3} C_{O_2}}$

This example shows that multistep reactions of commercial significance can be easily treated with this method to obtain general reaction rate equations. The complexity in the form of the general rate equation is no more than that in Langmuir-Hinshelwood rate equations, which have long been used in heterogeneous catalytic kinetics. Significantly, however, one can recover even simpler rate equations (*e.g.*, power-law) for situations where one step is rate determining or where a step or steps are irreversible. Note that this approach of starting with the general equation and then simplifying it for special limiting cases is fully consistent with the approach many take in chemical engineering education.

Extension to Non-Trace Intermediates

The general Helfferich method applies to simple pathways with all reactants, products, and free catalyst present in much higher concentrations than the intermediates. But, there are some reactions where the concentration of one or more intermediates rises above trace level, perhaps because the intermediate is a molecular product rather than being a reactive intermediate. In these cases, the pathway can be broken at those intermediates, and each of the fragments of the overall network can then be treated using the general method described in this article.^[6]

To illustrate, consider the acid-catalyzed dehydration of cyclohexanol in supercritical water^[13] as shown in Figure 2. This network is nonsimple because one of the intermediates, cyclohexene, is not at trace levels. Its concentration is comparable to that of the reactant cyclohexanol and end product methylcyclopentene. Therefore, one cannot use the general formula to write a single rate equation for the conversion of cyclohexanol to methylcyclopentene. One can break the complete network into two piece-wise simple portions, however, and apply Helfferich mathematics to each portion. These two piece-wise simple portions appear as Figure 3.

Using the general formula, one can write the rate equation for the first sequence, the conversion of cyclohexanol (A) to cyclohexene (B) plus water (W).

$$r_1 = \frac{\lambda_{01}\lambda_{12}C_A - \lambda_{10}\lambda_{21}C_B}{\lambda_{10} + \lambda_{12}} = \frac{k_{01}k_{12}C_A C_W C_{H_3O^+} - k_{10}k_{21}C_W^2 C_{H_3O^+} C_B}{(k_{10} + k_{12})C_W} = \frac{k_{01}k_{12}C_A C_{H_3O^+} - k_{10}k_{21}C_W C_{H_3O^+} C_B}{k_{10} + k_{12}} \quad (11)$$

The rate equation for the second portion is, for the general case of all steps being reversible,

$$r_2 = \frac{\lambda_{23}\lambda_{34}\lambda_{45}C_B - \lambda_{32}\lambda_{43}\lambda_{54}C_C}{\lambda_{34}\lambda_{45} + \lambda_{32}\lambda_{45} + \lambda_{32}\lambda_{43}} \quad (12)$$

Note that cyclohexene is designated as species 2 in the second sequence to maintain consistent species indexes. Methylcyclopentene (C) is species 5. Note too that for this second network, the first step (protonation) is irreversible, so $\lambda_{32} = 0$. The rate equation for the second portion then becomes simply

$$r_2 = \lambda_{23}C_B = k_{23}C_B C_{H_3O^+} \quad (13)$$

Akiya and Savage^[13] modeled the kinetics for this system using the two rate equations above. Doing so led to a model that contained only three parameters to be determined from experimental data; two in the first rate equation and one in the second. A numerical modeling approach based on an explicit accounting for each step would have necessitated the inclusion of nine different parameters. Using the Helfferich formula to develop analytical rate equations has certainly simplified the task of parameter estimation.

The interested reader is directed to Helfferich^[6-8] and the references therein for more information regarding additional extensions of this general method.

RATE EQUATION—CHRISTIANSEN MATHEMATICS (TRACE-LEVEL CATALYSIS)

The material presented thus far, when used for catalyzed reaction systems, applies when the concentration of free catalyst is much higher than concentrations of the intermediates. Examples of this situation include acid or base catalysis and many homogeneous transition metal catalyzed reactions. This section treats trace-level catalysis, where the free catalyst concentration is small, and a significant fraction of the total catalyst amount can be bound with intermediates. Enzyme catalysis and

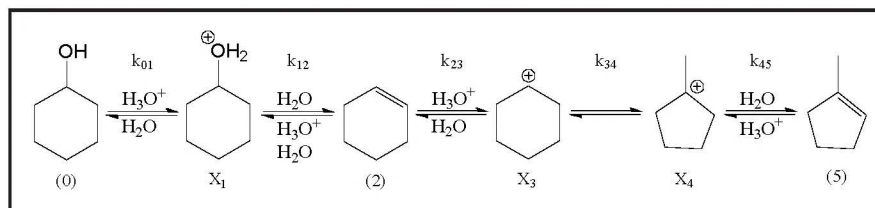


Figure 2. Multistep networks for cyclohexene formation from cyclohexanol (top) and methylcyclopentene formation (bottom) (adapted from Ref. [13])

some heterogeneously catalyzed reaction sequences (e.g., some isomerizations, Eley-Rideal reactions) are examples of simple reaction systems with trace-level catalysis. Christiansen^[9-11] developed the general treatment for systems of this type, Helfferich^[6] discusses it in some detail, and Boudart^[14] provided a short overview nearly 40 years ago.

