R&D NOTES

Second-Order Reaction in a Semibatch Reactor

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With growing emphasis in chemical manufacturing away from large-scale single-product facilities to smaller-scale facilities, often with multipurpose and multiproduct capability, many companies are aiming for greater flexibility in responding to demands of customers for new products and higher quality (Singh, 1986; Rotstein et al., 1994). Consistent with this trend is the increasing importance of processing involving batch and semibatch reactors and the need to better understand the performance of those reactors.

Semibatch reactors, in many applications, involve a substantial increase in the volume of reaction mixture during a processing cycle. For example, in emulsion polymerization the final volume of reaction mixture may be several multiples of the original volume (Fram et al., 1955; Wessling, 1968).

In general the performance of a semibatch reactor that undergoes a large volume change is influenced by two important factors—kinetics and dilution. For complex reaction systems, the relative importance of these two factors, and how they interact in influencing reactor performance, may not be obvious. Some insight can be gained by examining more tractable cases. Previous work developed an analytical solution for a second-order reaction in a semibatch reactor that is applicable over small changes in reactor volume. This article develops a solution for the same system that applies when volume changes are large.

If a second-order reaction of species A and B is conducted in a constant-volume batch reactor, and the concentration C_B is much greater than C_A, the operation can be modeled as a pseudo-first-order reaction in species A. For a semibatch reactor, this assumption provides an analytical solution that is valid during the early stage of operation, before dilution of B becomes important. Alternatively, a solution that is based on the assumption of constant mols of $B(N_B)$ takes dilution into account and is valid over an extended period of reactor operation.

The operation involves an isothermal, constant-density, reaction,

$$A + B \rightarrow P \tag{1}$$

in a well-mixed semibatch reaction vessel. The reactor initially contains a volume V_0 of solution of reactant B at a molar concentration, C_{B_0}. At time, $t = 0$, a solution containing species A at a molar concentration, C_{A_F}, begins flowing into the vessel at constant volumetric flow rate, ν_0. None of the liquid in the vessel is discharged, and the liquid volume increases with time.

The equation governing concentration-time behavior in the reactor is

$$C_{A_F} - C_A - \tau(-r_A) = \tau dC_A/d\tau, \tag{2}$$

and the volume-time behavior is

$$\tau = \tau_0 + t, \tag{3}$$

where $\tau = V/\nu_0$ and $\tau_0 = V_0/\nu_0$. To solve for C_A vs. τ, a kinetics expression is substituted in Eq. 2 for $(-r_A)$, and the equation integrated from τ_0 to τ. For simple first- and zero-order kinetics, an analytical solution can be found. When the kinetics of Eq. 1 are described by a mixed second-order rate expression (first order in each reactant), there are two assumptions that lead to approximate analytical solutions.

(a) $C_B \approx C_{B_0}$: For a discussion of this case, see Butt (1980) or Fogler (1992). The reaction term, $(-r_A)$, in Eq. 2 is replaced by kC_A, where k is the pseudo-first-order rate parameter, $k'C_{B_0}$. The analytical solution to Eq. 2 is

$$C_A = (C_{A_F}/k\tau)\{1 - e^{(k\tau_0 - k\tau)}\} \tag{4}$$

for an initial concentration of A of zero in the reactor.

(b) $N_B \approx N_{B_0}$: For this case, the rate of reaction is approximated as follows:

$$(-r_A) \approx k'(N_{B_0}/V)C_A = (V_0/V)k'C_{B_0}C_A, \tag{5a}$$

and using the same definition of the pseudo-first-order rate parameter, k, as before,

$$(-r_A) \approx (V_0/V)kC_A \quad \text{or} \quad = (\tau_0/\tau)kC_A. \tag{5b}$$

