SUPPLEMENTARY MATERIAL

MATHEMATICS-1964681

Kinetic analysis of one-step suicide substrate inactivation of an enzyme-catalyzed ping-pong reaction with one substrate undergoing disproportionation

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Note about section 3.3.1 of the main body of manuscript

A close-formed solution for the time dependent variation of [A] in Equation 53 can be represented as follows:

$$[\mathrm{A}] = \left(K_M^E + K_M^F\right) \times W\left[\frac{[\mathrm{A}]_0}{\left(K_M^E + K_M^F\right)} Exp\left(\frac{-\dfrac{2k_c k_f [\mathrm{E}]_0 t}{\left(k_c + k_f\right)} + [\mathrm{A}]_0}{\left(K_M^E + K_M^F\right)}\right)\right], \tag{S1}$$

where K_M^E and K_M^F are the Michaelis-Menten constants for the first and second stages of a ping-pong reaction in which the substrate undergoes disproportionation. More information about the symbols is given in Table 1.

Note about section 3.3.2 of the main body of manuscript

The two alternative approaches to solve analytically Reactions 8 and 9 presented in Case B of the section 3.3.2 are explained below.

1. Steady-state approximation for E and F

The non-linear ODE system [Equations (60) and (61)] of the time-dependent variation of the concentration for the participating compounds of Reactions (54) and (55) can easily be solved if the steady-state is invoked for [E] and, consequently, for [F] (*i.e.*, $[\mathrm{E}]' \approx 0$ and $[\mathrm{F}]' \approx 0$). If this is the case, the analytical solutions for [A], [E] and [F] with initial values for $[\mathrm{A}] = [\mathrm{A}]_0$ and $[\mathrm{E}] = [\mathrm{E}]_0$ are as follows:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-\frac{2k_a k_d}{k_a + k_d}[\mathrm{E}]_0 t}, \tag{S2}$$

$$[\mathrm{E}] = \frac{k_d}{k_a + k_d}[\mathrm{E}]_0, \tag{S3}$$

$$[\mathrm{F}] = \frac{k_a}{k_a + k_d}[\mathrm{E}]_0. \tag{S4}$$

Of interest is also the fact that the integrated solution for [A] [Equation (S1)] could also have been derived from the integration of Equation (50) if k_c and k_f were assumed to approach infinity. However, unless the condition $[\mathrm{A}]_0 >> [\mathrm{E}]_0$ still remains, the approximate integrated solution for [A] is not completely satisfactory. This can clearly be observed in Figure S1, in which the values for k_a and k_d were simply exchanged and the values for $[\mathrm{A}]_0$ and $[\mathrm{E}]_0$ were of similar order. The numerical and analytical solutions showed a better overlapping for conditions in which $k_a \le k_d$ when compared to $k_a > k_d$. The enzyme states E and F reach more rapidly steady-state when $k_a \le k_d$ and the match between the numerical and analytical solutions of the time-dependent variation of the concentration and rate for the substrate and (the sum of) products was maintained through a broader domain of time (Fig S1A, C and E). In contrast, when $k_a > k_d$, a more noticeable mismatch between the numerical and analytical solutions for the compounds were observed, even beyond the time at which E and F were already considered to be in steady-state (Fig S1B, D and F).

2. Non-steady-state approximation for E and F

At time around $t=0$, when $[\mathrm{E}] \approx [\mathrm{E}]_0$, the first terms of the power expansion series of the enzyme-dependent function of $[\mathrm{E}]'$ [Equation (66)] were obtained and only the partial sum of the first two polynomials of grade $n=1$ and $n=2$ were evaluated to find approximate solutions:

$$[\mathrm{E}]'_{n=1} = -k_a[\mathrm{E}]_0[\mathrm{A}]_0 - \left[k_a[\mathrm{E}]_0 + \left(k_a + k_d\right)[\mathrm{A}]_0\right]\left([\mathrm{E}]-[\mathrm{E}]_0\right) + \ldots, \tag{S5}$$

$$[\mathrm{E}]'_{n=2} = -k_a[\mathrm{E}]_0[\mathrm{A}]_0 - \left[k_a[\mathrm{E}]_0 + \left(k_a + k_d\right)[\mathrm{A}]_0\right]\left([\mathrm{E}]-[\mathrm{E}]_0\right) - k_a\left([\mathrm{E}]-[\mathrm{E}]_0\right)^2 + \ldots \tag{S6}$$

The approximate integrated solutions for Equations (S5) and (S6) were as follows:

$$[\mathrm{E}]_{n=1} = \frac{[\mathrm{E}]_0\left[k_a[\mathrm{E}]_0 + \left(k_a \mathrm{e}^{-k_{ad1}t} + k_d\right)[\mathrm{A}]_0\right]}{k_{ad1}}, \tag{S7}$$

$$[\mathrm{E}]_{n=2} = \frac{1}{2k_a}\left[k_{\overline{ad1}} + k_{ad2}\mathrm{Tanh}\left[\frac{1}{2}k_{ad2}t + \mathrm{ArcTanh}\left(\frac{k_{ad1}}{k_{ad2}}\right)\right]\right], \tag{S8}$$

where k_{ad1}, $k_{\overline{ad1}}$ and k_{ad2} were constants that depended on $[\mathrm{A}]_0$, $[\mathrm{E}]_0$ and the rate constants k_a and k_d as shown below:

$$k_{ad1} = k_a[\mathrm{E}]_0 + \left(k_a + k_d\right)[\mathrm{A}]_0, \tag{S9}$$

$$k_{\overline{ad1}} = k_a[\mathrm{E}]_0 - \left(k_a + k_d\right)[\mathrm{A}]_0, \tag{S10}$$

$$k_{ad2} = \left[k_a^2[\mathrm{E}]_0^2 - 2k_a\left(k_a - k_d\right)[\mathrm{E}]_0[\mathrm{A}]_0 + \left(k_a + k_d\right)^2[\mathrm{A}]_0^2\right]^{1/2}. \tag{S11}$$

