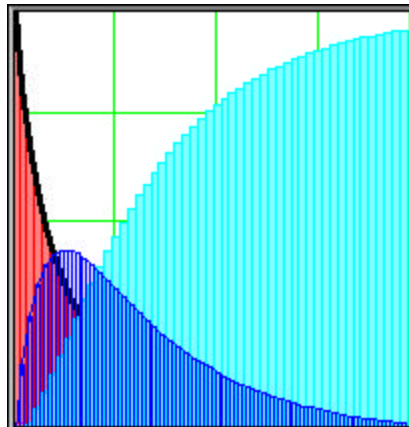


ABC

Chemical Kinetics

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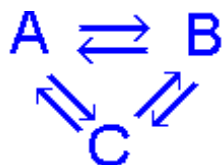
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Icons and Style/colour code used:

Roman underlined = hyperlinks

Green_highlighted = data entry

Light_yellow = important equations or intermediate results

Bright_yellow = important final results



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Concentrations as functions of time. Derivation of the Exact Solution for:



For this system, the differential equation that express the time dependence of [A] is:

$$-\left(\frac{d}{dt}[A]\right) = k_1 \cdot [A] \quad \text{which integrates directly as} \quad [A] = a \cdot e^{-k_1 \cdot t} \quad \text{where } a = [A]_0 \text{ (the [A] when } t=0)$$

This integration is easy and a classic exercise in "simple" reactions Kinetics, that you can practice by yourself. We concentrate next on the more complicated step. For the intermediate:

$$\frac{d}{dt}[B] = k_1 \cdot [A] - k_2 \cdot [B] = k_1 \cdot (a \cdot e^{-k_1 \cdot t}) - k_2 \cdot [B]$$

$$d[B] = a \cdot k_1 \cdot e^{-k_1 \cdot t} \cdot dt - k_2 \cdot [B] \cdot dt$$

$$d[B] + k_2 \cdot [B] \cdot dt = a \cdot k_1 \cdot e^{-k_1 \cdot t} \cdot dt \quad \text{(I)}$$

$$e^{k_2 \cdot t} \cdot (d[B] + k_2 \cdot [B] \cdot dt) = e^{k_2 \cdot t} \cdot (a \cdot k_1 \cdot e^{-k_1 \cdot t} \cdot dt)$$

$$d([B] \cdot e^{k_2 \cdot t}) = a \cdot k_1 \cdot e^{(k_2 - k_1) \cdot t} \cdot dt \quad \text{(II)}$$

$$\int_{t=0, [B]=0}^{t, [B]} 1 \cdot d([B] \cdot e^{k_2 \cdot t}) = a \cdot k_1 \cdot \int_{t=0}^t e^{(k_2 - k_1) \cdot t} dt \quad \text{assuming here that } [B] = 0 \text{ when } t = 0$$

$$[B] \cdot e^{k_2 \cdot t} - 0 \cdot e^{k_2 \cdot 0} = a \cdot k_1 \cdot \frac{e^{(k_2 - k_1) \cdot t}}{k_2 - k_1} - a \cdot k_1 \cdot \frac{e^{(k_2 - k_1) \cdot 0}}{k_2 - k_1}$$

$$[B] \cdot e^{k_2 \cdot t} = \frac{a \cdot k_1}{k_2 - k_1} \cdot e^{(k_2 - k_1) \cdot t} - \frac{a \cdot k_1}{k_2 - k_1}$$

$$[B] = \frac{a \cdot k_1}{k_2 - k_1} \cdot \left[\frac{e^{(k_2 - k_1) \cdot t}}{e^{k_2 \cdot t}} - \frac{1}{e^{k_2 \cdot t}} \right] \quad \text{P}$$

$$[B] = \frac{a \cdot k_1}{k_2 - k_1} \cdot (e^{-k_1 \cdot t} - e^{-k_2 \cdot t})$$

Finally, using the mass balance: $[C] = a - [A] - [B]$

$$[C] = a - (a \cdot e^{-k_1 \cdot t}) - \left[\frac{a \cdot k_1}{k_2 - k_1} \cdot (e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) \right] \quad \text{P}$$

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

(since no calculus is needed here we leave the work to you)

Checking

We will use the symbolic processor of Mathcad for checking the expressions obtained.

Working with the differential equation that describes the time dependence of [B] and the functions derived:

$$\frac{d}{dt}[B] = k_1 \cdot [A] - k_2 \cdot [B] \quad A(t) := a \cdot e^{-k_1 \cdot t} \quad B(t) := \frac{a \cdot k_1}{k_2 - k_1} \cdot (e^{-k_1 \cdot t} - e^{-k_2 \cdot t})$$

Don't worry in this moment by the "*this variable is not defined above*" error (red variables in the math expressions), because we will use this functions not for calculations but for the algebraic transformations below.

1) With the live symbolic processing we can use the functions names.

The right hand side: $k_1 \cdot A(t) - k_2 \cdot B(t)$ simplify $\rightarrow k_1 \cdot a \cdot \frac{-\exp(-k_1 \cdot t) \cdot k_1 + k_2 \cdot \exp(-k_2 \cdot t)}{k_2 - k_1}$

and the left hand side: $\frac{d}{dt}B(t)$ simplify $\rightarrow k_1 \cdot a \cdot \frac{-\exp(-k_1 \cdot t) \cdot k_1 + k_2 \cdot \exp(-k_2 \cdot t)}{k_2 - k_1}$ That's OK !

2) If you want to use the menu driven symbolic processor, you should work not with the functions names but with its complete expressions.

$$k_1 \cdot (a \cdot e^{-k_1 \cdot t}) - k_2 \cdot \left[\frac{a \cdot k_1}{k_2 - k_1} \cdot (e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) \right] \quad \text{simplifies to} \quad a \cdot k_1 \cdot \frac{\exp(-k_1 \cdot t) \cdot k_1 - k_2 \cdot \exp(-k_2 \cdot t)}{-k_2 + k_1}$$

$$\frac{d}{dt} \left[\frac{a \cdot k_1}{k_2 - k_1} \cdot (e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) \right] \quad \text{simplifies to} \quad a \cdot k_1 \cdot \frac{\exp(-k_1 \cdot t) \cdot k_1 - k_2 \cdot \exp(-k_2 \cdot t)}{-k_2 + k_1} \quad \text{This works too.}$$

3) The checking can be done directly, for example, rearranging the initial differential equation to:

$$\frac{d}{dt}[B] - k_1 \cdot [A] + k_2 \cdot [B] = 0 \quad \dots \text{and writing that in the live symbolic processor language} \quad \frac{d}{dt}B(t) - k_1 \cdot A(t) + k_2 \cdot B(t) \text{ simplify } \rightarrow 0$$

... we obtain the expected result.

With any of these strategies you can check the solution for [C] by yourself. Good luck!



Rate Expressions and Mass Balance for the system:



The analytical expressions for the reaction rates as a function of time in a reaction scheme of the type **A - B - C**, are obtained. By starting from the mass balance applied to this system, the relationship between the reaction rates is obtained, highlighting the case of initial rates. Mathcad Symbolic Processor is used when deriving the rate equations of [A], [B] and [C], and when evaluating the limits. The equations obtained are proven by means of an interactive graph. An animation is presented that summarizes the cases from $t = 0$ until the end of the reaction. General equations that permit these calculations and graphics, in the case in which $k_1 = k_2$, are presented.

Objective:

To obtain analytical equations for the reaction rates as a function of time and use the mass balance to show the relation between them in a particular reaction scheme.



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Rate Expressions and Mass Balance for the system:



For this system, the analytical equations that describe the time dependence of the concentrations are:

$$A(t) = a \cdot e^{-k_1 \cdot t} \quad B(t) = \frac{k_1}{k_2 - k_1} \cdot a \cdot \left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t} \right) \quad C(t) = a \cdot \left[1 + \left(\frac{k_1 \cdot e^{-k_2 \cdot t} - k_2 \cdot e^{-k_1 \cdot t}}{k_2 - k_1} \right) \right]$$

[Double click here to see the derivation of these equations](#)

Rate definitions according to each reaction participant and **Rate expressions:** (any time)

$$v_A = - \left(\frac{d}{dt} A(t) \right) = - \left[\frac{d}{dt} \left(a \cdot e^{-k_1 \cdot t} \right) \right] \quad \text{yields} \quad a \cdot k_1 \cdot \exp(-k_1 \cdot t)$$

$$v_B = \left(\frac{d}{dt} B(t) \right) = \frac{d}{dt} \left[\frac{k_1}{k_2 - k_1} \cdot a \cdot \left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t} \right) \right] \quad \text{yields} \quad \frac{k_1}{(k_2 - k_1)} \cdot a \cdot \left(-k_1 \cdot \exp(-k_1 \cdot t) + k_2 \cdot \exp(-k_2 \cdot t) \right)$$

$$v_C = \left(\frac{d}{dt} C(t) \right) = \frac{d}{dt} \left[a \cdot \left[1 + \left(\frac{k_1 \cdot e^{-k_2 \cdot t} - k_2 \cdot e^{-k_1 \cdot t}}{k_2 - k_1} \right) \right] \right] \quad \text{yields} \quad a \cdot \frac{(-k_1 \cdot k_2 \cdot \exp(-k_2 \cdot t) + k_2 \cdot k_1 \cdot \exp(-k_1 \cdot t))}{(k_2 - k_1)}$$

Initial rate expressions: (rate at $t = 0$)

$$\lim_{t \rightarrow 0} \left(a \cdot k_1 \cdot \exp(-k_1 \cdot t) \right) \quad \text{yields} \quad a \cdot k_1$$

$$\lim_{t \rightarrow 0} \left[\frac{k_1}{(k_2 - k_1)} \cdot a \cdot \left(-k_1 \cdot \exp(-k_1 \cdot t) + k_2 \cdot \exp(-k_2 \cdot t) \right) \right] \quad \text{yields} \quad a \cdot k_1$$

Note that the **initial rates** are in the relation:

$$v_A = v_B \quad \text{and} \quad v_C = 0$$

$$\lim_{t \rightarrow 0} \left[a \cdot \frac{(-k_1 \cdot k_2 \cdot \exp(-k_2 \cdot t) + k_2 \cdot k_1 \cdot \exp(-k_1 \cdot t))}{(k_2 - k_1)} \right] \quad \text{yields} \quad 0$$

