A Streamlined Approach to Solving Simple and Complex Kinetic Systems Analytically

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The topic of rate expression derivation for chemical reaction schemes in undergraduate and graduate chemical kinetics, physical organic, and physical inorganic chemistry courses necessarily involves a significant amount of mathematics. The success of students grasping the methodologies involved and making inferences about the consequences of rate-constant approximations, chemical equilibrium, and rate-determining steps largely depends on the student–teacher comfort level in dealing with the language of mathematics. Teachers of chemistry may find such a task daunting for a variety of reasons. Usually the situation exposes the deficiency in the mathematical training of chemical educators and the students' lack of problem-solving skills in realizing how concepts learned in one science course may be utilized to full advantage in another. The development of this extremely important critical skill is demanded by the ever growing trend to interdisciplinary research. The observation that students complain often of not seeing the relevance of learning something, particularly in mathematics, to "real-world" examples attests to the dilemma and is a direct result of the current and longstanding compartmentalized approach to science program curricula. This attitude pervades in educators' teaching and students' learning styles and results in both educators and students becoming increasingly dependent on the results themselves as given in standard texts while sacrificing the knowledge of how such results were obtained in the first place. The emerging trend of developing cross-disciplinary science courses such as the recently described Science One and Cooperative Science Option (CSO) offered at the University of British Columbia (*1*), is a small step in the right direction in rectifying this situation.

In this paper I apply well-established mathematical concepts to the solution of an important chemical problem, namely, the derivation of analytical rate expressions for simple and complex unimolecular and bimolecular chemical reaction schemes. There are excellent texts available on the subject (*2–6*), which give various treatments; however, the approaches taken either involve a mixture of several manipulations, which may appear confusing to the mathematically deficient reader, or give incomplete results. It is the intention here to develop a streamlined and accessible approach so as to present the material in a simple and unified form and to provide a firm grounding for students to tackle more complex kinetic examples.

Laplace Transforms Applied to Unimolecular Transformations

Chemical reaction mechanisms comprised of unimolecular reactions, such as those given in Table 1, involve elementary steps where one chemical species is transformed into another either reversibly or irreversibly. A wide variety of schemes is possible including consecutive, cyclic, and branched pathways, or any combination of these. The series of rate expressions for each chemical species in a scheme represents a set of linear ordinary differential equations (ODE's). This set of equations can be solved to obtain the time-dependent evolution of each chemical species with a boundary constraint defined by the initial concentration, or some other measured property, of each species at time zero. Marquis Pierre Simon de Laplace (1749–1827) devised an elegant method of solving simultaneous ordinary differential equations with boundary constraints that involves the transformation of these equations into a set of polynomial expressions that can be readily solved by elimination or matrix methods. As will be shown (see below), matrix methods are superior in dealing with reaction schemes involving combinations of consecutive, cyclic, or branched transformations.

The Laplace transform method is a widely established technique for solving simultaneous ordinary linear differential equations (*7–17*). It is a powerful method owing to its generality and straightforward implementation despite its unfortunate absence in chemical kinetics and physical organic–inorganic chemistry course syllabuses and in the mainstream education of chemistry undergraduate and graduate students. A variety of well-known reaction schemes will now be presented and solved by this technique. Interested readers are encouraged