After the respective substitution of $[\mathrm{E}]_{n=1}$ and $[\mathrm{E}]_{n=2}$ for $[\mathrm{E}]$ in Equation (62), the approximate integrate solutions for $[\mathrm{A}]_{n=1}$ and $[\mathrm{A}]_{n=2}$ were derived:

$$[\mathrm{A}]_{n=1} = [\mathrm{A}]_0 + \frac{\left(k_a^2 - k_d^2\right)[\mathrm{E}]_0\left(\dfrac{k_a[\mathrm{E}]_0 + \left(k_a\mathrm{e}^{-k_{ad1}t} + k_d\right)[\mathrm{A}]_0}{k_{ad1}} - 1\right) + 2k_ak_d[\mathrm{E}]_0\ln\left[\dfrac{k_a[\mathrm{E}]_0 + \left(\left(k_a + k_d\right)\mathrm{e}^{-k_{ad1}t}\right)[\mathrm{A}]_0}{k_{ad1}}\right]}{\left(k_a + k_d\right)^2}, \tag{S12}$$

$$[\mathrm{A}]_{n=2} = [\mathrm{A}]_0 - \frac{\left(k_a - k_d\right)\left(k_{ad1} - k_{ad2}\mathrm{Tanh}\left[\dfrac{k_{ad2}t}{2} + \mathrm{ArcTanh}\left(\dfrac{k_{ad1}}{k_{ad2}}\right)\right]\right)}{2k_a\left(k_a + k_d\right)} + \frac{2k_ak_d[\mathrm{E}]_0}{\left(k_a + k_d\right)^2}\mathrm{Ln}\left[\frac{k_ak_{\overline{ad1}} - k_dk_{ad1} + k_{ad2}\left(k_a + k_d\right)\mathrm{Tanh}\left[\dfrac{k_{ad2}t}{2} + \mathrm{ArcTanh}\left(\dfrac{k_{ad1}}{k_{ad2}}\right)\right]}{2k_a^2[\mathrm{E}]_0}\right]. \tag{S13}$$

The approximate analytical solutions for $[\mathrm{A}]$ and $[\mathrm{E}]$ together with their respective numerical solutions are shown in Figure 2S. The graphs illustrate how the matches between the numerical and approximate analytical solutions for $[\mathrm{A}]$ and $[\mathrm{E}]$ improve around $t=0$ under non-steady-state conditions as the grade of the polynomial increases. However, the approximate analytical solutions for $[\mathrm{A}]$ and $[\mathrm{E}]$ have the inconvenience of growing complexity as n increases. The mismatch between the numerical and approximate integrated solutions for [A] and [E] was more prominent as the reaction progressed and [A] became exhausted.