Mass balance $a = [A] + [B] + [C]$

as $a = \text{Constant}$

at any time $\frac{d}{dt} A(t) + \frac{d}{dt} B(t) + \frac{d}{dt} C(t) = 0$

or $-v_A + v_B + v_C = 0$

Then, at any time $v_A = v_B + v_C$

if at $t = 0$ $[B]_0 = [C]_0 = 0$, then $(v_C)_0 = 0$ (as C cannot be formed or consumed at $t = 0$)

and $(v_A)_0 = (v_B)_0$ *The same result obtained before.*

Checking

$$A(t) := a \cdot e^{-k_1 \cdot t} \quad B(t) := \frac{k_1}{k_2 - k_1} \cdot a \cdot \left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t} \right) \quad C(t) := a \cdot \left[1 + \left(\frac{k_1 \cdot e^{-k_2 \cdot t} - k_2 \cdot e^{-k_1 \cdot t}}{k_2 - k_1} \right) \right]$$

$$\text{rate}_A(t) := a \cdot k_1 \cdot e^{-k_1 \cdot t}$$

$$a \equiv 1 \frac{\text{mol}}{\text{L}}$$

$$\text{tang}_A(t) := (t_{\text{ref}} - t) \cdot \text{rate}_A(t_{\text{ref}}) + A(t_{\text{ref}})$$

$$\text{rate}_B(t) := \frac{a \cdot k_1}{k_2 - k_1} \cdot \left(k_2 \cdot e^{-k_2 \cdot t} - k_1 \cdot e^{-k_1 \cdot t} \right)$$

$$\text{tang}_B(t) := (t - t_{\text{ref}}) \cdot \text{rate}_B(t_{\text{ref}}) + B(t_{\text{ref}})$$

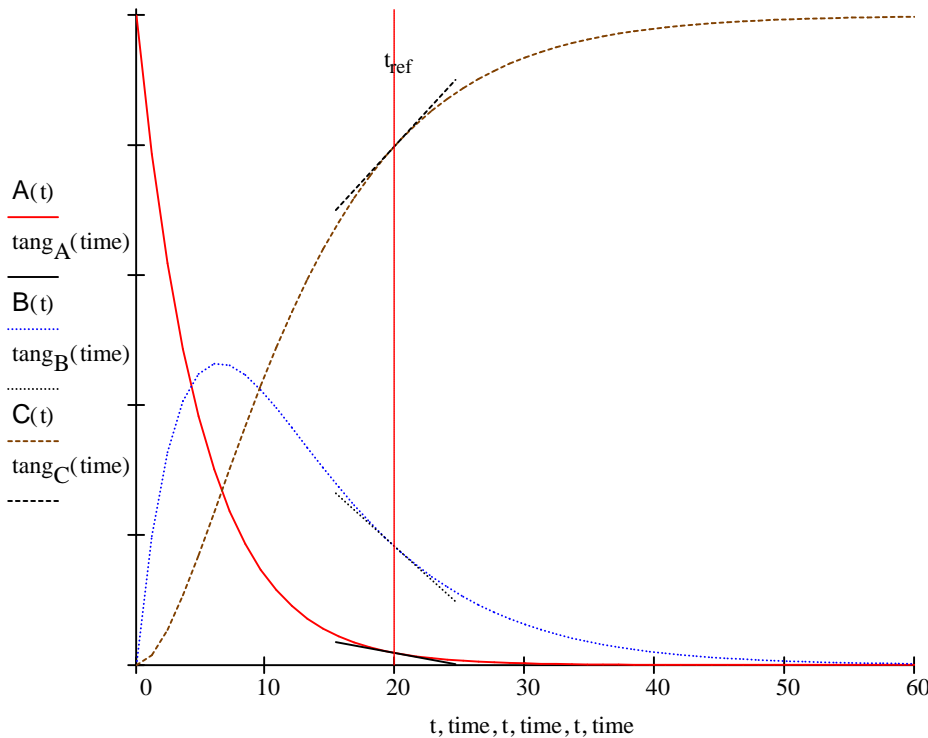
$$\text{rate}_C(t) := \frac{a}{k_2 - k_1} \cdot \left(k_2 \cdot k_1 \cdot e^{-k_1 \cdot t} - k_1 \cdot k_2 \cdot e^{-k_2 \cdot t} \right)$$

$$\text{tang}_C(t) := (t - t_{\text{ref}}) \cdot \text{rate}_C(t_{\text{ref}}) + C(t_{\text{ref}})$$

$$N_{\text{pts}} := 50 \quad t := 0s, \frac{t_{\text{fin}}}{N_{\text{pts}}} .. t_{\text{fin}} \quad \Delta t := \frac{t_{\text{fin}}}{13} \quad \text{time} := \begin{pmatrix} t_{\text{ref}} - \Delta t \\ t_{\text{ref}} + \Delta t \end{pmatrix}$$

$$A(t_{\text{ref}}) = 0.018 \frac{\text{mol}}{\text{L}} \quad B(t_{\text{ref}}) = 0.181 \frac{\text{mol}}{\text{L}} \quad C(t_{\text{ref}}) = 0.801 \frac{\text{mol}}{\text{L}}$$

$$\text{rate}_B(t_{\text{ref}}) + \text{rate}_C(t_{\text{ref}}) = 3.663 \times 10^{-3} \frac{\text{mol}}{\text{L} \cdot \text{s}}$$



$$\text{rate}_A(t_{\text{ref}}) = 3.663 \times 10^{-3} \frac{\text{mol}}{\text{L} \cdot \text{s}}$$

$$t_{\text{ref}} \equiv 20s$$

$$k_1 \equiv 0.2s^{-1}$$

$$k_2 \equiv 0.12s^{-1}$$

$$t_{\text{fin}} \equiv 60s$$

Change the value of t_{ref} from 0 (initial rates) to any reaction time and explore different cases. (Note the difference between rate and tangent line). You can also play with k_1 , k_2 and t_{fin} . Observe that the expressions used up to here are not "singularity proof" (see next page).


[ABC rates.avi](#)


Double click in this region to see an animation showing all the situations from $t = 0$ to $t_{\text{fin}} = 6$.

More general expressions for $B(t)$, $\text{rate}_B(t)$, $C(t)$ and $\text{rate}_C(t)$ that avoid the "division by zero" error when $k_1 = k_2$ can be used. The method for the derivation of such equations is presented in the worksheet **A-B-C $k_1 = k_2$** .

Double click here to see: [A-B-C \$k_1 = k_2\$](#)

$$B(t) = \begin{cases} \frac{k_1}{k_2 - k_1} \cdot a \cdot \left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t} \right) & \text{if } (k_1 \neq k_2) \\ a \cdot k_1 \cdot t \cdot e^{-k_1 \cdot t} & \text{otherwise} \end{cases}$$

$$\text{rate}_B(t) = \begin{cases} \frac{a \cdot k_1}{k_2 - k_1} \cdot \left(k_2 \cdot e^{-k_2 \cdot t} - k_1 \cdot e^{-k_1 \cdot t} \right) & \text{if } (k_1 \neq k_2) \\ a \cdot k_1 \cdot (1 - k_1 \cdot t) \cdot e^{-k_1 \cdot t} & \text{otherwise} \end{cases}$$

$$C(t) = \begin{cases} a \cdot \left[1 + \left(\frac{k_1 \cdot e^{-k_2 \cdot t} - k_2 \cdot e^{-k_1 \cdot t}}{k_2 - k_1} \right) \right] & \text{if } (k_1 \neq k_2) \\ a \cdot \left(e^{k_1 \cdot t} - k_1 \cdot t - 1 \right) \cdot e^{-k_1 \cdot t} & \text{otherwise} \end{cases}$$

$$\text{rate}_C(t) = \begin{cases} \frac{a}{k_2 - k_1} \cdot \left(k_1 \cdot k_2 \cdot e^{-k_1 \cdot t} - k_1 \cdot k_2 \cdot e^{-k_2 \cdot t} \right) & \text{if } (k_1 \neq k_2) \\ a \cdot k_1^2 \cdot t \cdot e^{-k_1 \cdot t} & \text{otherwise} \end{cases}$$


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Rate Expressions and Mass Balance for the system:



Exercise:

☉ Apply the method used in the worksheet to the system $A = B - C$. Compare the reaction rate equations obtained for this system with those for $A - B - C$, especially when $t = 0$. Comment on the results.

The analytical equations for [A], [B] and [C] in the system $A = B - C$ can be found in the references below and in the worksheet:

[A=B-C exact & numerical](#)

References:

C. W. Pyun, "Steady-State and Equilibrium Approximations in Chemical Kinetics", **J. Chem. Ed.**, Vol.48, pp. 194 - 196, March 1971.

V. Viossat and R. I. Ben-Alm, "A Test of the Validity of Steady State and Equilibrium Approximations in Chemical Kinetics", **J. Chem. Ed.**, Vol. 70, No. 9, pp. 732 - 738, Sept. 1993.



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Expressions for the time when [B] has its maximum value and has an inflection point in the system:



For the system **A - B - C** expressions are obtained that allow the time corresponding to the maximum in [B], t_{\max} , to be calculated, as well as t_{inf} , the time corresponding to the inflection point in [B] as a function of time. Mathcad Symbolic Processor is used for the evaluation of derivatives. The expressions obtained are verified through interactive graphics. General expressions are presented that allow t_{\max} and t_{inf} to be calculated avoiding the "division by zero" error when $k_1 = k_2$.

Objective:

To apply the mathematical methods for function analysis to kinetic equations, obtaining important information for describing a reaction system.



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Expressions for the time when [B] has its maximum value and has an inflection point in the system:



In a scheme of first order consecutive reactions, the expression for [B] in function of time is:

$$B(t) = \frac{a \cdot k_1}{k_2 - k_1} \cdot \left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t} \right)$$

Where k_1 and k_2 are the first order rate constants of the first and second step, respectively, and $a = [A]_0$.

[Double click here to see the derivation of this equation](#)

For the maximum of [B] the first derivative of B(t) becomes zero. In this way, the first step is to obtain the expression for $dB(t)/dt$. For this task we use the Symbolic Processor of Mathcad.

$$\frac{d}{dt_{\max}} \left[\frac{a \cdot k_1}{k_2 - k_1} \cdot \left(e^{-k_1 \cdot t_{\max}} - e^{-k_2 \cdot t_{\max}} \right) \right] = 0 \quad \text{yields} \quad a \cdot \frac{k_1}{(k_2 - k_1)} \cdot \left(-k_1 \cdot \exp(-k_1 \cdot t_{\max}) + k_2 \cdot \exp(-k_2 \cdot t_{\max}) \right) = 0$$

If at any point this expression is zero, this is only because the term between parenthesis including both exponential is zero. Cut and paste below that part of the obtained expression and solve it for t_{\max} .

$$\left(-k_1 \cdot \exp(-k_1 \cdot t_{\max}) + k_2 \cdot \exp(-k_2 \cdot t_{\max}) \right) = 0 \qquad k_2 \cdot \exp(-k_2 \cdot t_{\max}) = k_1 \cdot \exp(-k_1 \cdot t_{\max})$$

$$\frac{k_1}{k_2} = \frac{\exp(-k_2 \cdot t)}{\exp(-k_1 \cdot t)} = \exp[t_{\max} \cdot (k_1 - k_2)]$$

$$\ln \left(\frac{k_1}{k_2} \right) = t_{\max} \cdot (k_1 - k_2)$$

$$t_{\max} = \frac{\ln \left(\frac{k_1}{k_2} \right)}{(k_1 - k_2)}$$

(In version 7 and older of Mathcad, this last part of the work should be done "by hand". In later versions the Symbolic Processor can manage the solution up to the end).