Table 1. Example Reaction Schemes Involving Unimolecular Transformations

Scheme	Rate Equations
$A \xrightarrow{k} B$	$d[A]/dt = -k[A]$ $d[B]/dt = k[A]$
$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$	$d[A]/dt = -k_1[A] + k_2[B]$ $d[B]/dt = k_1[A] - k_2[B]$
$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \underset{k_4}{\overset{k_3}{\rightleftharpoons}} C$	$d[A]/dt = -k_1[A] + k_2[B]$ $d[B]/dt = k_1[A] - (k_2 + k_3)[B] + k_4[C]$ $d[C]/dt = k_3[B] - k_4[C]$
$A \rightleftharpoons B$, cyclic with C ($k_1, k_2, k_3, k_4, k_5, k_6$)	$d[A]/dt = -(k_1 + k_5)[A] + k_2[B] + k_6[C]$ $d[B]/dt = k_1[A] - (k_2 + k_4)[B] + k_3[C]$ $d[C]/dt = k_5[A] + k_4[B] - (k_3 + k_6)[C]$
$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_3} C$	$d[A]/dt = -k_1[A] + k_2[B]$ $d[B]/dt = k_1[A] - (k_2 + k_3)[B]$ $d[C]/dt = k_3[B]$
$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$, branched to C ($k_3, k_4$)	$d[A]/dt = -(k_1 + k_3)[A] + k_2[B]$ $d[B]/dt = k_1[A] - (k_2 + k_4)[B]$ $d[C]/dt = k_3[A] + k_4[B]$
$A \xrightarrow{k_1} B \xrightarrow{k_2} B$	$d[A]/dt = -k_1[A]$ $d[B]/dt = k_1[A] - k_2[B]$ $d[C]/dt = k_2[B]$

to apply the method to their own research problems and to include it in their course teaching. Before illustrating the method, preliminary definitions and important properties are presented.

Rate Equations for Elementary Steps

For a general elementary irreversible reaction involving p reactants and q products

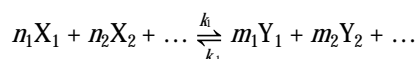$$n_1 X_1 + n_2 X_2 + \ldots \xrightarrow{k} m_1 Y_1 + m_2 Y_2 + \ldots$$
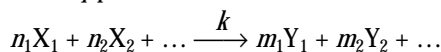
with rate constant k, the corresponding rate laws for disappearance of reactants and appearance of products are given by

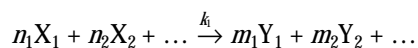$$\frac{d[X_i]}{dt} = -n_i \prod_{j=1}^{p} k[X_j]^{n_j} \tag{1a}$$

with $i = 1, 2, 3, \ldots, p$, and

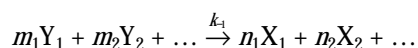$$\frac{d[Y_i]}{dt} = m_i \prod_{j=1}^{q} k[X_j]^{n_j} \tag{1b}$$

with $i = 1, 2, 3, \ldots, q$. For a general elementary reversible reaction

$$n_1 X_1 + n_2 X_2 + \ldots \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} m_1 Y_1 + m_2 Y_2 + \ldots$$

with forward and reverse rate constants k_1 and k_{-1}, the corresponding rate laws are found by first separating the above chemical equation into its two constituent directions and determining the corresponding rate equations for each chemical equation. Hence, for the forward reaction

$$n_1 X_1 + n_2 X_2 + \ldots \xrightarrow{k_1} m_1 Y_1 + m_2 Y_2 + \ldots$$

eqs 1a and 1b apply, and for the reverse reaction

$$m_1 Y_1 + m_2 Y_2 + \ldots \xrightarrow{k_{-1}} n_1 X_1 + n_2 X_2 + \ldots$$

we have

$$\frac{d[X_i]}{dt} = n_i \prod_{j=1}^{p} k_{-1}[Y_j]^{m_j} \tag{2a}$$

with $i = 1, 2, 3, \ldots, p$, and

$$\frac{d[Y_i]}{dt} = -m_i \prod_{j=1}^{q} k_{-1}[Y_j]^{m_j} \tag{2b}$$

with $i = 1, 2, 3, \ldots, q$.

The pairs of equations 1a–2a and 1b–2b are then combined to give the overall rate law for each reactant species

$$\frac{d[X_i]}{dt} = -n_i \prod_{j=1}^{p} k_1[X_j]^{n_j} + n_i \prod_{j=1}^{p} k_{-1}[Y_j]^{m_j} \tag{3a}$$

where $i = 1, 2, 3, \ldots, p$, and the corresponding one for each product species

$$\frac{d[Y_i]}{dt} = -m_i \prod_{j=1}^{q} k_1[X_j]^{n_j} + m_i \prod_{j=1}^{q} k_{-1}[Y_j]^{m_j} \tag{3b}$$

where $i = 1, 2, 3, \ldots, q$.