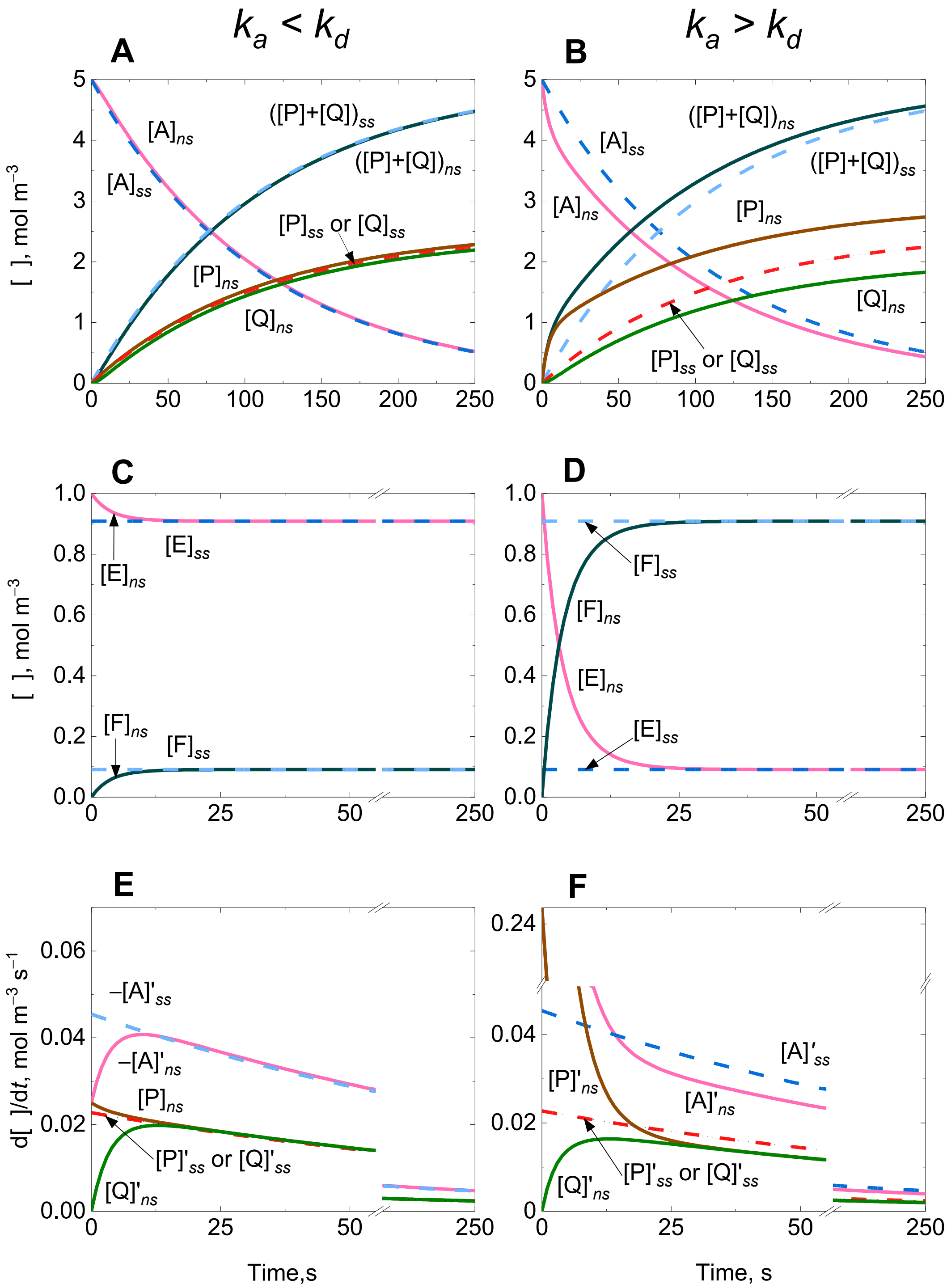


Figure S1. Representative numerical (dashed lines, subscript *ns*) and analytical (solid lines, subscript *ss*) solutions of the time-dependent variation of (**A**–**D**) the concentration for the substrate A, the products P and Q, and the two active enzyme states E and F and (**E**, **F**) the reaction rate for A, P and Q of an enzyme-catalyzed ping-pong reaction. The substrate A follows disproportionation and the accumulation of the intermediate substrate-enzyme complexes EA and FA is negligible. For the analytical solution, E and F were assumed to be in steady-state. Initial conditions: $[A]_0 = 5$ mol m^{-3}, $[E]_0 = 1$ mol m^{-3}, and (**A**, **C** and **E**) $k_a = 5\times10^{-3}$ m^3(mol s)$^{-1}$ and $k_d = 5\times10^{-2}$ m^3(mol s)$^{-1}$ or (**B**, **D** and **F**) $k_a = 5\times10^{-2}$ m^3(mol s)$^{-1}$ and $k_d = 5\times10^{-3}$ m^3(mol s)$^{-1}$.