At an inflection point, the second derivative of the function is equal to zero. In order to obtain the expression for the time when [B] inflects, a similar procedure as in the previous case is followed: the second derivative $d^2B(t)/dt^2$ is solved with the aid of the Symbolic Processor of Mathcad,

$$\frac{d^2}{dt_{\text{inf}}^2} \left[\frac{a \cdot k_1}{k_2 - k_1} \cdot \left(e^{-k_1 \cdot t_{\text{inf}}} - e^{-k_2 \cdot t_{\text{inf}}} \right) \right] = 0 \quad \text{yields} \quad a \cdot \frac{k_1}{(k_2 - k_1)} \cdot \left(k_1^2 \cdot \exp(-k_1 \cdot t_{\text{inf}}) - k_2^2 \cdot \exp(-k_2 \cdot t_{\text{inf}}) \right) = 0$$

$$\text{which means that: } \left(k_1^2 \cdot \exp(-k_1 \cdot t_{\text{inf}}) - k_2^2 \cdot \exp(-k_2 \cdot t_{\text{inf}}) \right) = 0$$

then, the relevant part of the expression obtained is solved for t_{inf} .

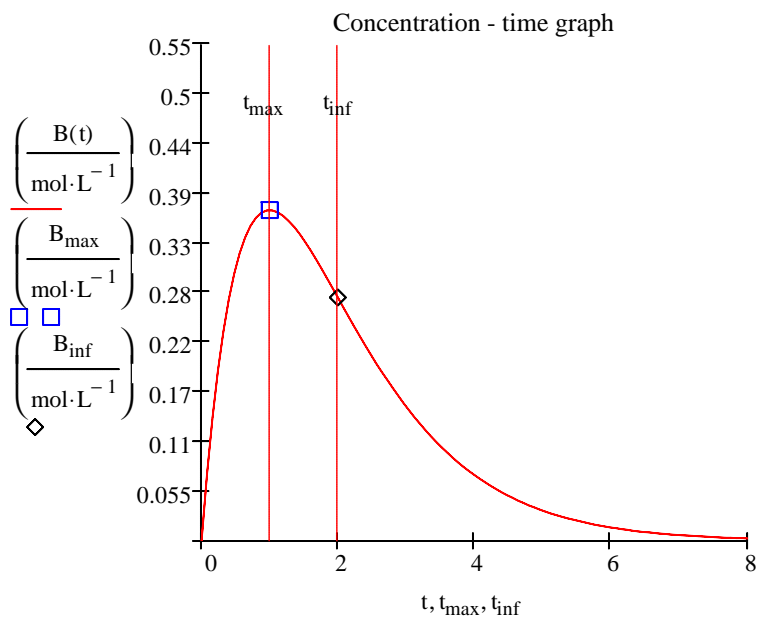
$$t_{\text{inf}} = 2 \cdot \frac{\ln \left(\frac{k_1}{k_2} \right)}{k_1 - k_2}$$

Note that:

$$t_{\text{inf}} = 2 \cdot t_{\max}$$

CONFIRMATION

(The equations used in the construction of these graphs are defined in the next page).



The general validity of the obtained expressions can be verified by changing the values of k_1 and k_2 in the green shaded areas below.

DATA

$$a \equiv 1 \cdot \frac{\text{mol}}{\text{L}}$$

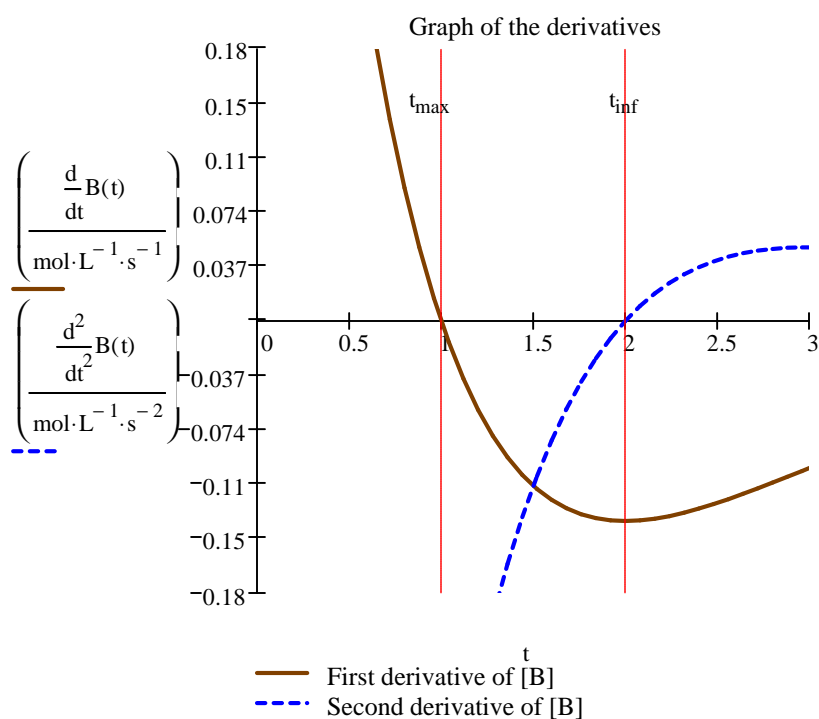
$$k_1 \equiv 1 \cdot \text{s}^{-1}$$

$$k_2 \equiv 1 \cdot \text{s}^{-1}$$

RESULTS

$$t_{\text{max}} = 1 \text{ s}$$

$$t_{\text{inf}} = 2 \text{ s}$$



Here it is demonstrated that the

1st derivative equals zero at t_{max}

and that the

2nd derivative equals zero at t_{inf}

More general expressions are used for $B(t)$, t_{\max} and, t_{\inf} that avoid the "division by zero" error when $k_1 = k_2$. The method for the derivation of such equations is presented in the following part, the worksheet [A-B-C \$k_1 = k_2\$](#) .

$$B(t) \equiv \begin{cases} \frac{k_1}{k_2 - k_1} \cdot a \cdot \left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t} \right) & \text{if } (k_1 \neq k_2) \\ a \cdot k_1 \cdot t \cdot \exp(-k_1 \cdot t) & \text{otherwise} \end{cases}$$

Double click here to see: [A-B-C \$k_1 = k_2\$](#)

$$t_{\max} \equiv \begin{cases} \frac{1}{(k_1 - k_2)} \cdot \ln\left(\frac{k_1}{k_2}\right) & \text{if } (k_1 \neq k_2) \\ \left(\frac{1}{k_1}\right) & \text{otherwise} \end{cases}$$

$$B_{\max} \equiv B(t_{\max})$$

$$t_{\text{fin}} \equiv 8 \cdot t_{\max}$$

$$t_{\inf} \equiv \begin{cases} \frac{2}{(k_1 - k_2)} \cdot \ln\left(\frac{k_1}{k_2}\right) & \text{if } (k_1 \neq k_2) \\ \left(\frac{2}{k_1}\right) & \text{otherwise} \end{cases}$$

$$B_{\inf} \equiv B(t_{\inf})$$

$$t \equiv 0 \cdot s, \frac{t_{\text{fin}}}{100} \dots t_{\text{fin}}$$



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Expressions for the time when [B] has its maximum value and has an inflection point in the system:



Exercises:

⊙ The dependence of [C] with time in the system $A - B - C$, has an inflection point. Find the equation for calculating the time corresponding to this point. Compare with the equations obtained in the worksheet.

⊙ Apply the method used in the worksheet to the system $A = B - C$. Compare the equations obtained for this system with those for $A - B - C$. Comment on the results.

The analytical equations for [A], [B] and [C] in the system $A = B - C$ can be found in any of the references below and in the worksheet:

[A=B-C exact & numerical](#)

References:

C. W. Pyun, "Steady-State and Equilibrium Approximations in Chemical Kinetics", **J. Chem. Ed.**, Vol.48, pp. 194 - 196, March 1971.

V. Viossat and R. I. Ben-Alm, "A Test of the Validity of Steady State and Equilibrium Approximations in Chemical Kinetics", **J. Chem. Ed.**, Vol. 70, No. 9, pp. 732 - 738, Sept. 1993.



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General Kinetic Expressions for the System: Considering the case when $k_1 = k_2$



The method is developed that allows general equations to be obtained that avoid the singularity error presented in several important kinetics equations for the systems under study. Mathcad Symbolic Processor is used in the evaluation of limits and derivatives. The presented method is applicable to other important equations used in the description of the system **A - B - C**, as well as for the **A = B - C** and other related kinetic schemes.

Objective:

To solve indeterminate forms in kinetics equations, using Calculus methods and automatic symbolic processing.