Definition of Laplace Transform

The Laplace transform, $F(s)$, of a function $f(t)$ is given by the integral

$$F(s) = \int_0^{\infty} \exp(-st) f(t) \, dt \tag{4}$$

In this expression the function $f(t)$ is transformed through the integral operation into a function of s and is called the inverse Laplace transform of $F(s)$. The shorthand notation describing the relationship between the Laplace transform pair is given by

$$F(s) = L\{f(t)\} \tag{5a}$$

and

$$f(t) = L^{-1}\{F(s)\} \tag{5b}$$

Properties

Two essential properties applicable to both Laplace and inverse Laplace transforms are the scaling and linearity properties. These are given by the relationships

$$L\{cf(t)\} = cL\{f(t)\} \tag{6a}$$

and

$$L^{-1}\{cf(t)\} = cL^{-1}\{f(t)\} \tag{6b}$$

for the scaling property, where c is any positive- or negative-valued scaling factor; and by the relationships

$$L\{f(t) + g(t)\} = L\{f(t)\} + L\{g(t)\} \tag{7a}$$

and

$$L^{-1}\{f(t) + g(t)\} = L^{-1}\{f(t)\} + L^{-1}\{g(t)\} \tag{7b}$$

for the linearity property. In addition to these, the first-derivative theorem is given by

$$L\{f'(t)\} = sL\{f(t)\} - f(0) \tag{8}$$

which is required for taking the Laplace transform of differential terms as $d[A]/dt$ appearing in rate expressions. Verification of the above expressions is given in various mathematical texts (7–17) and the reader is referred to these for further reading.

Outline of the Method

The basic idea of the method is to substitute the difficult task of solving simultaneous ordinary differential equations (functions of t) that describe the rate expressions for each chemical species in a reaction scheme by transforming them into a set of simple polynomial equations (functions of s) using the properties given above. Initial conditions are applied and these equations can then be readily solved to obtain Laplace transform functions corresponding to each chemical species (functions of s). Once these are determined, the desired time-dependent function for a given chemical species is found by obtaining the corresponding inverse Laplace transform function (a function of t). In practice this is done by simply looking up Laplace transform pairs in extensively compiled tables (18, 19). For most purposes a very small subset of these tables is used. It should be noted that there is a unique correspondence between two functions constituting a Laplace transform pair; that is, a Laplace transform function is associated with only one inverse Laplace transform function and vice versa.

The method is illustrated in full detail for the following reaction scheme

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$
$$k_3 \downarrow$$
$$C$$
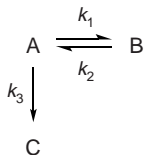
with initial conditions $[A] = [A]_0$, $[B] = 0$, and $[C] = 0$ at time zero. The corresponding rate laws are given by the following set of differential equations

$$d[A]/dt = -(k_1 + k_3)[A] + k_2[B] \qquad (9a)$$

$$d[B]/dt = k_1[A] - k_2[B] \qquad (9b)$$

$$d[C]/dt = k_3[A] \qquad (9c)$$

Letting

$$[A] = x, \quad [B] = y, \quad [C] = z, \quad \text{and} \quad [A]_0 = a \qquad (10)$$

leads to simplification of the equations in (9a-c) to

$$x'(t) + (k_1 + k_3)x(t) - k_2 y(t) = 0 \qquad (11a)$$

$$y'(t) - k_1 x(t) + k_2 y(t) = 0 \qquad (11b)$$

$$z'(t) - k_3 x(t) = 0 \qquad (11c)$$

Applying Laplace transforms to eqs 11a–c using the properties given in eqs 6a, 7a, and 8 yields

