Lindemann Mechanism (Unimolecular Decomposition)

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

Differential Rate Law:

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2[B]$$

Exact Solution via laplace transform or matrix methods (see Johnston p. 329) :

$$[A] = \frac{[A_0]}{\lambda_2 - \lambda_3}\left[(k_1 - \lambda_3)e^{(-\lambda_2 t)} - (k_1 - \lambda_2)e^{(-\lambda_3 t)}\right] \qquad \lambda_2\lambda_3 = k_1k_2$$

$$[B] = \frac{[A_0]k_1}{\lambda_2 - \lambda_3}\left[-e^{(-\lambda_2 t)} + e^{(-\lambda_3 t)}\right] \qquad \lambda_2 + \lambda_3 = k_1 + k_{-1} + k_2$$

$$[C] = [A_0]\left[1 + \frac{\lambda_2\lambda_3}{\lambda_2 - \lambda_3}\frac{e^{(-\lambda_2 t)}}{\lambda_2} - \frac{e^{(-\lambda_3 t)}}{\lambda_3}\right] \qquad (k_1 - \lambda_2)(k_1 - \lambda_3) = -k_1k_{-1}$$

If $k_1 << (k_{-1} + k_2)$ the exact solutions reduce to:

$$[A] = \frac{[A_0]}{k_{-1} + k_2}\left[\frac{k_1 k_{-1}}{k_{-1} + k_2} e^{(-(k_{-1}+k_2)t)} + (k_{-1} + k_2) e^{\left(-\frac{k_1 k_2}{(k_{-1}+k_2)} t\right)}\right]$$

$$[B] = \frac{[A_0] k_1}{k_{-1} + k_2}\left[e^{(-(k_{-1}+k_2)t)} + e^{\left(-\frac{k_1 k_2}{(k_{-1}+k_2)} t\right)}\right]$$

$$[C] = [A_0]\left[1 + \frac{k_1 k_2}{k_{-1} + k_2}\left\{\frac{e^{(-(k_{-1}+k_2)t)}}{k_{-1} + k_2} - \frac{(k_{-1} + k_2)}{k_1 k_2} e^{\left(-\frac{k_1 k_2}{(k_{-1}+k_2)} t\right)}\right\}\right]$$

FROM H.S. JOHNSTON GAS PHASE REACTION RATE THEORY

pp. 331-332

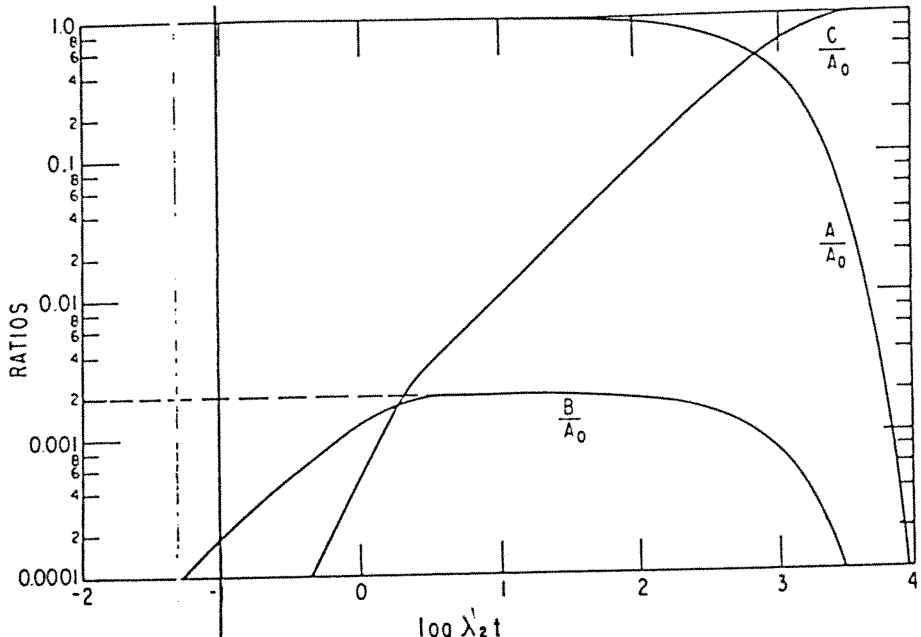


Fig. A-1. Comparison of exact integrated function (solid curve) with steady-state solution (dashed curve) for the mechanism $A \underset{b}{\overset{a}{\rightleftarrows}} B \overset{c}{\longrightarrow} C$. The rate constants are $a = 0.002$, $b = c = 0.5$.