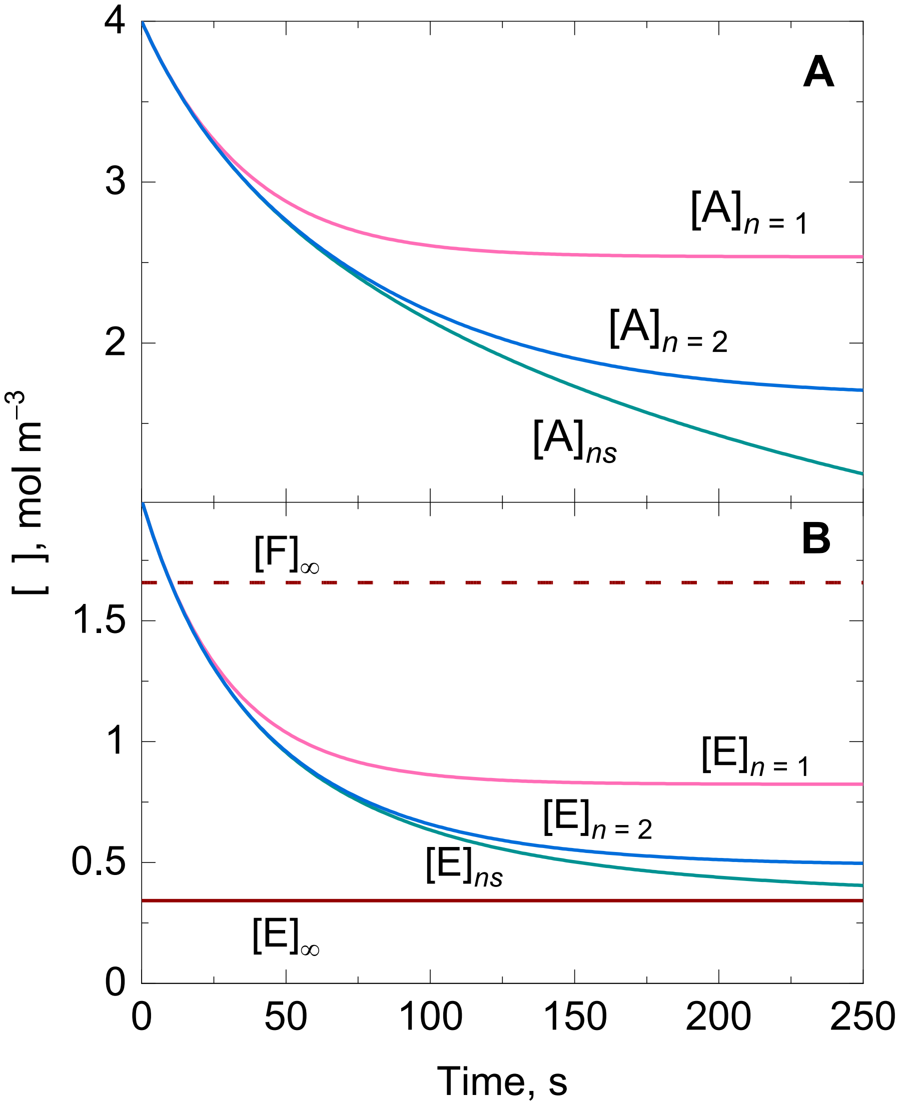


Figure S2. Representative numerically (subscript *ns*) and analytically (subscript $n=1$ or 2) integrated solutions of the time-dependent variation of the concentration for (**A**) the substrate A and (**B**) the two active enzyme states E and F of an enzyme catalyzed ping-pong reaction under non-steady-state conditions. The substrate A undergoes disproportionation and the substrate-enzyme complexes AE and AF do not accumulate. The numerical solutions (*ns*) for $[\mathrm{A}]$ and $[\mathrm{E}]$ are shown together with two approximate integrated solutions around $t=0$ obtained using the first terms ($n=1$ or 2) of the power expansion series of the enzyme-dependent function of $[\mathrm{E}]'$. Horizontal solid and dashed lines are the limit values of the analytical solution for $[\mathrm{E}]$ and $[\mathrm{F}]$ (*i.e.*, $[\mathrm{E}]_\infty$ and $[\mathrm{F}]_\infty$, Equation 52) when the times goes forward and $[\mathrm{A}]$ becomes exhausted. Initial conditions: $[\mathrm{A}]_0 = 4\ \mathrm{mol\ m^{-3}}$, $[\mathrm{E}]_0 = 2\ \mathrm{mol\ m^{-3}}$, $k_a = 5\times10^{-3}\ \mathrm{m^3(mol\ s)^{-1}}$ and $k_d = 10^{-3}\ \mathrm{m^3(mol\ s)^{-1}}$.

Wolfram language scripts
in pdf format

Irreversible Uni-Uni Michaelis-Menten Model in the Absence of Suicide Substrate Inactivation

$$\mathrm{A} + \mathrm{E} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} \mathrm{EA} \overset{k_c}{\rightarrow} \mathrm{E} + \mathrm{P}$$

Quasi-steady-state approximation

```
-cA'[t] == ka * cE[t] * cA[t] - kb * cEA[t]
cEA'[t] == ka * cE[t] * cA[t] - (kb + kc) * cEA[t]
-cE'[t] == ka * cE[t] * cA[t] - (kb + kc) * cEA[t]
cP'[t] == kc * cEA[t]
```

```
-cA′[t] == -kb cEA[t] + ka cA[t] × cE[t]

cEA′[t] == -((kb + kc) cEA[t]) + ka cA[t] × cE[t]

-cE′[t] == -((kb + kc) cEA[t]) + ka cA[t] × cE[t]

cP′[t] == kc cEA[t]

Solve[cEA′[t] == -((kb + kc) cEA[t]) + ka cA[t] × cE[t] /.
  {cEA′[t] → 0, cE[t] → cEo - cEA[t]}, cEA[t]]
```

$$\left\{\left\{\mathrm{cEA}[t] \to \frac{\mathrm{cEo\ ka\ cA}[t]}{\mathrm{kb} + \mathrm{kc} + \mathrm{ka\ cA}[t]}\right\}\right\}$$

$$\mathrm{Solve}\left[-\mathrm{cA}'[t] == \mathrm{kc} * \mathrm{cEA}[t]\ /.\ \mathrm{cEA}[t] \to \frac{\mathrm{cEo\ ka\ cA}[t]}{\mathrm{kb} + \mathrm{kc} + \mathrm{ka\ cA}[t]},\ \mathrm{cA}'[t]\right]$$

Out[•]= $$\left\{\left\{\mathrm{cA}'[t] \to -\frac{\mathrm{cEo\ ka\ kc\ cA}[t]}{\mathrm{kb} + \mathrm{kc} + \mathrm{ka\ cA}[t]}\right\}\right\}$$

Closed-form solution for the time-dependent variation of [A] (Lambert function)

In[•]:= $$\mathrm{DSolve}\left[\left\{-\mathrm{cA}'[t] == \frac{\mathrm{cEo\ kc\ cA}[t]}{\mathrm{km} + \mathrm{cA}[t]},\ \mathrm{cA}[0] == \mathrm{cAo}\right\},\ \{\mathrm{cA}[t]\},\ t\right]$$

••• Solve: Inverse functions are being used by Solve, so some solutions may not be found; use Reduce for complete solution information.

••• Solve: Inverse functions are being used by Solve, so some solutions may not be found; use Reduce for complete solution information.