$$L\{x'(t) + (k_1 + k_3)x(t) - k_2 y(t)\} = 0 \qquad (12a)$$

$$L\{y'(t) - k_1 x(t) + k_2 y(t)\} = 0 \qquad (12b)$$

$$L\{z'(t) - k_3 x(t)\} = 0 \qquad (12c)$$

or

$$sx(s) - x(0) + (k_1 + k_3)x(s) - k_2 y(s) = 0 \qquad (13a)$$

$$sy(s) - y(0) - k_1 x(s) + k_2 y(s) = 0 \qquad (13b)$$

$$sz(s) - z(0) - k_3 x(s) = 0 \qquad (13c)$$

Further applying the initial condition criteria to eqs 13a–c yields

$$[s + k_1 + k_3]x(s) - k_2 y(s) = a \qquad (14a)$$

$$-k_1 x(s) + [k_2 + s]y(s) = 0 \qquad (14b)$$

$$sz(s) - k_3 x(s) = 0 \qquad (14c)$$

The set of equations 14a–c is solved for $x(s)$, $y(s)$, and $z(s)$ using the matrix method. This method is the easiest one to employ for simultaneous linear equations. Other names for this method include the method of determinants and Cramer's method (20). The set of equations 14a–c is written first in matrix form:

$$\begin{bmatrix} s+k_1+k_3 & -k_2 & 0 \\ -k_1 & k_2+s & 0 \\ -k_3 & 0 & s \end{bmatrix} \begin{bmatrix} x(s) \\ y(s) \\ z(s) \end{bmatrix} = \begin{bmatrix} a \\ 0 \\ 0 \end{bmatrix} \qquad (15)$$

The determinant of the left-hand matrix is obtained as follows:

$$D = \begin{vmatrix} s+k_1+k_3 & -k_2 & 0 \\ -k_1 & k_2+s & 0 \\ -k_3 & 0 & s \end{vmatrix} = s\left(s^2 + (k_1+k_2+k_3)s + k_3 k_2\right)$$

For convenience the determinant, D, can be written as

$$D = s(s + \gamma_1)(s + \gamma_2) \qquad (16)$$

where

$$\gamma_1 \gamma_2 = k_2 k_3 \qquad (17a)$$

$$\gamma_1 + \gamma_2 = k_1 + k_2 + k_3 \qquad (17b)$$

Solving for $x(s)$, $y(s)$, and $z(s)$ yields

$$x(s) = \frac{1}{D}\begin{vmatrix} a & -k_2 & 0 \\ 0 & k_2+s & 0 \\ 0 & 0 & s \end{vmatrix} = \frac{a(k_2+s)}{(s+\gamma_1)(s+\gamma_2)} \qquad (18)$$

$$y(s) = \frac{1}{D}\begin{vmatrix} s+k_1+k_3 & a & 0 \\ -k_1 & 0 & 0 \\ -k_3 & 0 & s \end{vmatrix} = \frac{ak_1}{(s+\gamma_1)(s+\gamma_2)} \qquad (19)$$

and

$$z(s) = \frac{1}{D}\begin{vmatrix} s+k_1+k_3 & -k_2 & a \\ -k_1 & k_2+s & 0 \\ -k_3 & 0 & 0 \end{vmatrix} = \frac{ak_3(k_2+s)}{s(s+\gamma_1)(s+\gamma_2)} \qquad (20)$$

The corresponding inverse Laplace transforms of $x(s)$, $y(s)$, and $z(s)$ found from tables of transforms yield the functions $x(t)$, $y(t)$, and $z(t)$:

$$x(t) = a\left[\left(\frac{k_2-\gamma_1}{\gamma_2-\gamma_1}\right)\exp(-\gamma_1 t) - \left(\frac{k_2-\gamma_2}{\gamma_2-\gamma_1}\right)\exp(-\gamma_2 t)\right] \qquad (21a)$$

$$y(t) = a\left(\frac{k_1}{\gamma_2-\gamma_1}\right)\left[\exp(-\gamma_1 t) - \exp(-\gamma_2 t)\right] \qquad (21b)$$

$$z(t) = a\left[\frac{k_2 k_3}{\gamma_1 \gamma_2} + \left(\frac{k_3(k_2-\gamma_1)}{\gamma_1(\gamma_1-\gamma_2)}\right)\exp(-\gamma_1 t) + \left(\frac{k_3(k_2-\gamma_2)}{\gamma_2(\gamma_2-\gamma_1)}\right)\exp(-\gamma_2 t)\right] \qquad (21c)$$

Finally, the set of equations 21a–c can be rewritten in the familiar form

$$[A] = [A]_0\left[\left(\frac{k_2-\gamma_1}{\gamma_2-\gamma_1}\right)\exp(-\gamma_1 t) - \left(\frac{k_2-\gamma_2}{\gamma_2-\gamma_1}\right)\exp(-\gamma_2 t)\right] \qquad (22a)$$