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General Kinetic Expressions for the System: Considering the case when $k_1 = k_2$



For the intermediate:

$$B(t) = \frac{k_1}{k_2 - k_1} \cdot a \cdot \left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t} \right)$$

[Double click here to see the derivation of the equations for B\(t\) and C\(t\)](#)

The singularity error when $k_2 = k_1$ can be avoided:

I) applying L'Hôpital's rule step-by-step : $\lim_{x \rightarrow a} \left(\frac{f(x)}{g(x)} \right) = \lim_{x \rightarrow a} \left(\frac{f'(x)}{g'(x)} \right)$

taking $f(k_2) = k_1 \cdot a \cdot \left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t} \right)$ $f'(k_2) = \frac{d}{dk_2} k_1 \cdot a \cdot \left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t} \right) \rightarrow f'(k_2) = k_1 \cdot a \cdot t \cdot \exp(-k_2 \cdot t)$

and $g(k_2) = (k_2 - k_1)$ $g'(k_2) = \frac{d}{dk_2} (k_2 - k_1) \rightarrow g'(k_2) = 1$

then $\frac{k_1 \cdot a \cdot t \cdot \exp(-k_2 \cdot t)}{1}$ becomes $k_1 \cdot a \cdot t \cdot \exp(-k_1 \cdot t)$ when $k_2 = k_1$

or, II) directly, using the Mathcad Symbolic Processor to evaluate the limit:

$$\lim_{k_2 \rightarrow k_1} \left[\frac{k_1}{k_2 - k_1} \cdot a \cdot \left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t} \right) \right] \text{ yields } k_1 \cdot \exp(-k_1 \cdot t) \cdot t \cdot a$$

This last method will be applied in all the following cases:

For the product:

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

$$\lim_{k_2 \rightarrow k_1} \left[a \cdot \left[1 + \left(\frac{k_1 \cdot e^{-k_2 \cdot t} - k_2 \cdot e^{-k_1 \cdot t}}{k_2 - k_1} \right) \right] \right] \text{ yields } a \cdot (\exp(k_1 \cdot t) - k_1 \cdot t - 1) \cdot \exp(-k_1 \cdot t)$$

The time for $[B]_{\max}$

$$t_{\max} = \frac{1}{(k_1 - k_2)} \cdot \ln \left(\frac{k_1}{k_2} \right)$$

$$\lim_{k_2 \rightarrow k_1} \frac{1}{(k_1 - k_2)} \cdot \ln \left(\frac{k_1}{k_2} \right) \text{ yields } \frac{1}{k_1}$$

The time for the inflection in $[B]$

$$t_{\text{inf}} = \frac{2}{(k_1 - k_2)} \cdot \ln \left(\frac{k_1}{k_2} \right)$$

$$\lim_{k_2 \rightarrow k_1} \frac{2}{(k_1 - k_2)} \cdot \ln \left(\frac{k_1}{k_2} \right) \text{ yields } \frac{2}{k_1}$$

Then, the following are general equations that avoid the singularity point and work with all possible values of rate constants in this reaction scheme:

$$B(t) = \text{if} \left[(k_1 = k_2), (\exp(-k_1 \cdot t) \cdot t \cdot a \cdot k_1), \left[\frac{k_1}{k_2 - k_1} \cdot a \cdot (e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) \right] \right]$$

$$C(t) = \text{if} \left[(k_1 = k_2), [a \cdot (\exp(k_1 \cdot t) - k_1 \cdot t - 1) \cdot \exp(-k_1 \cdot t)], \left[a \cdot \left[1 + \left(\frac{k_1 \cdot e^{-k_2 \cdot t} - k_2 \cdot e^{-k_1 \cdot t}}{k_2 - k_1} \right) \right] \right] \right]$$

$$t_{\max} = \text{if} \left[(k_1 = k_2), \left(\frac{1}{k_1} \right), \left[\frac{1}{(k_1 - k_2)} \cdot \ln \left(\frac{k_1}{k_2} \right) \right] \right]$$

$$t_{\min} = \text{if} \left[(k_1 = k_2), \left(\frac{2}{k_1} \right), \left[\frac{2}{(k_1 - k_2)} \cdot \ln \left(\frac{k_1}{k_2} \right) \right] \right]$$

A less compact but perhaps more clear way for defining these functions is using the Mathcad's programming structure, as in the example in the right:

$$B(t) = \begin{cases} \frac{k_1}{k_2 - k_1} \cdot a \cdot (e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) & \text{if } (k_1 \neq k_2) \\ a \cdot k_1 \cdot t \cdot \exp(-k_1 \cdot t) & \text{otherwise} \end{cases}$$


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General Kinetic Expressions for the System: Considering the case when $k_1 = k_2$



Exercises:

⊙ Apply the method used in the worksheet to the system $A = B - C$. Compare the equations obtained for this system with those in $A - B - C$. Analyze the practical conditions required for the equations for $A = B - C$, to give the singularity error.

The analytical equations for [A], [B] and [C] in the system $A = B - C$ can be found in the last two references below and in the worksheet:

[A=B-C exact & numerical](#)

⊙ L'Hôpital's rule has a number of other applications in Chemical Kinetics. Mathcad can help you to find the expressions for the derivatives and limits. Consider, for example, the following case.

if: $\frac{dx}{dt} = k \cdot (a - x)^2$ is a particular case of: $\frac{dx}{dt} = k \cdot (a - x) \cdot (b - x)$ (when the initial concs. are equal)

then, the solution $\frac{1}{a-x} - \frac{1}{a} = k \cdot t$ should be the limiting case of: $\frac{1}{a-b} \cdot \ln \left[\frac{b \cdot (a-x)}{a \cdot (b-x)} \right] = k \cdot t$ (when $a \rightarrow b$)

Demonstrate the above statement by the two methods: evaluating the limit and applying the L'Hôpital's rule step-by-step.

References:

C. W. Pyun and I. Lipschitz, "Resolution of indeterminate forms in Chemical Kinetics", **J. Chem. Ed.**, Vol. 53, pp. 293 - 294, May 1976.

C. W. Pyun, "Steady-State and Equilibrium Approximations in Chemical Kinetics", **J. Chem. Ed.**, Vol.48, pp. 194 - 196, March 1971.

V. Viossat and R. I. Ben-Alm, "A Test of the Validity of Steady State and Equilibrium Approximations in Chemical Kinetics", **J. Chem. Ed.**, Vol. 70, No. 9, pp. 732 - 738, Sept. 1993.



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Comparison of the Exact Solution with the Steady State Approximation for:



An approximate expression is obtained for [B] in the system **A - B - C**, applying the Steady State Approximation. By means of an interactive graph the behavior of the approximate equation is compared with the exact analytical equation for the concentration of B as a function of time. The analysis of different cases allows important conclusions to be made concerning the conditions of applicability of the Steady State Approximation to this system.

Objective:

To evaluate, by means of an interactive graph, the Steady State Approximation, applying it to a system where the exact analytical solution is known.



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Comparison of the Exact Solution with the Steady State Approximation for:



For this system, the analytical equations that describe the **exact** time dependence of the concentrations are:

$$A(t) := a \cdot e^{-k_1 \cdot t} \quad B(t) := \frac{a \cdot k_1}{k_2 - k_1} \cdot \left(e^{-k_1 \cdot t} - e^{-k_2 \cdot t} \right) \quad C(t) := a \cdot \left[1 + \left(\frac{k_1 \cdot e^{-k_2 \cdot t} - k_2 \cdot e^{-k_1 \cdot t}}{k_2 - k_1} \right) \right]$$

[Double click here to see the derivation of these equations](#)

Where k_1 and k_2 are the first order rate constants of the first and second step, respectively, and $a = [A]_0$.

On the other hand, the **Steady State Approximation** $\frac{d}{dt}[B] = 0$

applied to the intermediate of the outlined mechanism, implies that for B:

$$\sum v_{\text{formation}} = \sum v_{\text{consumption}} \quad \text{that is to say, } k_1 \cdot [A] = k_2 \cdot [B] \quad \text{then: } [B] = \frac{k_1}{k_2} \cdot [A]$$

Substituting in this expression the equation for $A(t)$ yields: $B_{\text{ss}}(t) := \frac{k_1}{k_2} \cdot \left(a \cdot e^{-k_1 \cdot t} \right)$

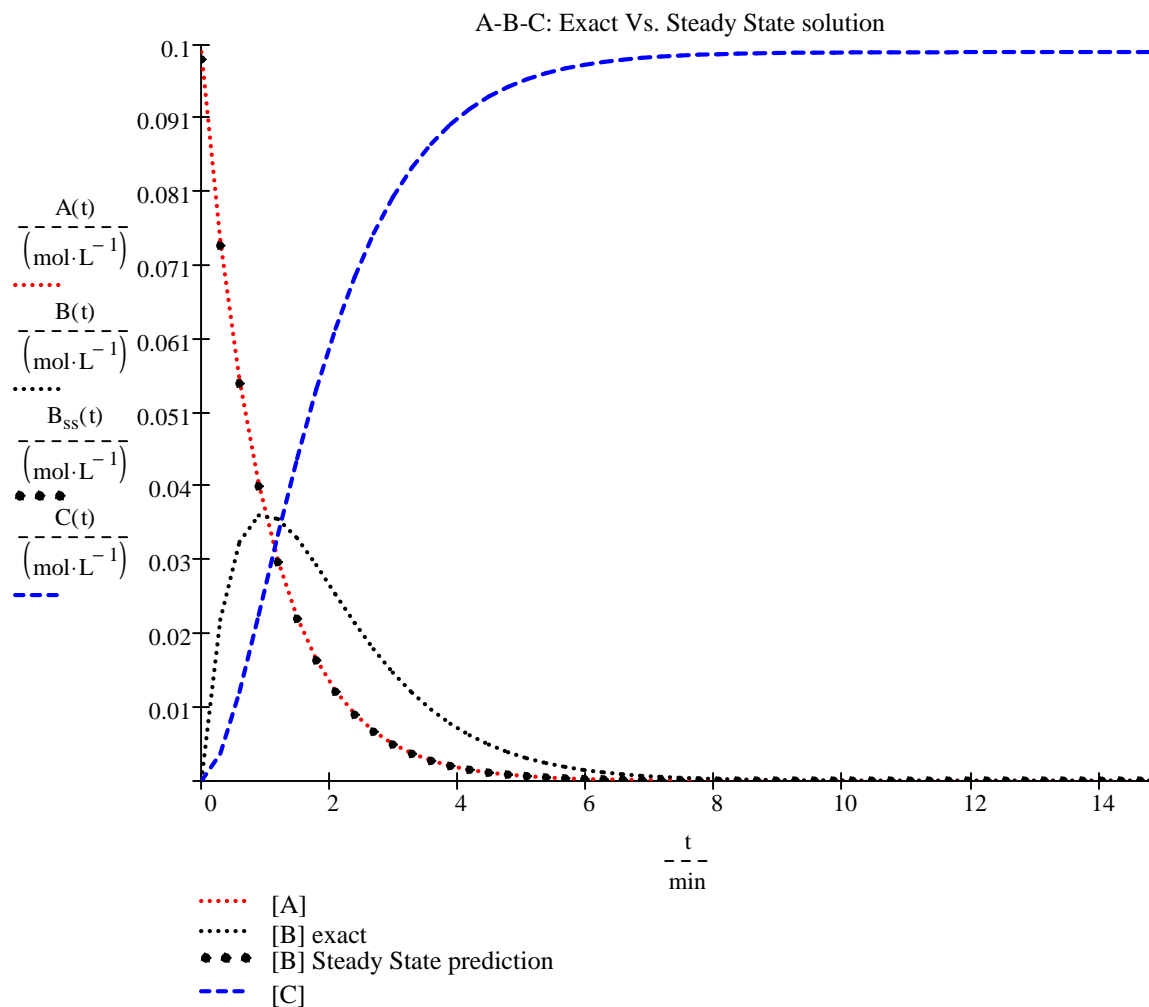
This allows the dependence of $[B]$ with time to be calculated, according to the Steady State Approximation.