Out[•]= $$\left\{\left\{\mathrm{cA}[t] \to \mathrm{km\ ProductLog}\left[\frac{\mathrm{cAo}\ e^{\frac{\mathrm{cAo}}{\mathrm{km}} - \frac{\mathrm{cEo\ kc\ t}}{\mathrm{km}}}}{\mathrm{km}}\right]\right\}\right\}$$

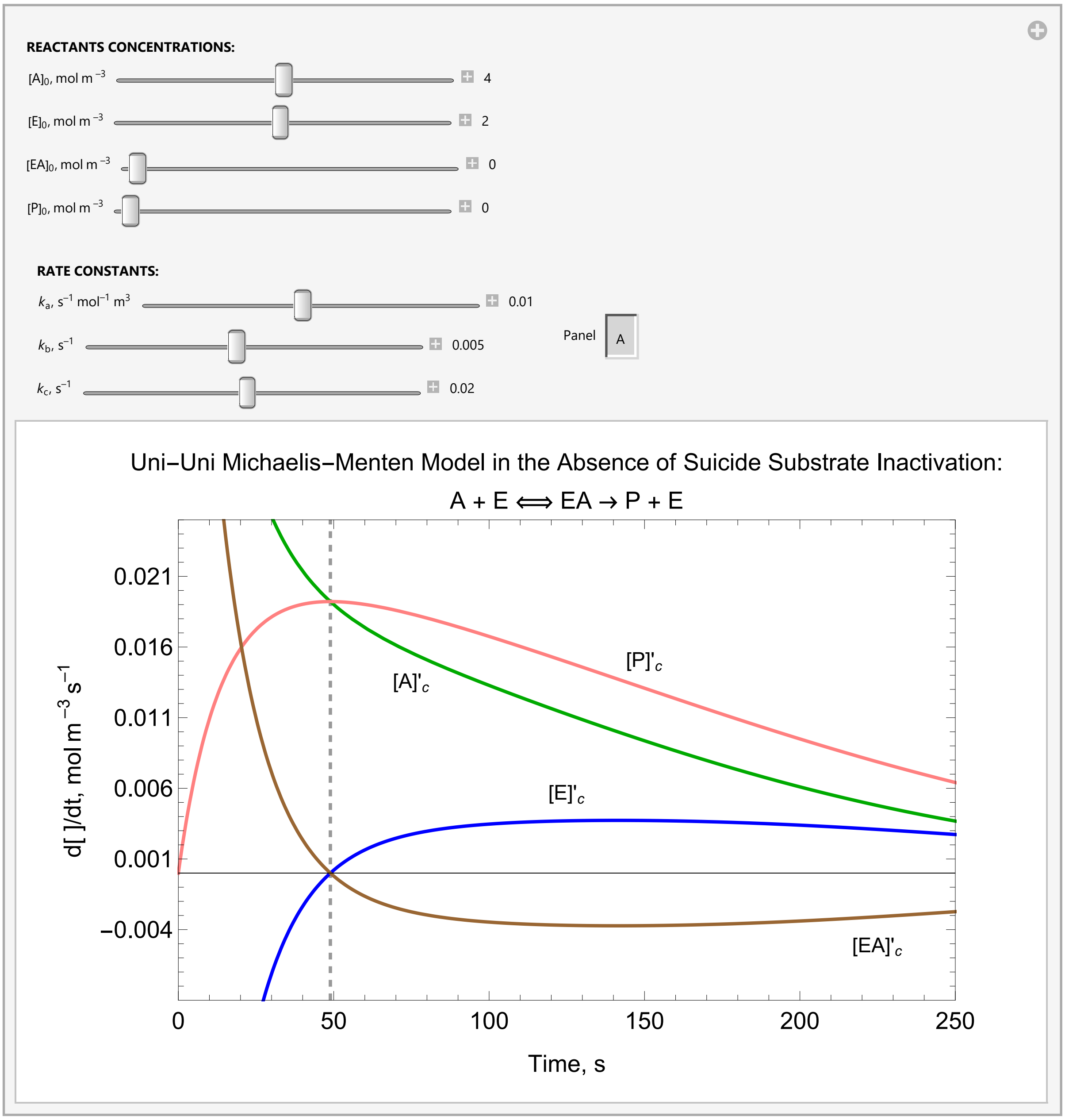
Figure 1A (Mathematics-1964681). Representative numerical solutions of the time-dependent variation of the reaction rate for the participating compounds of an enzymatic system with one substrate and one substrate-enzyme complex in the absence (subscript c) of one-step suicide substrate inactivation under non-steady-state conditions.

```
In[1]:= Manipulate[
  Module[{StandardModel1, soln, plot1},
```

```
StandardModel1 = Sequence[
  PlotRange → {{0, 250}, {-0.009, 0.025}},
  PlotLabel → Style["Uni-Uni Michaelis-Menten
      Model in the Absence of Suicide Substrate Inactivation:
A + E ⟺ EA → P + E", FontSize → 14],
  Frame → True,
  FrameLabel → {"Time, s", "d[ ]/dt, mol m^-3 s^-1"},
  LabelStyle → {FontSize → 14},
  ImageSize → 1.2 {480, 310}];
soln = NDSolve[{-cA'[t] == ka * cE[t] * cA[t] - kb * cEA[t],
   cEA'[t] == ka * cE[t] * cA[t] - (kb + kc) * cEA[t],
   -cE'[t] == ka * cE[t] * cA[t] - (kb + kc) * cEA[t], cP'[t] == kc * cEA[t], cA[0] == cAo,
   cE[0] == cEo, cEA[0] == cEAo, cP[0] == cPo}, {cA, cE, cEA, cP}, {t, 0, 300}];
plot1 = Plot[{-cA'[t] /. soln,
   cP'[t] /. soln,
   cE'[t] /. soln,
   cEA'[t] /. soln}, {t, 0, 250},
  GridLines → {{
     {t /. Last[FindMaximum[cEA[t] /. soln, {t, 0}]], {Black, Thick, Dashed}}}, {}},
  Evaluate@StandardModel1,
  PlotStyle →
   {{Thick, Darker[Green]}, {Thick, Pink}, {Thick, Blue}, {Thick, Brown}},
  Epilog → {
    Inset[Style["[A]'_c", 12, Background → White],
     {75, -0.002 - cA'[75] /. soln[[1]]}],
    Inset[Style["[P]'_c", 12, Background → White],
     {150, 0.002 + cP'[150] /. soln[[1]]}],
    Inset[Style["[E]'_c", 12, Background → White],
     {125, 0.002 + cE'[125] /. soln[[1]]}],
    Inset[Style["[EA]'_c", 12, Background → White],
     {225, -0.002 + cEA'[225] /. soln[[1]]}]}];
Pane[
 Switch[StandardModel,
  1, Show[plot1]
 ], ImageSize → 1.2 {480, 310}]],
Row[{
 Column[{

   Style["REACTANTS CONCENTRATIONS:", Bold],
   Control@{{cAo, 4, "[A]_0, mol m^-3"}, 0.1, 8, Appearance → "Labeled"},
   Control@{{cEo, 2, "[E]_0, mol m^-3"}, 0.1, 4, Appearance → "Labeled"},
   Control@{{cEAo, 0, "[EA]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
   Control@{{cPo, 0, "[P]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"}
  }],
 Column[{

   Style["RATE CONSTANTS:", Bold],
   Control@{{ka, 0.01, "k_a, s^-1 mol^-1 m^3"}, 0.001, 0.02, Appearance → "Labeled"},
   Control@{{kb, 0.005, "k_b, s^-1"}, 0.001, 0.01, Appearance → "Labeled"},
   Control@{{kc, 0.02, "k_c, s^-1"}, 0.001, 0.04, Appearance → "Labeled"}
  }],
```

```
  Control@{{StandardModel, 1, "Panel"}, {
     1 → "A"
    }, ControlType → Setter}}]
]
```