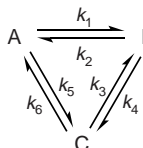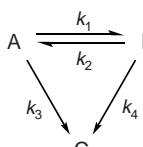$$[B] = [A]_0\left(\frac{k_1}{\gamma_2-\gamma_1}\right)\left[\exp(-\gamma_1 t) - \exp(-\gamma_2 t)\right] \qquad (22b)$$

$$[C] = [A]_0\left[1 + \left(\frac{k_3(k_2-\gamma_1)}{\gamma_1(\gamma_1-\gamma_2)}\right)\exp(-\gamma_1 t) + \left(\frac{k_3(k_2-\gamma_2)}{\gamma_2(\gamma_2-\gamma_1)}\right)\exp(-\gamma_2 t)\right] \qquad (22c)$$

using the definitions given in eqs 10 and 17a–b.

Table 2 summarizes the results of common reaction schemes solved by this method. In the case of the example involving a reversible reaction between two chemical species (entry 2 in Table 2), it can be shown that the equilibrium limit of the ratio of the product and reactant concentrations is equal to the ratio of the forward and reverse rate constants. Moreover, in the case of the cycle depicted by the fourth entry in Table 2 it can be shown that the algebraic sum of the loga-

Table 2. Reaction Schemes Involving Unimolecular Transformations Solved by the Laplace Transform Method

Scheme	Initial Conditions	Rate Equations
$A \xrightarrow{k} B$	$[A]_0 = a$; $[B]_0 = 0$	$[A] = a \exp(-kt)$ $[B] = a[1 - \exp(-kt)]$
$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$	$[A]_0 = a$; $[B]_0 = 0$	$[A] = \dfrac{a}{k_1 + k_2}\left[k_2 + k_1\exp(-(k_1+k_2)t)\right]$ $[B] = \dfrac{ak_1}{k_1 + k_2}\left[1 - \exp(-(k_1+k_2)t)\right]$

Scheme: $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \underset{k_4}{\overset{k_3}{\rightleftharpoons}} C$
Initial Conditions: $[A]_0 = a$; $[B]_0 = 0$; $[C]_0 = 0$

$$[A] = a\left[\frac{k_2 k_4}{\gamma_1 \gamma_2} - \frac{k_1(\gamma_1 - k_3 - k_4)}{\gamma_1(\gamma_2 - \gamma_1)}e^{-\gamma_1 t} - \frac{k_1(k_3 + k_4 - \gamma_2)}{\gamma_2(\gamma_2 - \gamma_1)}e^{-\gamma_2 t}\right]$$

$$[B] = ak_1\left[\frac{k_4}{\gamma_1 \gamma_2} + \frac{k_4 - \gamma_1}{\gamma_1(\gamma_1 - \gamma_2)}e^{-\gamma_1 t} + \frac{k_4 - \gamma_2}{\gamma_2(\gamma_2 - \gamma_1)}e^{-\gamma_2 t}\right]$$

$$[C] = ak_1 k_3\left[\frac{1}{\gamma_1 \gamma_2} + \frac{1}{\gamma_1(\gamma_1 - \gamma_2)}e^{-\gamma_1 t} - \frac{1}{\gamma_2(\gamma_1 - \gamma_2)}e^{-\gamma_2 t}\right]$$

where
$\gamma_1 \gamma_2 = k_2 k_4 + k_1 k_3 + k_1 k_4$
$\gamma_1 + \gamma_2 = k_1 + k_2 + k_3 + k_4$