Now we are able to compare the result predicted by the Steady State Approximation for the dependence of $[B]$ with time to the variation calculated by the exact analytical equation.

Steady State, a good approximation?

Parameters for the construction of the graph: $t_{\text{fin}} := \frac{15}{(k_1 - k_2)} \cdot \ln\left(\frac{k_1}{k_2}\right)$ $t := 0 \text{min}, 0.02t_{\text{fin}}, \dots, t_{\text{fin}}$

$$a \equiv 0.1 \frac{\text{mol}}{\text{L}}$$



$$k_1 \equiv 1 \text{ min}^{-1}$$

$$k_2 \equiv 1.01 \cdot k_1$$

By changing the relative values of k_1 and k_2 the different cases can be explored, checking when the Steady State Approximation reproduces the behavior of the system predicted by the exact equations.

PARTICULAR CASES

The result should show that when the system satisfies the condition that $k_2 \geq 50 \cdot k_1$, the expression derived from the Steady State Approximation offers very similar results to those of the exact equation. In this case we observe that the intermediate hardly accumulates; it reacts quickly after being formed. After a very short "induction period" the state is reached where $d[B]/dt$ is approximately zero, in comparison with the slopes of the concentration curves of the other species.

Under these conditions the Steady State Approximation is a good approach.

If, for example, $k_2 = 2 \cdot k_1$ the result is different to the previous case. The accumulation of the intermediate is observed, and the Steady State condition for B ($d[B]/dt = 0$) is only approximately accomplished after very long times, when the reaction is practically completed.

Under these conditions the Steady State Approximation is a bad approach.

We have shown that in the reaction scheme $A \rightarrow B \rightarrow C$ where both steps follow first order kinetics, for the the Steady State Approximation to give good results, it is not sufficient that k_2 is simply larger than k_1 , but rather it is required that $k_2 \gg k_1$, namely a factor of 50 or more larger.

In addition, the Steady State Approximation never makes good predictions when $t \approx 0$ (during the so called "induction period"). For example, during the induction period graphs

show that $\left(\frac{d[B]}{dt}\right)_{t=0} < 0$ and $([B])_0 \neq 0$, both of which are erroneous predictions.

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Comparison of the Exact Solution with the Steady State Approximation for:



Exercise:

© Applying the Steady State Approximation to the system **A - B - C**, find the equation for $[C]_{ss}(t)$. Modify the worksheet to perform an interactive graphical comparison between the exact and approximate dependencies of $[C]$, and use it to examine the validity of this approximation to different particular cases.

References:

V. Viossat and R. I. Ben-Alm, "Validity of the Quasi-Stationary-State Approximation in the Case of Two Successive Reversible First-Order Reactions", **J. Chem. Ed.**, Vol. 75, No. 9, pp. 1165 - 1169, Sept. 1998.

C. W. Pyun, "Steady-State and Equilibrium Approximations in Chemical Kinetics", **J. Chem. Ed.**, Vol. 48, pp. 194 - 196, March 1971.

V. Viossat and R. I. Ben-Alm, "A Test of the Validity of Steady State and Equilibrium Approximations in Chemical Kinetics", **J. Chem. Ed.**, Vol. 70, No. 9, pp. 732 - 738, Sept. 1993.

G. I. Gellene, "Application of Kinetic Approximations to the **A = B - C** Reaction System", **J. Chem. Ed.**, Vol. 72, No. 3, pp. 196 - 199, March 1995.

L. Volk, W. Richardson, K. H. Lau, M. Hall and S. H. Lin, "Steady State and Equilibrium Approximations in Reaction Kinetics", **J. Chem. Ed.**, Vol 54, No. 2, pp. 95 - 97, Feb. 1977.



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Comparison of the Exact Solution with the Steady State and pre-Equilibrium Approximations for the system:



The concentration - time dependencies predicted by the Steady State Approximation and for the pre-Equilibrium Approximation are compared, through an interactive graph, with the exact analytical solution for a reaction set of the type $A = B - C$. A systematic search exploring different possible cases is proposed, and a table is presented with the results of 8 model situations. This visual analysis allows the conditions of applicability of these approximate methods, widely used in the study of reaction mechanisms in Chemical Kinetics, to be defined. The generic nature of the procedure developed in this worksheet makes it applicable to a wide range of chemical mechanisms of interest, including enzymatic kinetics, reactions of industrial or pharmacological importance, etc.

Objective:

To evaluate, by means of an interactive graph, the Steady State and pre-Equilibrium Approximations, applying them to a system where the exact analytical solution is known.



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Comparison of the Exact Solution with the Steady State and pre-Equilibrium Approximations for the system:



Initial concentrations (at $t=0$): $[A]_0 = 1 \text{ M}$ $a \equiv 1 \frac{\text{mol}}{\text{L}}$ and $[B]_0 = [C]_0 = 0$

Number of points and time interval to consider: $N_{\text{pts}} \equiv 50$ $t := 0, \frac{t_{\text{fin}}}{N_{\text{pts}}} \dots t_{\text{fin}}$

Exact Solution

$$p := k_1 + k_{-1} + k_2 \quad q := \sqrt{p^2 - 4k_1 \cdot k_2} \quad \lambda_1 := \frac{p - q}{2} \quad \lambda_2 := \frac{p + q}{2}$$

$$p = 17 \text{ s}^{-1} \quad q = 14.457 \text{ s}^{-1} \quad \lambda_1 = 1.272 \text{ s}^{-1} \quad \lambda_2 = 15.728 \text{ s}^{-1}$$

$$A(t) := \frac{a}{\lambda_2 - \lambda_1} \cdot \left[(\lambda_2 - k_1) \cdot e^{-\lambda_1 \cdot t} - (\lambda_1 - k_1) \cdot e^{-\lambda_2 \cdot t} \right]$$

$$B(t) := \frac{a \cdot k_1}{\lambda_2 - \lambda_1} \cdot \left(e^{-\lambda_1 \cdot t} - e^{-\lambda_2 \cdot t} \right) \quad K_{\text{eq}} := \frac{k_1}{k_{-1}}$$

As **reference**, the time to
double $[B]_{\text{max}}$ is used

$$t_{\text{ref}} := \frac{2}{\lambda_2 - \lambda_1} \ln \left(\frac{\lambda_2}{\lambda_1} \right)$$

$$C(t) := a \cdot \left(1 - \frac{\lambda_2}{\lambda_2 - \lambda_1} \cdot e^{-\lambda_1 \cdot t} + \frac{\lambda_1}{\lambda_2 - \lambda_1} \cdot e^{-\lambda_2 \cdot t} \right)$$

Approximate Solutions

Expressions for $[B](t)$ according to: **Steady State**

$$B_{\text{ss}}(t) := \frac{k_1 \cdot A(t)}{(k_{-1} + k_2)}$$

and **pre-Equilibrium**

$$B_{\text{eq}}(t) := \frac{k_1 \cdot A(t)}{k_{-1}}$$

Errors, relative to the result obtained by the exact solution, for the values of $[B]$ in t_{ref}
predicted by both approximate methods.

reference error, **Steady State** $\text{Error}_{\text{ss}} := \frac{B_{\text{ss}}(t_{\text{ref}}) - B(t_{\text{ref}})}{B(t_{\text{ref}})}$

reference error, **pre-Equilibrium** $\text{Error}_{\text{eq}} := \frac{B_{\text{eq}}(t_{\text{ref}}) - B(t_{\text{ref}})}{B(t_{\text{ref}})}$