Helfferich^[6] shows that the rate of conversion of reactant A into product P via the general linear network $\text{cat} \rightleftharpoons X_1 \rightleftharpoons \dots \rightleftharpoons X_{k-1} \rightleftharpoons \text{P}$, is

$$r_p = \frac{\left(\prod_{i=0}^{k-1} \lambda_{i,i+1} - \prod_{i=0}^{k-1} \lambda_{i+1,i} \right) C_T}{D_k^{\text{CH}}} \quad (14)$$

where D_k^{CH} is the Christiansen denominator for a network with k reaction steps. The Christiansen numerator contains C_T , the total catalyst concentration (sum of the concentrations of the free catalyst and all catalyst-containing intermediates). In trace-level catalysis, it is often the total catalyst concentration (amount added to the reactor) that is known. Its distribution among the different catalyst-containing species is not easily measured in engineering applications.

The denominator is the sum of all terms in the Christiansen matrix, and Helfferich describes how to generate these terms.

For a generic 3-step reaction network, $\text{cat}_0 \rightleftharpoons X_1 \rightleftharpoons X_2 \rightleftharpoons \text{cat}_3$, the Christiansen matrix is

$$\begin{vmatrix} \lambda_{12}\lambda_{23} & \lambda_{10}\lambda_{23} & \lambda_{10}\lambda_{21} \\ \lambda_{23}\lambda_{01} & \lambda_{21}\lambda_{01} & \lambda_{21}\lambda_{32} \\ \lambda_{01}\lambda_{12} & \lambda_{32}\lambda_{12} & \lambda_{32}\lambda_{10} \end{vmatrix} \quad (15)$$

An important property of this matrix is that the sum of the terms in each row is proportional to the concentration of one of the catalyst-containing species in the reaction network.^[6] The sum of the terms in the first row is proportional to the

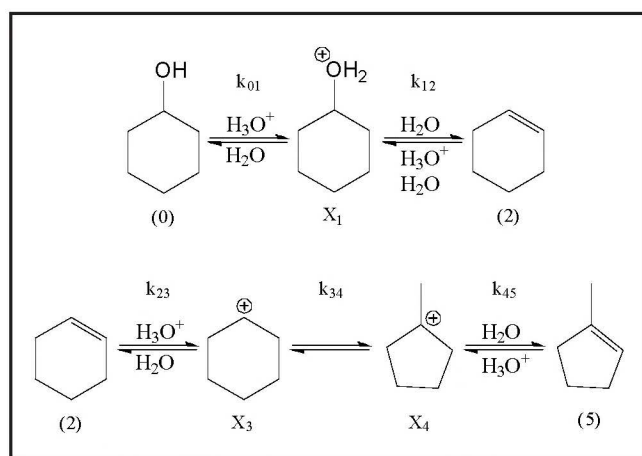
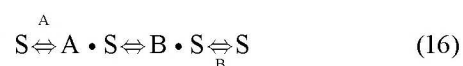


Figure 3. Multistep network for methylcyclopentene formation from cyclohexanol (adapted from Ref. [13])

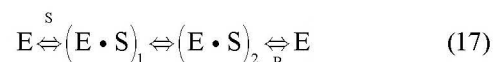
concentration of the free catalyst. The sum of the terms in the second row is proportional to the concentration of intermediate X_1 , and so on. This relationship between the relative abundances of the different catalyst containing species and the relative magnitudes of the sums of the terms in each row allows one to simplify the denominator for cases in which one or more of the catalyst-containing species are present in much higher (or lower) concentrations than the others. For example, if X_2 is the most abundant catalyst species (*macs*), then the sum of the terms in the third row of the matrix will be much larger than the sums of the terms from the other rows. Therefore, one can neglect the small contributions from the other rows, and to a very good approximation the Christiansen denominator can be taken to be the sum of the terms in the third row alone. The number of denominator terms for a network with k steps can therefore be reduced from k^2 to k when there exists a *macs*. Likewise, one can obtain simplification if there exists a *lacs* (least abundant catalyst species). In this case, one can neglect the small contribution made by the sum of the terms in the matrix row corresponding to the reactive intermediate that is the *lacs*.