Scheme: $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$, with k_5, k_3 and k_6, k_4 to C
Initial Conditions: $[A]_0 = a$; $[B]_0 = 0$; $[C]_0 = 0$

$$[A] = a\left[\frac{\beta}{\gamma_1 \gamma_2} + \frac{\alpha\gamma_1 - \gamma_1^2 - \beta}{\gamma_2 - \gamma_1}e^{-\gamma_1 t} + \frac{\gamma_2^2 - \alpha\gamma_2 + \beta}{\gamma_2 - \gamma_1}e^{-\gamma_2 t}\right]$$

$$[B] = a\left[\frac{\varepsilon}{\gamma_1 \gamma_2} + \frac{k_1\gamma_1 - \varepsilon}{\gamma_2 - \gamma_1}e^{-\gamma_1 t} + \frac{\varepsilon - k_1\gamma_2}{\gamma_2 - \gamma_1}e^{-\gamma_2 t}\right]$$

$$[C] = a\left[\frac{\delta}{\gamma_1 \gamma_2} + \frac{k_5\gamma_1 - \delta}{\gamma_2 - \gamma_1}e^{-\gamma_1 t} + \frac{\delta - k_5\gamma_2}{\gamma_2 - \gamma_1}e^{-\gamma_2 t}\right]$$

where
$\alpha = k_2 + k_3 + k_4 + k_6$; $\beta = k_2 k_4 + k_2 k_6 + k_3 k_6$;
$\varepsilon = k_1 k_4 + k_1 k_6 + k_4 k_5$; $\delta = k_1 k_3 + k_2 k_5 + k_3 k_5$;
$\gamma_1 \gamma_2 = \beta + \varepsilon + \delta$; $\gamma_1 + \gamma_2 = \alpha + k_1 + k_5$

Scheme: $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_3} C$
Initial Conditions: $[A]_0 = a$; $[B]_0 = 0$; $[C]_0 = 0$

$$[A] = \frac{a}{\gamma_2 - \gamma_1}\left[(k_2 + k_3 - \gamma_1)e^{-\gamma_1 t} - (k_2 + k_3 - \gamma_2)e^{-\gamma_2 t}\right]$$

$$[B] = \frac{ak_1}{\gamma_2 - \gamma_1}\left[e^{-\gamma_1 t} - e^{-\gamma_2 t}\right]$$

$$[C] = a\left[1 + \frac{k_1 k_3}{\gamma_1(\gamma_1 - \gamma_2)}e^{-\gamma_1 t} + \frac{k_1 k_3}{\gamma_2(\gamma_2 - \gamma_1)}e^{-\gamma_2 t}\right]$$

where
$\gamma_1 \gamma_2 = k_1 k_3$; $\gamma_1 + \gamma_2 = k_1 + k_2 + k_3$

Scheme: $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$, with k_3 and k_4 to C
Initial Conditions: $[A]_0 = a$; $[B]_0 = 0$; $[C]_0 = 0$

$$[A] = \frac{a}{\gamma_2 - \gamma_1}\left[(k_2 + k_3 - \gamma_1)e^{-\gamma_1 t} - (k_2 + k_3 - \gamma_2)e^{-\gamma_2 t}\right]$$

$$[B] = \frac{ak_1}{\gamma_2 - \gamma_1}\left[e^{-\gamma_1 t} - e^{-\gamma_2 t}\right]$$

$$[C] = a\left[1 - \frac{\gamma_2 - k_4}{\gamma_2 - \gamma_1}e^{-\gamma_1 t} - \frac{\gamma_1 + k_4}{\gamma_1 - \gamma_2}e^{-\gamma_2 t}\right]$$

where
$\gamma_1 \gamma_2 = k_1 k_3 + k_2 k_4 + k_3 k_4$; $\gamma_1 + \gamma_2 = k_1 + k_2 + k_3 + k_4$

Scheme: $A \xrightarrow{k_1} B \xrightarrow{k_2} B$
Initial Conditions: $[A]_0 = a$; $[B]_0 = 0$; $[C]_0 = 0$

$$[A] = a\exp(-k_1 t)$$

$$[B] = \frac{ak_1}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right]$$

$$[C] = a\left[1 - \frac{k_2}{k_2 - k_1}\exp(-k_1 t) - \frac{k_1}{k_1 - k_2}\exp(-k_2 t)\right]$$

Table 3. Reaction Schemes Involving Bimolecular Transformations as Given in Reference 2