RESULTS

$$\frac{k_1}{k_{-1} + k_2} = 0.133$$

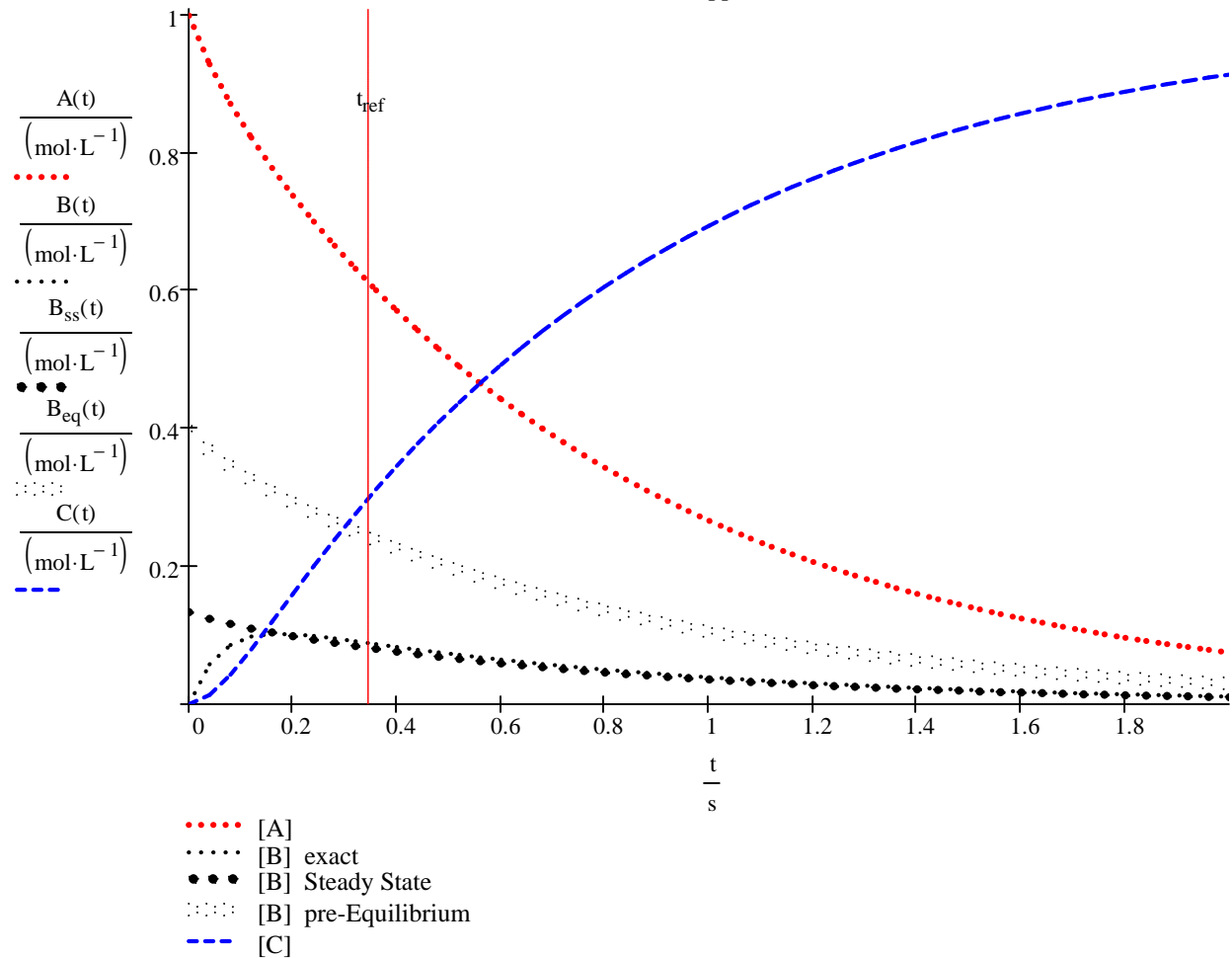
Error_{ss} = -7.8%

$$\frac{k_2}{k_{-1} + k_1} = 1.429$$

Error_{eq} = 176.5%

$$K_{eq} = 0.4$$

A=B-C: Exact and Approximate solutions



$$k_1 \equiv 2 \cdot \text{s}^{-1}$$

$$k_{-1} \equiv 5 \cdot \text{s}^{-1}$$

$$k_2 \equiv 10 \cdot \text{s}^{-1}$$

$$t_{fin} \equiv 2 \text{ s}$$

Changing the values of the rate constants, all particular cases can be explored (see next page). In some cases it could be necessary to adjust the final time too.

Systematic study of particular cases

As we have seen in the study of the $A \rightarrow B \rightarrow C$ system, $k_2 \geq 50 \cdot k_1$ can be reasonably used as a reference condition for the validity of Steady State Approximation. Below, the results obtained when the rate constants are systematically varied by a factor of 50 with respect to each other, are detailed.

Case	k_1	k_{-1}	k_2	$\left(\frac{\text{Error}_{ss}}{\%}\right)$	$\left(\frac{k_1}{k_{-1} + k_2}\right)$	$\left(\frac{\text{Error}_{eq}}{\%}\right)$	$\left(\frac{k_2}{k_{-1} + k_1}\right)$	K_{eq}
I	1	1	1	-16.4	0.5	67.2	0.5	1
II	1	1	50	-1.9	0.02	4900	25	1
III	1	50	1	-0.02	0.02	2	0.02	0.02
IV	50	1	1	-48.2	25	3.7	0.02	50
V	1	50	50	-0.51	0.01	99	0.98	0.02
VI	50	1	50	-48.7	0.98	2500	0.98	50
VII	50	50	1	-1	0.98	1	0.01	1
VIII	50	50	50	-15.9	0.5	68.2	0.5	1

[Click here to see A-B-C steady state](#)

The change in the appearance of the graph can be substantial for different situations. However, by observing the coincidence between the traces drawn using the exact and approximate equations and the numerical result values, the following general observations can be made about the validity of Steady State and pre-Equilibrium Approximations:

Steady State valid when: $(k_{-1} + k_2) \gg k_1$ Cases II, III and V.

pre-Equilibrium valid when: $(k_{-1} + k_1) \gg k_2$ Cases III, IV and VII.

Both approximations work: $k_{-1} \gg k_2$ Cases III, and VII. Here $B_{ss} \rightarrow B_{eq}$ (see equations).

No approximation works: Cases VI, and I \approx VIII. This implies $\frac{2}{7} = 28.6\%$ or $\frac{3}{8} = 37.5\%$ of all the mathematical possibilities (!).

Analysis

The chemical applicability condition for the Steady State Approximation in this system includes the fast consumption of B, not only in the forward direction (very reactive intermediate) but here the backward decay is also important (unstable intermediate). In fact, a large (k_{-1} / k_1) ratio can compensate low (k_2 / k_1) , or both can collaborate $(k_{-1} + k_2) \gg k_1$ to give a quick disappearance of B.

The "rapid equilibrium" (a kinetic requisite) required for the pre-Equilibrium Approximation to be applied, is independent of a large value of K_{eq} (a thermodynamic parameter). Cases where this approach makes good predictions can be associated with large as well as with moderate or even small values of K_{eq} . The fundamental concept here is that, at least one of the rate constants in

$K_{eq} = \frac{k_1}{k_{-1}}$ must be large compared to the rate constant of the second step.

Following visual analysis of the graph and numerical results, a systematic study of particular cases leads to the conclusion that working with a chemical system which can be modeled by a scheme of the type **A = B - C**, the majority of the situations can be successfully managed with the Steady State Approximation and/or with the pre-Equilibrium Approximation. Nevertheless, must be recognized that there is a non-negligible proportion of cases in which neither of these approximate methods work well. And the chemist, of course, can not choose the relationship between rate constants in a real reaction!

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Comparison of the Exact Solution with the Steady State and pre-Equilibrium Approximations for the system:



Exercises:

- ⊙ Find the equations used in the worksheet for $B_{ss}(t)$ and for $B_{eq}(t)$.

- ⊙ The reference condition found in the previous worksheet, when exploring the applicability of Steady State Approximation to the system **A - B - C**, is $k_2 \geq 50 \cdot k_1$. Now, in the system **A = B - C** explore situations with, for example, $(k_{-1} \approx k_2) \approx (10k_1)$ where such a condition is not fulfilled. Comment on the results

- ⊙ The case with rate constants in the relation: $k_1 = 50$, $k_{-1} = 50$ and $k_2 = 1$ belongs to the interesting kind of situations where the Steady State Approximation works well even though the algebraic definition of "steady state" for **B**: $\left(\frac{d[B]}{dt}\right) \approx 0$ is not satisfied. Explore this case with the graph and comment on the results.

References:

V. Viossat and R. I. Ben-Alm, "Validity of the Quasi-Stationary-State approximation in the case of two successive reversible first-order reactions", **J. Chem. Ed.**, Vol. 75, No. 9, pp. 1165 - 1169, Sept. 1998.

C. W. Pyun, "Steady-State and Equilibrium approximations in Chemical Kinetics", **J. Chem. Ed.**, Vol.48, pp. 194 - 196, March 1971.

V. Viossat and R. I. Ben-Alm, "A test of the validity of Steady State and Equilibrium approximations in Chemical Kinetics", **J. Chem. Ed.**, Vol. 70, No. 9, pp. 732 - 738, Sept. 1993.

G. I. Gellene, "Application of Kinetic approximations to the **A = B - C** reaction system", **J. Chem. Ed.**, Vol. 72, No. 3, pp. 196 - 199, March 1995.

L. Volk, W. Richardson, K. H. Lau, M. Hall and S. H. Lin, "Steady State and Equilibrium approximations in Reaction Kinetics", **J. Chem. Ed.**, Vol 54, No. 2, pp. 95 - 97, Feb. 1977.



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Comparison of the exact Analytical Solution with the Numerical Solution for the system:



The Mathcad numerical method for solving ordinary differential equations is presented, with application to the kinetic analysis of a reaction scheme of the type $A = B - C$. Through an interactive graph and by means of a table of values, the results calculated numerically are compared with those obtained by the exact analytical equations of concentrations as a function of time for this system. This Mathcad worksheet allows a similar analysis to reactions of the type $A - B$, $A = B$ and $A - B - C$, to be applied as particular cases of the implemented general model. In all the practical cases it is proven that the accuracy offered by the numeric method is sufficient. This conclusion is reflected directly in the following worksheet, which makes intensive use of the Mathcad ODE-solver.

Objective:

To evaluate, numerically and by means of an interactive graph, the usefulness of Mathcad ODE-solver in Chemical Kinetics, applying it to a system with known analytical solution.



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Comparison of the exact Analytical Solution with the Numerical Solution for the system:



Analytical Solution

$$p := k_1 + k_{-1} + k_2$$

$$q := \sqrt{p^2 - 4k_1 \cdot k_2}$$

$$\lambda_1 := \frac{p - q}{2}$$

$$\lambda_2 := \frac{p + q}{2}$$

$$p = 5$$

$$q = 4.123$$

$$\lambda_1 = 0.438$$

$$\lambda_2 = 4.562$$

$$A(t) := \frac{a}{\lambda_2 - \lambda_1} \cdot \left[(\lambda_2 - k_1) \cdot e^{-\lambda_1 \cdot t} - (\lambda_1 - k_1) \cdot e^{-\lambda_2 \cdot t} \right]$$

$$B(t) := \frac{a \cdot k_1}{\lambda_2 - \lambda_1} \cdot \left(e^{-\lambda_1 \cdot t} - e^{-\lambda_2 \cdot t} \right)$$

$$t := 0, \frac{t_{\text{fin}}}{N_{\text{pts}}} .. t_{\text{fin}}$$

$$C(t) := a \cdot \left(1 - \frac{\lambda_2}{\lambda_2 - \lambda_1} \cdot e^{-\lambda_1 \cdot t} + \frac{\lambda_1}{\lambda_2 - \lambda_1} \cdot e^{-\lambda_2 \cdot t} \right)$$

Numerical Solution

Differential equations for the reacting system

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

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

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

Defining:

$$x_0 = [A]$$

$$x_1 = [B]$$

$$x_2 = [C]$$

Differential eqns. in Mathcad format

$$D(t, x) := \begin{bmatrix} -k_1 \cdot x_0 + k_{-1} \cdot x_1 \\ k_1 \cdot x_0 - (k_{-1} + k_2) \cdot x_1 \\ k_2 \cdot x_1 \end{bmatrix} \begin{matrix} d[A]/dt \\ d[B]/dt \\ d[C]/dt \end{matrix}$$

Starting point for the numerical ODE-solver (at $t = 0$) $a \equiv 1$

$$x := \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} \begin{matrix} [A]_0 = a \\ [B]_0 = 0 \\ [C]_0 = 0 \end{matrix}$$

Number of points to consider in the calculation: $N_{\text{pts}} \equiv 50 \quad i := 0..N_{\text{pts}}$