Application

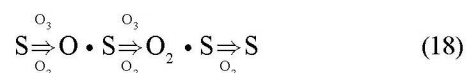
Consider the generic three-step sequence $\text{cat} \rightleftharpoons X_1 \rightleftharpoons X_2 \rightleftharpoons \text{ca}$, which has two catalyst-containing reactive intermediates. Any number of co-reactants or co-products can appear in any of the three steps. Numerous catalytic systems have reaction mechanisms of this form. For example, the solid-catalyzed isomerization $A = B$ can occur through a three-step sequence of adsorption of A, isomerization on the surface, and desorption of B from a surface site (S) back into the fluid phase. The reactive intermediates X_1 and X_2 are surface bound A ($A \cdot S$) and B ($B \cdot S$) respectively.



Some enzyme-catalyzed reactions that convert a substrate, S, into a product, P, proceed through two different enzyme-substrate complexes ($E \cdot S$).^[5] Each complex is a catalyst-containing reactive intermediate.



The heterogeneously catalyzed decomposition of ozone over MnO_2 is another example of a specific reaction that has the same structure as the network under consideration.^[15, 16]



The acid-catalyzed isomerization of cyclohexene (C) to methylcyclopentene (M),^[13] which was examined previously, is one more example.

The general form of the Christiansen rate equation for a

single catalytic cycle with three steps is

$$r = \frac{(\lambda_{01}\lambda_{12}\lambda_{23} - \lambda_{10}\lambda_{21}\lambda_{32})C_T}{\lambda_{12}\lambda_{23} + \lambda_{10}\lambda_{23} + \lambda_{10}\lambda_{21} + \lambda_{23}\lambda_{01} + \lambda_{21}\lambda_{01} + \lambda_{21}\lambda_{32} + \lambda_{01}\lambda_{12} + \lambda_{32}\lambda_{12} + \lambda_{32}\lambda_{10}} \quad (19)$$

To derive this rate equation manually would require algebraic manipulations with two QSSA expressions (one for each intermediate) and the catalyst balance (since the distribution of catalyst material amongst the different forms is not known). This task is tedious, and a tremendous amount of algebra is required to obtain the simplified form of the rate equation above.

Table 1 (page 213) shows the general rate equation for each of the specific application systems in view. The parameters (k_i) in these rate equations are collections of rate constants for individual steps. Rarely does one need to retain all of the terms in the general rate equation. For example, in heterogeneous catalysis, such as the isomerization example, one often assumes that one of the steps is rate determining and that all others are in quasi-equilibrium. If we assume that step 2, the surface reaction ($A \cdot S \rightleftharpoons B \cdot S$), is rate determining ($\lambda_{12}, \lambda_{21} \ll \text{other } \lambda_{ij}$), then the rate equation becomes

$$r = \frac{(\lambda_{01}\lambda_{12}\lambda_{23} - \lambda_{10}\lambda_{21}\lambda_{32})C_T}{\lambda_{10}\lambda_{23} + \lambda_{23}\lambda_{01} + \lambda_{32}\lambda_{10}} \quad (20)$$

Replacing the pseudo-first-order rate coefficients with the rate constants and species concentrations and then simplifying, leads to

$$r = \frac{k_{12}K_{01}C_T(C_A - C_B/K_e)}{1 + K_{01}C_A + K_{32}C_B} \text{ where } K_e = K_{01}K_{12}K_{23} \text{ and } K_{ij} = \frac{\lambda_{ij}}{\lambda_{ji}} \quad (21)$$

as the rate equation. This Langmuir-Hinshelwood-Hougen-Watson rate equation shows precisely the same dependence of the rate on the concentrations of A and B as the general rate equation for this system in Table 1. Thus, no simplification in form resulted from assuming the existence of a rate-determining step.

For enzyme-catalyzed reactions, step 3, product formation ($(E \cdot S)_2 \rightleftharpoons_p E$), is often irreversible and rate determining ($\lambda_{32}=0; \lambda_{23} \ll \text{other } \lambda_{ij}$). The rate equation for this case is

$$r = \frac{(\lambda_{01}\lambda_{12}\lambda_{23})C_T}{\lambda_{10}\lambda_{21} + \lambda_{21}\lambda_{01} + \lambda_{01}\lambda_{12}} \quad (22)$$

Upon replacing the pseudo-first-order rate coefficients with the appropriate rate constants and concentrations, one obtains the rate equation,

$$r = \frac{\left(\frac{k_{12}k_{23}}{k_{21} + k_{12}} \right) C_E^0 C_S}{\left(\frac{k_{10}k_{21}}{k_{01}(k_{21} + k_{12})} \right) + C_S} = \frac{V_{\max} C_S}{K_m + C_S} \quad (23)$$

which is the familiar Michaelis-Menten result. V_{\max} is the maximum reaction velocity (rate). C_E^0 is the total enzyme concentration.