Scheme	Initial Conditions	Rate Equations
A + B $\xrightarrow{k}$ C	$[A]_0 = a$; $[B]_0 = b$; $[C]_0 = 0$	$kt = \dfrac{1}{b-a}\ln\left(\dfrac{a(b-x)}{b(a-x)}\right)$
		where $x = [C]$ at time t
A + B $\xrightarrow{k}$ C	$[A]_0 = a$; $[B]_0 = a$; $[C]_0 = 0$	$[A] = \dfrac{a}{1+kat}$
2A $\xrightarrow{k}$ B	$[A]_0 = a$; $[B]_0 = 0$	$\dfrac{1}{a-x} - \dfrac{1}{a} = 2kt$
		where $x = [B]$ at time t

rithms of the ratios of product and reactant concentrations around the cycle is identically zero at equilibrium.

An important realization is that the method of Laplace transforms cannot be applied to chemical systems involving bimolecular transformations because there is no distributive property for product functions; that is, the Laplace transform of a product of functions does not equal the product of the Laplace transforms of those functions:

$$L\{f(t)g(t)\} \neq L\{f(t)\}L\{g(t)\}$$

Differential equations describing bimolecular transformations are classified as nonlinear and are generally solved by numerical methods, with the exception of simple cases (see below), which are solved by integration methods.

A point of caution with respect to refs 2 and 3 is that the tables of transforms given therein do *not* refer to Laplace transforms according to the formal definition given in eq 4 and stated throughout the mathematical literature (7–17). Rather, they are obtained using the Laplace–Carson transform given by the analogous definition

$$G(s) = s\int_0^\infty \exp(-st)\,f(t)\,\mathrm{d}t = LC\{f(t)\} = sL\{f(t)\} \quad (23)$$

Note that use of this definition results in the addition or omission of terms in the numerators and denominators of the Laplace transform expressions as appropriate. Scaling and linearity properties also hold for the Laplace–Carson transform; however, the statement of the first-derivative theorem differs and is given by

$$LC\{f(t)\} = sG(s) - sf(0) \quad (24)$$

There is no practical advantage in using one definition over the other.

Integral Method Applied to Simple Bimolecular Transformations

Capellos and Bielski (2) give rate expressions for a number of bimolecular kinetic schemes as shown in Table 3. A more complete set of solutions derived in the present work is shown in Table 4. The method used to arrive at these expressions is illustrated in full detail for the scheme

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$
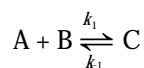
with initial conditions $[A]_0 = a$, $[B]_0 = b$, and $[C]_0 = 0$ at time zero. The corresponding rate laws are given by the following set of differential equations:

$$d[A]/dt = -k_1[A][B] + k_{-1}[C] \quad (25a)$$

$$d[B]/dt = -k_1[A][B] + k_{-1}[C] \quad (25b)$$

$$d[C]/dt = k_1[A][B] - k_{-1}[C] \quad (25c)$$

From eqs 25a–c it is readily apparent that

$$d[A]/dt = d[B]/dt = -d[C]/dt \quad (26)$$

whereupon subsequent integration using the boundary conditions leads immediately to the relationships

$$[A] - [A]_0 = [B] - [B]_0 \quad (27a)$$

$$[C] = [A]_0 - [A] \quad (27b)$$

Substitution of eqs 27a–b into eq 25a and integration over the boundary conditions leads to

$$k_1 t(\gamma_1 - \gamma_2) = \ln\left[\frac{([A]+\gamma_1)([A]_0+\gamma_2)}{([A]+\gamma_2)([A]_0+\gamma_1)}\right] \quad (28)$$

where

$$\gamma_1\gamma_2 = \frac{[A]_0 k_{-1}}{k_1}$$

and

$$\gamma_1 + \gamma_2 = [A]_0 - [B]_0 - \frac{k_{-1}}{k_1}$$

The expressions for [B] and [C] are found by replacing [A] in eq 28 with the appropriate expression defined by eqs 27a–b. Thus, the relationships

$$k_1 t(\gamma_1 - \gamma_2) = \ln\left[\frac{([B]-[B]_0+[A]_0+\gamma_1)([A]_0+\gamma_2)}{([B]-[B]_0+[A]_0+\gamma_2)([A]_0+\gamma_1)}\right] \quad (29a)$$

$$k_1 t(\gamma_1 - \gamma_2) = \ln\left[\frac{([A]_0-[C]+\gamma_1)([A]_0+\gamma_2)}{([A]_0-[C]+\gamma_2)([A]_0+\gamma_1)}\right] \quad (29b)$$

are obtained. The expressions appearing in Table 4 are rewritten as proper concentration–time-dependent functions.