Out[1]=



In[•]:=
```
Module[{soln, cEA, cE},
 soln = ParametricNDSolve[{-cA'[t] == ka * cE[t] * cA[t] - kb * cEA[t], cEA'[t] ==
     ka * cE[t] * cA[t] - (kb + kc) * cEA[t], -cE'[t] == ka * cE[t] * cA[t] - (kb + kc) * cEA[t],
    cP'[t] == kc * cEA[t], cA[0] == cAo, cE[0] == cEo, cEA[0] == cEAo, cP[0] == cPo},
   {cA, cP, cE, cEA}, {t, 0.1, 300}, {cAo, cPo, cEo, cEAo, ka, kb, kc}];
 cEA = NMaximize[{cEA[cAo, cPo, cEo, cEAo, ka, kb, kc][t] /. soln /. {cAo → 4, cPo -> 0,
      cEo → 2, cEAo -> 0, ka -> 0.01, kb → 0.005, kc → 0.02}, 0.1 < t < 100}, t];
 cE = NMinimize[{cE[cAo, cPo, cEo, cEAo, ka, kb, kc][t] /. soln /. {cAo → 4, cPo -> 0,
      cEo → 2, cEAo -> 0, ka -> 0.01, kb → 0.005, kc → 0.02}, 0.1 < t < 100}, t];
 {cEA,
  cE}]
```

Out[•]=
```
{{0.960769, {t → 48.9194}}, {1.03923, {t → 48.9194}}}
```

Irreversible Uni-Uni Michaelis-Menten Model in the Presence of Suicide Substrate Inactivation

$$A + E \underset{k_b}{\overset{k_a}{\rightleftharpoons}} EA \overset{k_c}{\rightarrow} E + P$$