Solution to the ODEs system (*Runge-Kutta with adaptive step size method*)

$$S := \text{Rkadapt}(x, 0, t_{\text{fin}}, N_{\text{pts}}, D)$$

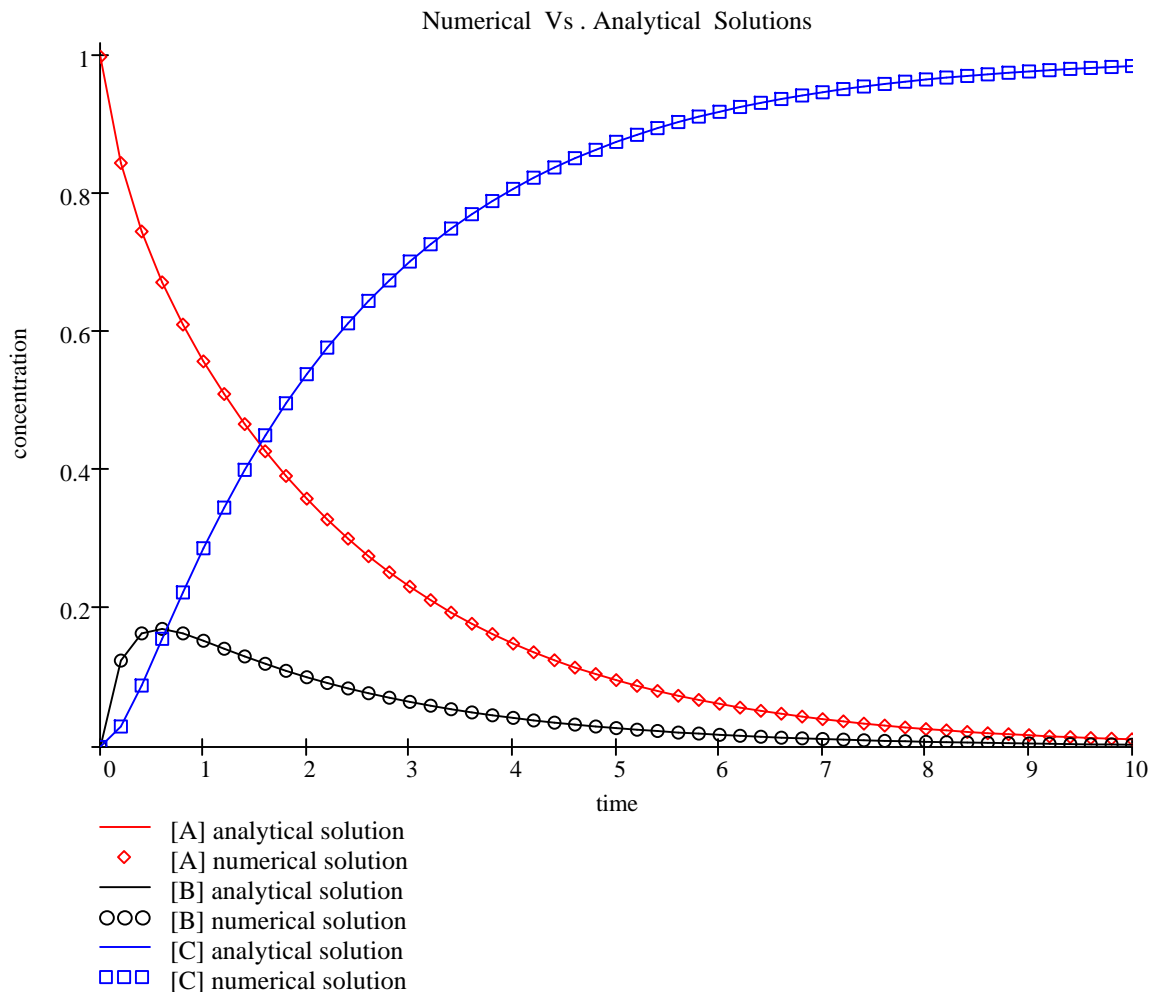
Extraction of concentration - time values: $t_{\text{num}} := S^{\langle 0 \rangle}$

$$A_{\text{num}} := S^{\langle 1 \rangle}$$

$$B_{\text{num}} := S^{\langle 2 \rangle}$$

$$C_{\text{num}} := S^{\langle 3 \rangle}$$

RESULTS



$k_1 \equiv 1$

$k_{-1} \equiv 2$

$k_2 \equiv 2$

$t_{fin} \equiv 10$

By changing below the values of the k_1 , k_{-1} and k_2 different situations can be explored. In some cases it could be necessary to adjust t_{fin} too.

Reactions like: $A \rightarrow B$,	$k_1 \neq 0$	$k_{-1} = 0$	$k_2 = 0$
$A \rightleftharpoons B$	$k_1 \neq 0$	$k_{-1} \neq 0$	$k_2 = 0$
and $A \rightarrow B \rightarrow C$	$k_1 \neq 0$	$k_{-1} = 0$	$k_2 \neq 0$
can be modeled here as particular cases			
of $A \rightleftharpoons B \rightarrow C$	$k_1 \neq 0$	$k_{-1} \neq 0$	$k_2 \neq 0$

A(t) =	A _{num,1} =
1.000000	1.000000
0.845979	0.845979
0.746817	0.746817
0.672818	0.672818
0.611794	0.611793
0.558608	0.558608
0.510978	0.510978
0.467785	0.467785
0.428395	0.428395
0.392382	0.392382
0.359420	0.359420
0.329238	0.329238
0.301593	0.301593
0.276272	0.276272
0.253077	0.253077
0.231830	0.231830
0.212367	0.212367
0.194537	0.194537
0.178205	0.178205
0.163244	0.163244
0.149539	0.149539
0.136984	0.136984
0.125484	0.125484
0.114949	0.114949
0.105298	0.105298
0.096458	0.096458
0.088360	0.088360
0.080942	0.080942
0.074146	0.074146
0.067921	0.067921
0.062219	0.062219
0.056996	0.056996
0.052210	0.052210
0.047827	0.047827
0.043812	0.043812
0.040134	0.040134
0.036764	0.036764
0.033678	0.033678
0.030850	0.030850
0.028260	0.028260
0.025888	0.025888

The singularity when $\lambda_1 = \lambda_2$ can be managed in the same way as in

[A-B-C k1 = k2](#)

On the left, both the analytical and numerical solutions for the starting species are shown. The table can be used to discover the difference in the values calculated at any time on the graph on the previous page.

It can be observed that in all cases the coincidence is sufficiently good to consider the numerical solution as not only "similar", but as a very good approximation to the exact analytical solution.



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Comparison of the exact Analytical Solution with the Numerical Solution for the system:



Exercises:

⊙ Use the Mathcad ODE-solver for simulating an enzyme kinetics experiment using the following data: initial concentrations $[\text{Substrate}_0] = 1\text{mM}$ and $[\text{Enzyme}_0] = 0.01\text{mM}$, rate constants $k_1 = 0.2\text{mM}^{-1}\text{s}^{-1}$, $k_{-1} = 0.04\text{s}^{-1}$ and $k_2 = 0.01\text{s}^{-1}$. Follow the instructions given in Bruist's paper and use the concentration - time graph for obtaining the necessary values, and calculate the Michaelis - Menten parameters (v_{MAX} and K_{M}) that characterize this system.

⊙ Apply the method used in the worksheet to the system $A = B = C$. The analytical equations for [A], [B] and [C] in this system can be found in the Viossat's paper.

References:

R. R. Pavlis, "Kinetics without Steady State Approximations", **J. Chem. Ed.**, Vol. 74, No. 9, pp. 1139 - 1140, Sept. 1997.

S. W. Orchard and M. B. Mooiman, "Simulation of first-Order Kinetics mechanisms", **J. Chem. Ed.**, Vol. 58, No. 5, pg. 409, May 1981.

M. F. Bruist, "Use of a Spreadsheet to Simulate Enzyme Kinetics", **J. Chem. Ed.**, Vol. 75, No. 3, pp. 372 - 375, March 1998.

V. Viossat and R. I. Ben-Alm, "Validity of the Quasi-Stationary-State Approximation in the Case of Two Successive Reversible First-Order Reactions", **J. Chem. Ed.**, Vol. 75, No. 9, pp. 1165 - 1169, Sept. 1998.

A very instructive set of documents on the applications of Mathcad numerical ODE-solver to Chemical Kinetics is the series by Flick Coleman, "Kinetics of Complex Reactions", "The Steady State and Equilibrium Approximations. Background Readings" and "Kinetics of Complex Reactions - Steady State and Equilibrium Approximations", published in the web site :

<http://bluehawk.monmouth.edu/~tzielins/mathcad/> (in the **Topic Area** click on "**Chemical Kinetics**")



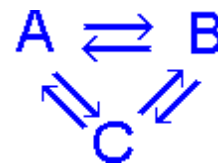
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Generalized Numerical Calculations for the Kinetic System of Three Species Related to Each Other Through Elementary Reversible or Non-Reversible Reactions



It has been shown that Mathcad allows very exact solutions to be obtained in a simple and effective way for systems of ordinary differential equations (ODE) that represent reaction mechanisms. In this worksheet the Mathcad ODE-solver is applied to a general scheme of three chemical species related to each other through elementary reversible or non-reversible reactions. Assigning values to the appropriate rate constants and reaction orders, it is possible to reproduce the mechanisms corresponding to the typical cases of "simple" and "complex" reactions studied in Chemical Kinetics, without having to face the analytical solution. Although the model implemented considers reactions involving only one reagent at each stage, adaptation to other reaction schemes is readily achieved.

Objective:

To model a general system that includes most of the "simple" and "complex" reactions studied in Chemical Kinetics and solve it using the Mathcad numerical ODE-solver, showing the results by means of an interactive graph.