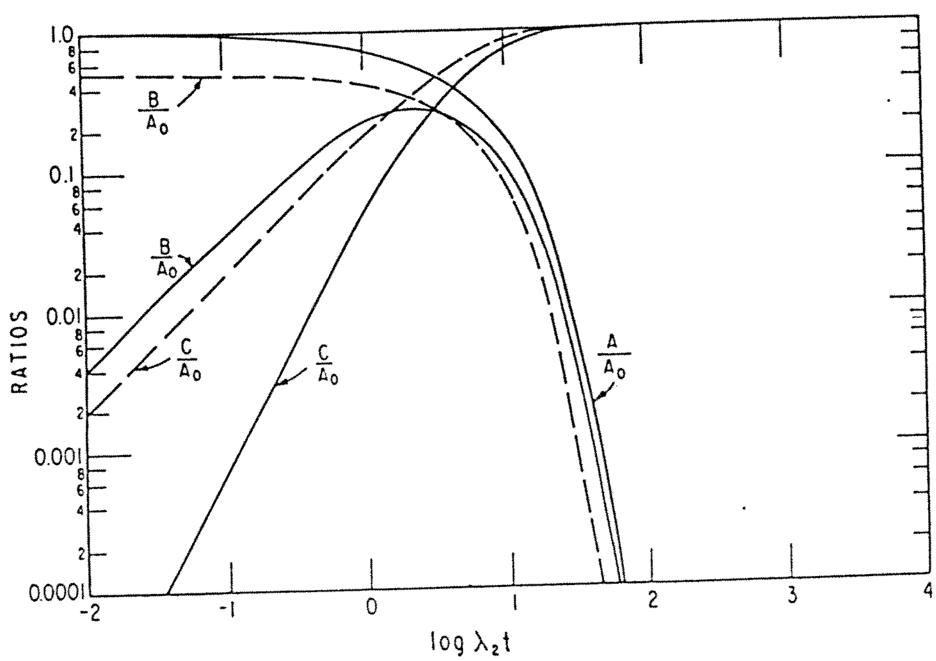
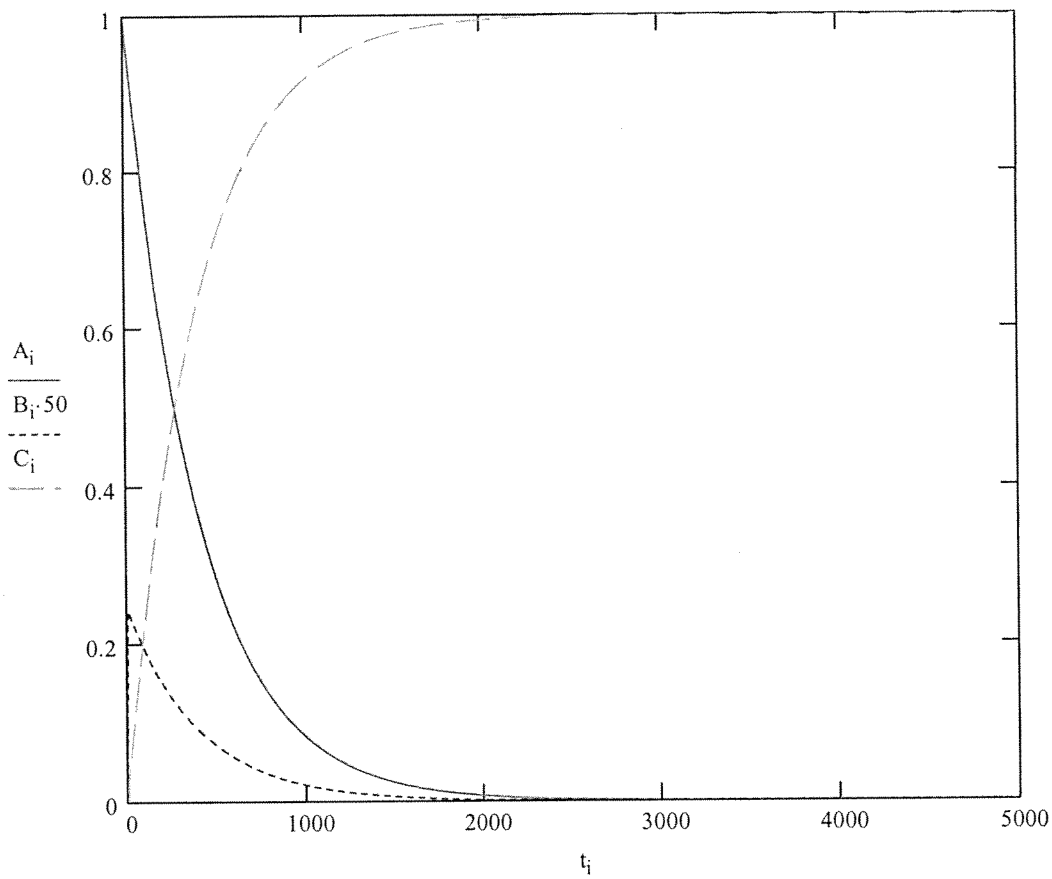


Fig. A-2. The same as Fig. 1, except that the rate constants are $a = b = c = 1.0$.

k1 := 0.005 k1inv := 0.5 k2 := 0.5



k1 := 0.5 k1inv := 0.5 k2 := 0.5