Summary

The powerful utility of Laplace transforms has been demonstrated for deriving rate expressions for any reaction mechanism comprising only unimolecular reactions. The method is not applicable to schemes involving bimolecular elementary steps; however, integration methods may be used to obtain rate expressions for simple cases. Incorporation of these techniques in chemical kinetics, physical organic, and physical inorganic chemistry courses should be a great asset for students' understanding of rate expression derivations for a wide variety of chemical reactions and reaction mechanism phenomena.

Table 4. Reaction Schemes Involving Bimolecular Transformations Solved by the Integration Method

Scheme	Initial Conditions	Rate Equations
$A + B \xrightarrow{k} C$	$[A]_0 = a;\ [B]_0 = b;$ $[C]_0 = 0$	$[A] = (b-a)\left[\dfrac{b}{a}\exp((b-a)kt) - 1\right]^{-1}$ $[B] = (a-b)\left[\dfrac{a}{b}\exp((a-b)kt) - 1\right]^{-1}$ $[C] = a\left[\dfrac{a-b}{b\exp((b-a)kt) - a} + 1\right]$
$A + B \xrightarrow{k} C$	$[A]_0 = a;\ [B]_0 = a;$ $[C]_0 = 0$	$[A] = \dfrac{a}{kta + 1}$ $[B] = \dfrac{a}{kta + 1}$ $[C] = \dfrac{kta^2}{kta + 1}$
$2A \xrightarrow{k} B$	$[A]_0 = a;\ [B]_0 = 0$	$[A] = \dfrac{a}{2kta + 1}$ $[B] = \dfrac{kta^2}{2kta + 1}$
$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C$	$[A]_0 = a;\ [B]_0 = b;$ $[C]_0 = 0$	$[A] = \dfrac{\gamma_1 - R\gamma_2}{R - 1}$ $[B] = \dfrac{(a-b+\gamma_1) - R(a-b+\gamma_2)}{R - 1}$ $[C] = \dfrac{a+\gamma_1 - R(a+\gamma_2)}{1 - R}$ where $\gamma_1\gamma_2 = -\dfrac{ak_2}{k_1};\ \ \gamma_1 + \gamma_2 = b - a + \dfrac{k_2}{k_1};$ $R = \left(\dfrac{a+\gamma_1}{a+\gamma_2}\right)e^{-k_1(\gamma_2-\gamma_1)t}$
$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C$	$[A]_0 = a;\ [B]_0 = a;$ $[C]_0 = 0$	$[A] = \dfrac{\gamma_1 - \gamma_2 R}{R - 1}$ $[B] = \dfrac{\gamma_1 - R\gamma_2}{R - 1}$ $[C] = \dfrac{a+\gamma_1 - R(a+\gamma_2)}{1 - R}$ where $\gamma_1\gamma_2 = -\dfrac{ak_2}{k_1};\ \ \gamma_1 + \gamma_2 = \dfrac{k_2}{k_1};$ $R = \left(\dfrac{a+\gamma_1}{a+\gamma_2}\right)e^{-2k_1(\gamma_2-\gamma_1)t}$
$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$	$[A]_0 = a;\ [B]_0 = 0$	$[A] = \dfrac{\gamma_1 - \gamma_2 R}{R - 1}$ $[B] = \dfrac{a+\gamma_1 - R(a+\gamma_2)}{2(1 - R)}$ where $\gamma_1\gamma_2 = -\dfrac{ak_2}{2k_1};\ \ \gamma_1 + \gamma_2 = \dfrac{k_2}{2k_1};$ $R = \left(\dfrac{a+\gamma_1}{a+\gamma_2}\right)e^{-2k_1(\gamma_2-\gamma_1)t}$

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