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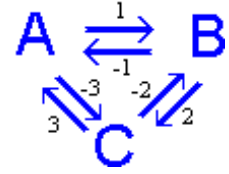
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Generalized Numerical Calculations for the Kinetic System of Three Species Related to Each Other Through Elementary Reversible or Non-Reversible Reactions



Defining: Starting point (at $t = 0$) ODE system for the complete mechanism

$$\begin{array}{l}
 x_0 = [A] \\
 x_1 = [B] \\
 x_2 = [C]
 \end{array}
 \quad
 x := \begin{pmatrix} a \\ b \\ c \end{pmatrix}
 \quad
 D(t, x) := \begin{cases}
 k_{-1} \cdot (x_1)^{n_{-1}} + k_3 \cdot (x_2)^{n_3} - k_1 \cdot (x_0)^{n_1} - k_{-3} \cdot (x_0)^{n_{-3}} & d[A]/dt \\
 k_1 \cdot (x_0)^{n_1} - k_{-1} \cdot (x_1)^{n_{-1}} - k_2 \cdot (x_1)^{n_2} + k_{-2} \cdot (x_2)^{n_{-2}} & d[B]/dt \\
 k_{-3} \cdot (x_0)^{n_{-3}} + k_2 \cdot (x_1)^{n_2} - k_3 \cdot (x_2)^{n_3} - k_{-2} \cdot (x_2)^{n_{-2}} & d[C]/dt
 \end{cases}$$

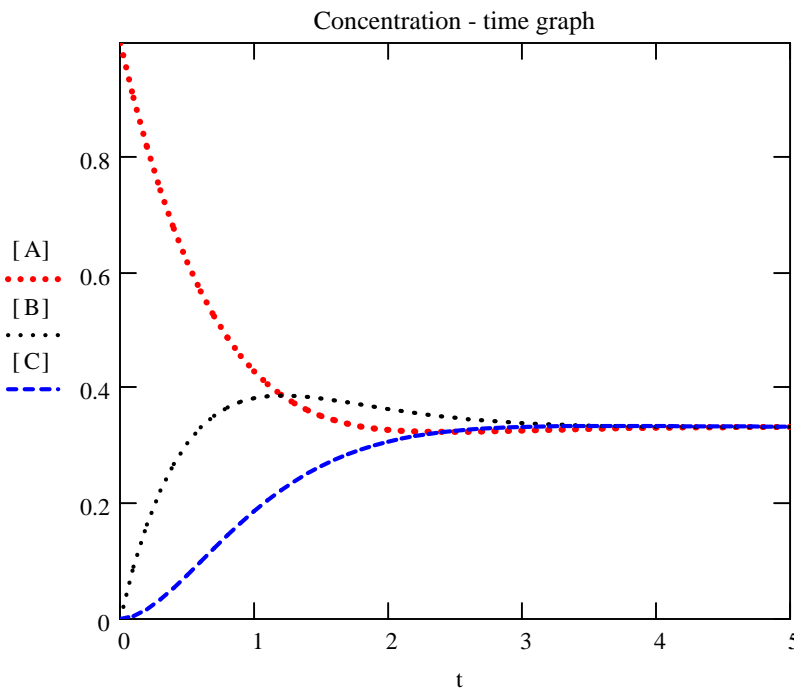
Solution to the ODE system and extraction of concentration values

$$\begin{array}{l}
 S := \text{Rkadapt}(x, 0, t_{\text{fin}}, n_{\text{ptos}}, D) \\
 [A] := S^{\langle 1 \rangle} \quad [B] := S^{\langle 2 \rangle} \quad [C] := S^{\langle 3 \rangle} \\
 t := S^{\langle 0 \rangle}
 \end{array}$$

DATA

$$t_{\text{fin}} \equiv 5 \quad \begin{array}{l} \text{final time} \\ \text{to explore} \end{array}$$

$$\begin{array}{l}
 \text{Init. Concentrations} \\
 [A]_0 \quad [B]_0 \quad [C]_0 \\
 a \equiv 1 \quad b \equiv 0 \quad c \equiv 0
 \end{array}$$



Rate constant and Reaction order for each reaction:

$$\begin{array}{l}
 A \leftrightarrow B \quad \begin{array}{l} k_1 \equiv 1 \\ K_1 = \text{"ne"} \end{array} \quad \begin{array}{l} n_1 \equiv 1 \\ n_{-1} \equiv 1 \end{array}
 \end{array}$$

$$\begin{array}{l}
 B \leftrightarrow C \quad \begin{array}{l} k_2 \equiv 1 \\ K_2 = \text{"ne"} \end{array} \quad \begin{array}{l} n_2 \equiv 1 \\ n_{-2} \equiv 1 \end{array}
 \end{array}$$

$$\begin{array}{l}
 C \leftrightarrow A \quad \begin{array}{l} k_3 \equiv 1 \\ K_3 = \text{"ne"} \end{array} \quad \begin{array}{l} n_3 \equiv 1 \\ n_{-3} \equiv 1 \end{array}
 \end{array}$$

"ne" = "do not exist"

Number of points to consider in the calculation: $n_{\text{ptos}} \equiv 50$

Changing the values of the appropriate data (rate constants and reaction orders), all particular cases can be explored (see next page).

In some cases it could be necessary to adjust the final time and/or initial concentrations to obtain a meaningful graph.

If any equilibrium exist, the corresponding equilibrium constant(s) have the value obtained below:

$$\begin{array}{l}
 K_1 \equiv \text{if} \left(k_{-1} = 0, \text{"ne"}, \frac{k_1}{k_{-1}} \right) \quad K_2 \equiv \text{if} \left(k_{-2} = 0, \text{"ne"}, \frac{k_2}{k_{-2}} \right) \quad K_3 \equiv \text{if} \left(k_{-3} = 0, \text{"ne"}, \frac{k_3}{k_{-3}} \right)
 \end{array}$$

Some of the Chemically Interesting Particular Cases:

Kinetic description

$A \rightarrow B$	$k_1 \neq 0 \quad (k_{-1} = k_2 = k_{-2} = k_3 = k_{-3}) = 0$	one step irreversible
$A \rightleftharpoons B$	$k_1 \neq 0 \quad k_{-1} \neq 0 \quad (k_2 = k_{-2} = k_3 = k_{-3}) = 0$	one step reversible
$A \rightarrow B$ and $A \rightarrow C$	$k_1 \neq 0 \quad k_{-3} \neq 0 \quad (k_{-1} = k_2 = k_{-2} = k_3) = 0$	two parallel irreversible steps
$A \rightarrow B \rightarrow C$	$k_1 \neq 0 \quad k_2 \neq 0 \quad (k_{-1} = k_{-2} = k_3 = k_{-3}) = 0$	two consecutive irreversible steps
$A \rightarrow B \rightarrow C \rightarrow A \dots$	$k_1 \neq 0 \quad k_2 \neq 0 \quad k_3 \neq 0 \quad (k_{-1} = k_{-2} = k_{-3}) = 0$	three <i>irreversible</i> cyclic steps
$A \rightleftharpoons B \rightarrow C$	$k_1 \neq 0 \quad k_{-1} \neq 0 \quad k_2 \neq 0 \quad (k_{-2} = k_3 = k_{-3}) = 0$	two consecutive: 1 st step reversible and 2 nd irreversible
$A \rightarrow B \rightleftharpoons C$	$k_1 \neq 0 \quad k_2 \neq 0 \quad k_{-2} \neq 0 \quad (k_{-1} = k_3 = k_{-3}) = 0$	two consecutive: 1 st step irreversible and 2 nd reversible
$A \rightleftharpoons B \rightleftharpoons C$	$k_1 \neq 0 \quad k_{-1} \neq 0 \quad k_{-2} \neq 0 \quad k_2 \neq 0 \quad (k_3 = k_{-3}) = 0$	two consecutive steps, both reversible

With this approach, numerical and graphical solutions for differential equations that represent chemical mechanisms can be obtained in an easy and precise way. The use of the ODE-solver allows one to avoid the often difficult determination of analytical solutions and can thus provide a numerical solution even for cases in which no analytical solution exist. At the same time, it is important to note that the numerical integrator even can solve systems of equations that have no chemical sense.

For example, it is easily demonstrated that the "three cyclic *irreversible* steps" (the fifth case propose above) achieves an equilibrium state, and the numerical integrator results can be illustrated in the form of a convincing graph. However, detailed balancing requires that the mechanism be formed by three **reversible** cyclic steps (see Moore and Pearson pg. 308) and the rate constant must obey the relationship: $k_1 \cdot k_2 \cdot k_3 = k_{-1} \cdot k_{-2} \cdot k_{-3}$. Other k's combination could be associated with a numerical solutions that do not make chemical sense.

In conclusion, the numerical ODE-solvers are powerful tools, very useful in Chemical Kinetics, but the chemist is the responsible of using any program correctly, to outline the problem with chemical sense and of interpreting the results correctly.

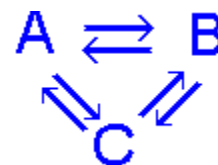

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Generalized Numerical Calculations for the Kinetic System of Three Species Related to Each Other Through Elementary Reversible or Non-Reversible Reactions



Exercises:

⊙ Use the worksheet to obtain the typical "simple" and "complex" reaction graphs: **A - B** (irreversible), **A = B** (reversible), **A - B - C** (consecutive), **A - B** and **A - C** (parallel). Try different reaction orders.

⊙ Alcohol absorption by our bodies is first-order with a rate constant $k_1 = 10.4 \text{hr}^{-1}$, and this step is followed by a zero-order metabolic oxidation of alcohol: $k_2 = 0.16 \frac{\text{gm}}{\text{hr}}$ (we here use the Mathcad symbols for "grams" and "hours"). Consider a driver who drinks enough to reach an initial concentration of 1 gm/L of alcohol in his body. Use the worksheet and model the transit of alcohol in the driver's body with an scheme **A - B - C**, where **A** = unabsorbed ethanol, **B** = absorbed ethanol and **C** = ethanol oxidized (see Ball's paper). In the resulting graph, find the time corresponding to the maximum alcohol in the blood and the time the driver should wait before driving again (look up for the legal limit of alcohol in the bloodstream in your State). The differential equations that represent the change of concentrations with time in this system can be easily integrated "by hand" thanks to the circumstance that the second step is zero-order (and don't forget the mass balance!). Find the analytical equations for **[A]**, **[B]**, **[C]** and t_{MAX} , and use them to answer the same questions as before. Compare the exact results with those obtained using the numerical integrator.

⊙ One case of **A** → **B** reactions not considered in the "general" model implemented in the worksheet is the autocatalytic case. The differential equations for such a system are:

$$\frac{d[A]}{dt} = -(k_1 \cdot [A] + k_c \cdot [A] \cdot [B]) \quad \text{and} \quad \frac{d[B]}{dt} = k_1 \cdot [A] + k_c \cdot [A] \cdot [B] \quad k_c \text{ is the autocatalytic rate constant}$$

Use the Mathcad ODE solver to analyze this system. Vary the rate constants and the initial concentrations to explore the variety of responses this system is capable of.

(Noggle, Example 10.6, pg. 211)

References:

I. Novak, "Chemical Kinetics without Calculus", **J.Chem.Ed.**, Vol. 75, No. 12, pp. 1574-1575, Dec. 1998.

J. Noggle, **Physical Chemistry Using Mathcad**, Pike Creek Publishing Co., Newark (Delaware), 1997.

D. W. Ball, "Kinetic of Consecutive Reactions: First Reaction, First-Order; Second Reaction, Zero-Order", **J. Chem. Ed.**, Vol. 75, No. 7, pp. 917 - 919, July 1998.

J. W. Moore and R. G. Pearson, **Kinetics and Mechanism**, John Wiley & Sons, New York, 1981.



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