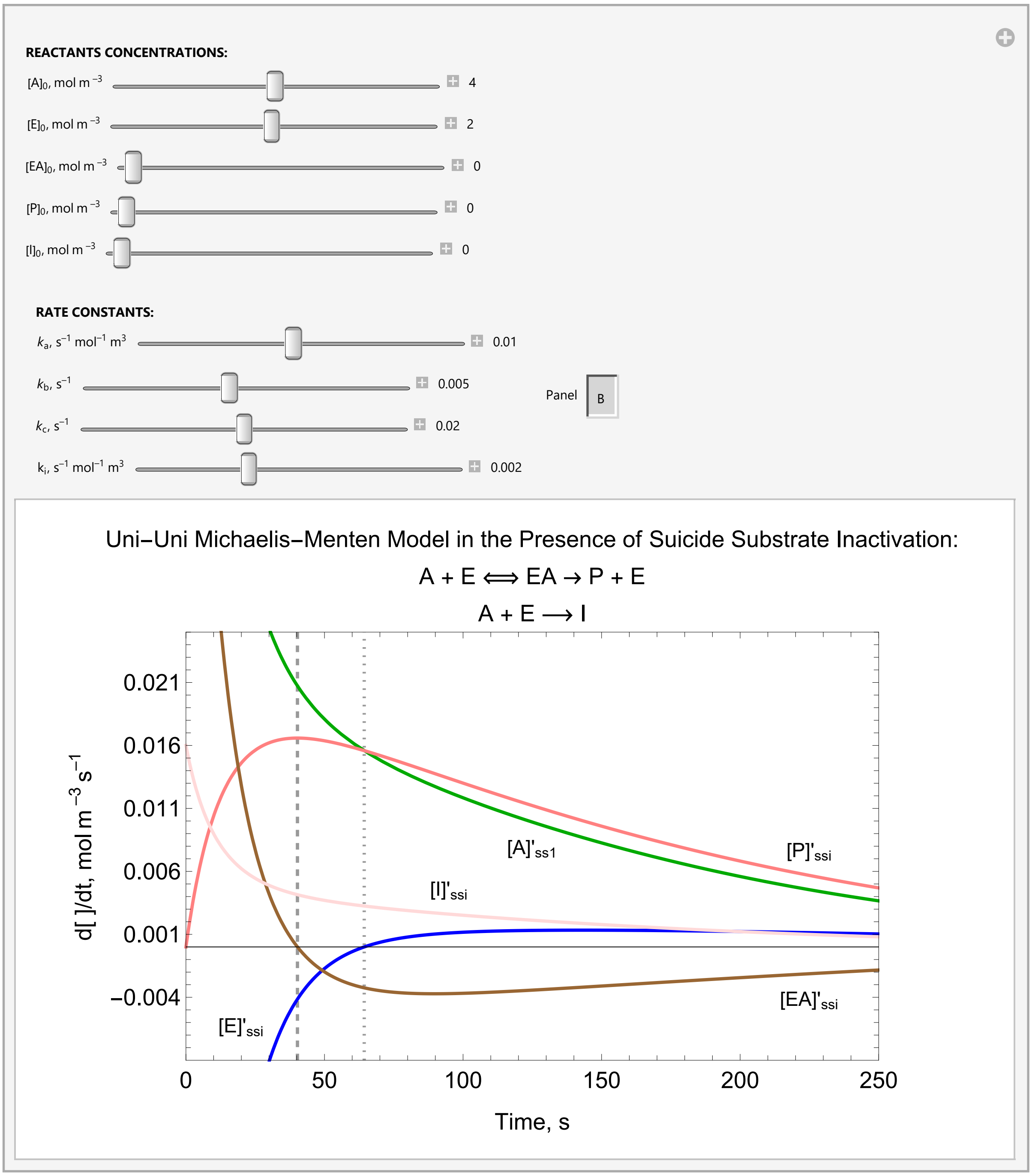
$$A + E \overset{k_i}{\rightarrow} I$$

Figure 1B (Mathematics-1964681). Representative numerical solutions of the time-dependent variation of the reaction rate for the participating compounds of an enzymatic system with one substrate and one substrate-enzyme complex in the presence of one-step suicide substrate inactivation (subscript ssi) under non-steady-state conditions.

```
In[4]:= Manipulate[
  Module[{StandardModel1, solne, plot1},
   StandardModel1 = Sequence[
     PlotRange → {{0, 250}, {-0.009, 0.025}},
     PlotLabel → Style["Uni-Uni Michaelis-Menten
         Model in the Presence of Suicide Substrate Inactivation:
A + E ⟺ EA → P + E
A + E ⟶ I", FontSize → 14],
     Frame → True,
     FrameLabel → {"Time, s", "d[ ]/dt, mol m^-3 s^-1"},
     LabelStyle → {FontSize → 14},
     ImageSize → 1.2 {480, 310}];
   solne = NDSolve[{-cA'[t] == (ka + ki) * cE[t] * cA[t] - kb * cEA[t],
      cEA'[t] == ka * cE[t] * cA[t] - (kb + kc) * cEA[t],
      -cE'[t] == (ka + ki) * cE[t] * cA[t] - (kb + kc) * cEA[t], cP'[t] == kc * cEA[t],
      cI'[t] == ki * cE[t] * cA[t], cA[0] == cAo, cE[0] == cEo, cEA[0] == cEAo,
      cP[0] == cPo, cI[0] == cIo}, {cA, cE, cEA, cP, cI}, {t, 0, 300}];
   plot1 = Plot[{
      -cA'[t] /. solne,
      cP'[t] /. solne,
      cE'[t] /. solne,
      cEA'[t] /. solne,
      cI'[t] /. solne}, {t, 0, 250},
     GridLines → {{
        {t /. Last[FindMaximum[cEA[t] /. solne, {t, 0}]], {Black, Thick, Dashed}},
        {t /. Last[FindMinimum[cE[t] /. solne, {t, 0}]], {Black, Thick, Dotted}}}, {}},
     Evaluate@StandardModel1,
     PlotStyle → {{Thick, Darker[Green]},
       {Thick, Pink}, {Thick, Blue}, {Thick, Brown}, {Thick, LightRed}},
     Epilog → {
       Inset[Style["[A]'ss1", 12, Background → White],
        {125, -0.002 + -cA'[125] /. solne[[1]]}],
```

```
      Inset[Style["[P]'ssi", 12, Background → White],
       {225, 0.002 + cP'[225] /. solne[[1]]}],
      Inset[Style["[E]'ssi", 12, Background → White], {20, cE'[35] /. solne[[1]]}],
      Inset[Style["[EA]'ssi", 12, Background → White],
       {225, -0.002 + cEA'[225] /. solne[[1]]}], Inset[Style["[I]'ssi",
        12, Background → White], {95, 0.002 + cI'[95] /. solne[[1]]}]}];
  Pane[
   Switch[StandardModel,
    1, Show[plot1]
   ], ImageSize → 1.2 {480, 310}]],
 Row[{
   Column[{

     Style["REACTANTS CONCENTRATIONS:", Bold],
     Control@{{cAo, 4, "[A]0, mol m^-3"}, 0.1, 8, Appearance → "Labeled"},
     Control@{{cEo, 2, "[E]0, mol m^-3"}, 0.1, 4, Appearance → "Labeled"},
     Control@{{cEAo, 0, "[EA]0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
     Control@{{cPo, 0, "[P]0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
     Control@{{cIo, 0, "[I]0, mol m^-3"}, 0, 0, Appearance → "Labeled"}
    }],
   Column[{

     Style["RATE CONSTANTS:", Bold],
     Control@{{ka, 0.01, "ka, s^-1 mol^-1 m^3"}, 0.001, 0.02, Appearance → "Labeled"},
     Control@{{kb, 0.005, "kb, s^-1"}, 0.001, 0.01, Appearance → "Labeled"},
     Control@{{kc, 0.02, "kc, s^-1"}, 0, 0.04, Appearance → "Labeled"},
     Control@{{ki, 0.002, "ki, s^-1 mol^-1 m^3"}, 0.001, 0.004, Appearance → "Labeled"}
    }],
   Control@{{StandardModel, 1, "Panel"}, {
      1 → "B"
     }, ControlType → Setter}}]
]
```