The term V_0/V (or τ_0/τ) accounts for dilution of B. If the rate expression is combined with Eq. 2, the result is

$$C_{A_F} - C_A - k\tau_0 C_A = \tau dC_A/d\tau. \tag{6}$$

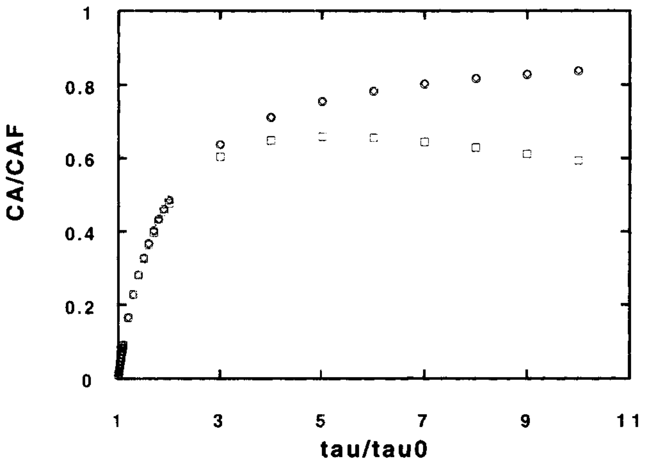

Figure 1. Concentration-time profile for $k\tau_0 = 0.1$.

Symbols: circles, Eq. 7; squares, Eq. 4; diamonds, numerical solution for $C_{B_0}/C_{A_F} = 10$.

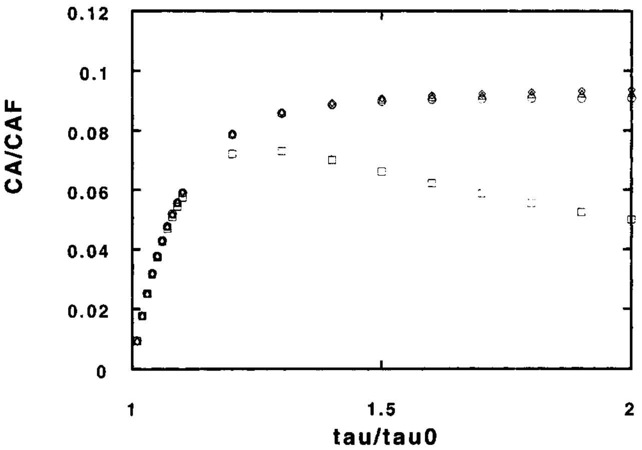

Figure 3. Concentration-time profile for $k\tau_0 = 10$.

Symbols: circles, Eq. 7; squares, Eq. 4; diamonds, numerical solution for $C_{B_0}/C_{A_F} = 20$; triangles, numerical solution for $C_{B_0}/C_{A_F} = 30$.

After separating variables, and integrating from $(\tau_0, 0)$ to (τ, C_A), the solution becomes

$$C_A = [C_{A_F}/(1+k\tau_0)]\{1-(\tau/\tau_0)^{-(1+k\tau_0)}\}. \tag{7}$$

Figures 1 to 3 show solutions to Eqs. 4 and 7 for kinetic parameters, $k\tau_0 = 0.1$, 1, and 10. Each figure also shows one or more solution determined by numerically solving the reactor model Eq. 2 by a fourth-order Runge-Kutta method (Smith, 1981) using the kinetic equation, $(-r_A) = k' C_B C_A$, where the variations of both concentrations are taken into account. The numerical solutions depend upon C_{B_0}/C_{A_F}, the ratio of the initial concentration of B and the feed concentration of A.

In Figures 1 to 3, the numerical solutions show a steep slope at low values of τ/τ_0, and a much more gradual slope, at higher values of τ/τ_0. The approximate solution, Eq. 4, for the case, $C_B \approx C_{B_0}$, agrees well with the numerical solutions during the most dynamic part of the profiles, abruptly reaches a maximum, and declines rapidly, diverging from the numerical solutions. The approximate solution, Eq. 7, for the case, $N_B \approx N_{B_0}$, follows the trend of the numerical solutions. However, at very high values of τ/τ_0, the approximate solution and numerical solutions diverge because Eq. 7 approaches an asymptotic limit, $C_{A_F}/(1+k\tau_0)$, while the numerical solutions continue to gradually increase. At very high values of τ/τ_0, the agreement is improved if C_{B_0}/C_{A_F} is increased. For example, Figure 3 shows numerical solutions for $C_{B_0}/C_{A_F} = 20$ and 30. Over the range of τ/τ_0 shown, the approximate profile compares best with the latter.