For ozone decomposition, Oyama and coworkers^[15,16] reported that all three steps are irreversible and that absorbed O atoms are the *lacs*. Thus, all reverse rate coefficients will be zero, and the denominator will omit the terms in the second row of the Christiansen matrix. The resulting rate equation is shown below.

$$r = \frac{\lambda_{01}\lambda_{12}\lambda_{23}C_T}{\lambda_{12}\lambda_{23} + \lambda_{01}\lambda_{12}} = \frac{k_{01}C_{O_3}C_T}{1 + \frac{k_{01}k_{12}}{k_{12}k_{23}}C_{O_3}} \quad (24)$$

This example illustrates the utility of Christiansen mathematics for single catalytic cycles. The general rate equation can be written quickly, and then rate laws for special cases (rate determining steps, irreversible steps, *lacs*, etc.) can be recovered by omitting the terms that are negligible.

CLOSING REMARKS

This article outlines and illustrates methods for quickly getting closed-form analytical rate equations for multistep networks using only the QSSA. These methods were developed at an industrial R&D center to deal with practical kinetics issues in chemical process development. Uncatalyzed reactions and those catalyzed by acid, base, homogeneous transition metal complexes, enzymes, and solid surfaces can all be handled by these methods. The chief constraint is that each step must be unimolecular in reactive intermediate. This constraint reduces the utility of this method for chain reactions that include branching, termination, and initiation steps and for heterogeneous catalysis with bimolecular surface reactions.

Though components of these approaches have been in the literature for decades, these methods do not appear in many popular chemical reaction engineering textbooks. I have been teaching these methods in our core chemical reaction engineering graduate course, a senior/graduate elective class on chemical kinetics, and continuing education courses on reaction kinetics. Graduate students or practicing professionals are probably the proper audience for this material. The students appreciate learning about this approach, which allows them to develop a rate equation very quickly for a general case and then simplify it to recover results for numerous special cases. Simplifying the general equation also reinforces the concepts of rate-determining steps, quasi-equilibrium steps, *macs*, and *lacs*.

A more detailed tutorial on the use and teaching of these methods is available from the author upon request. In addition, Helfferich^[6] provides a detailed treatment and many examples.

REFERENCES

1. Fogler, H.S., *Elements of Chemical Reaction Engineering*, 4th ed., Prentice-Hall, Upper Saddle River, NJ (2006)
2. Masel, R.I., *Chemical Kinetics and Catalysis*, Wiley-Interscience, New York (2001)
3. Davis, M.E., and R.J. Davis, *Fundamentals of Chemical Reaction Engineering*, McGraw-Hill, New York (2003)
4. Schmidt, L.D., *The Engineering of Chemical Reactions*, 2nd ed., Oxford University Press, New York (2005)
5. Roberts, G.W., *Chemical Reactions and Chemical Reactors*, Wiley (2009)
6. Helfferich, F.G., *Kinetics of Multistep Reactions*, 2nd ed., Elsevier, Amsterdam (2004)
7. Helfferich, F.G., *J. Phys. Chem.* **93**, 6676 (1989)
8. Chern, J-M, and F.G. Helfferich, *AIChE J.* **36**, 1200 (1990)
9. Christiansen, J.A.Z., *Physik. Chem. Bodenstein-Festband* **69** (1931)
10. Christiansen, J.A.Z., *Physik. Chem.* **B 28**, 303 (1935)
11. Christiansen, J.A., *Adv. Catal.* **5**, 311 (1953)
12. Gates, B.C., *Catalytic Chemistry*, John Wiley & Sons, New York (1992)
13. Akiya, N., and P.E. Savage, *Ind. Eng. Chem. Res.*, **40**, 1822 (2001)
14. Boudart, M., *Kinetics of Chemical Processes*, Prentice-Hall, Englewood Cliffs, NJ (1968)
15. Li, W., G.V. Gibbs, and S.T. Oyama, *J. Am. Chem. Soc.*, **120**, 9041 (1998)
16. Li, W., and S.T. Oyama, *J. Am. Chem. Soc.*, **120**, 9047 (1998) □