The accuracy of the approximated values of C_A/C_{A_F} depends upon the extent to which N_B differs from the initial value, N_{B_0}. The fractional conversion of B equals the ratio of reacted mols of A to the initial mols of B,

$$\begin{aligned} f_B &= (C_{A_F}\nu_0 t - C_A V)/C_{B_0}V_0 \\ &= [(\tau/\tau_0)(1 - C_A/C_{A_F}) - 1]/(C_{B_0}/C_{A_F}). \end{aligned} \tag{8}$$

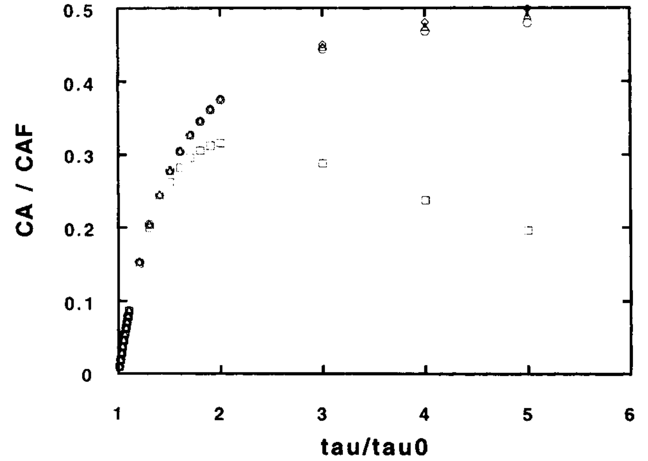

Figure 2. Concentration-time profile for $k\tau_0 = 1$.

Symbols: circles, Eq. 7; squares, Eq. 4; diamonds, numerical solution for $C_{B_0}/C_{A_F} = 10$; triangles, numerical solution for $C_{B_0}/C_{A_F} = 20$.

Table 1. Approximate Error in Estimates Using Eq. 7

$k \times \text{tau}_0$	C_{B_0}/C_{A_F}	tau/tau$_0$	$fB \times 100$ Eqs. 7 and 8	$fB \times 100$ by Num. Int.	% Error in C_A/C_{A_F} Calc. by Eq. 7
0.1	10	10	6.3	6.1	−0.2
0.1	10	20	14.9	13.9	−0.6
1	10	4	11.3	10.8	−2.6
1	10	5	16.0	15.0	−3.9
1	10	6	20.8	19.2	−5.2
1	20	6	10.4	10.0	−2.7
1	20	8	15.3	14.5	−4.2
1	20	10	20.3	18.8	−5.6
10	10	2	8.2	8.1	−5.9
10	20	2	4.1	4.1	−3.0
10	20	3	8.6	8.5	−6.7
10	30	2	2.7	2.7	−2.0
10	30	3	5.8	5.7	−4.5
10	30	4	8.8	8.7	−7.0

At a given value of τ/τ_0, exact values of f_B are calculated using values of C_A/C_{A_F} determined by numerically integrating Eq. 2. However, for small values of f_B, Eq. 8 provides a reasonable estimate of f_B using C_A/C_{A_F} values determined from Eq. 7. Table 1 shows exact and approximate values of f_B and errors in approximate values of C_A/C_{A_F} for various values of τ/τ_0, kinetic parameters, and C_{B_0}/C_{A_F}. The table shows that the accuracy of the Eq. 7 predictions improves the lower kinetic parameter and the greater ratio, C_{B_0}/C_{A_F}.

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