Out[4]=


REACTANTS CONCENTRATIONS:
[A]0, mol m −3 4
[E]0, mol m −3 2
[EA]0, mol m −3 0
[P]0, mol m −3 0
[I]0, mol m −3 0
RATE CONSTANTS:
ka, s−1 mol−1 m3 0.01
kb, s−1 0.005
kc, s−1 0.02
ki, s−1 mol−1 m3 0.002
Panel B
Uni–Uni Michaelis–Menten Model in the Presence of Suicide Substrate Inactivation:
A + E ⟺ EA → P + E
A + E ⟶ I
d[ ]/dt, mol m−3 s−1
0.021
0.016
0.011
0.006
0.001
−0.004
[A]'ss1
[P]'ssi
[I]'ssi
[EA]'ssi
[E]'ssi
0
50
100
150
200
250
Time, s

```
In[•]:= Module[{solne, cEA, cE},
  solne = ParametricNDSolve[{-cA'[t] == (ka + ki) * cE[t] * cA[t] - kb * cEA[t],
     cEA'[t] == ka * cE[t] * cA[t] - (kb + kc) * cEA[t],
     -cE'[t] == (ka + ki) * cE[t] * cA[t] - (kb + kc) * cEA[t],
     cP'[t] == kc * cEA[t], cI'[t] == ki * cE[t] * cA[t], cA[0] == cAo, cE[0] == cEo,
     cEA[0] == cEAo, cP[0] == cPo, cI[0] == cIo}, {cA, cP, cE, cEA, cI},
    {t, 0.1, 300}, {cAo, cPo, cEo, cEAo, cIo, ka, kb, kc, ki}];
  cEA = NMaximize[{cEA[cAo, cPo, cEo, cEAo, cIo, ka, kb, kc, ki][t] /. solne /.
       {cAo → 4, cPo -> 0, cEo → 2, cEAo -> 0, cIo → 0, ka -> 0.01,
        kb → 0.005, kc → 0.02, ki → 0.002}, 0.1 < t < 100}, t];
  cE = NMinimize[{cE[cAo, cPo, cEo, cEAo, cIo, ka, kb, kc, ki][t] /. solne /.
       {cAo → 4, cPo -> 0, cEo → 2, cEAo -> 0, cIo → 0, ka -> 0.01,
        kb → 0.005, kc → 0.02, ki → 0.002}, 0.1 < t < 100}, t];
  {cEA,
   cE}]

Out[•]= {{0.829297, {t → 40.2416}}, {0.838855, {t → 64.3389}}}
```

Irreversible Uni-Uni Michaelis-Menten Model in the Presence of Suicide Substrate Inactivation

$$A + E \underset{k_b}{\overset{k_a}{\rightleftharpoons}} EA \xrightarrow{k_c} E + P$$

$$A + E \xrightarrow{k_i} I$$

Figure 2 (Mathematics-1964681). Representative approximate analytically-integrated solutions of the time-dependent variation of the concentration for the participating compounds of an irreversible uni-uni Michaelis-Menten model in the absence (dashed lines, subscript c) and presence of suicide substrate inactivation (solid lines, subscript ssi) following a one-step mechanism.

1. In the presence of inactivation

```
solne = NDSolve[{-cA'[t] == (ka + ki) * cE[t] * cA[t] - kb * cEA[t],
    cEA'[t] == ka * cE[t] * cA[t] - (kb + kc) * cEA[t],
    -cE'[t] == (ka + ki) * cE[t] * cA[t] - (kb + kc) * cEA[t], cP'[t] == kc * cEA[t],
    cI'[t] == ki * cE[t] * cA[t], cA[0] == cAo, cE[0] == cEo, cEA[0] == cEAo,
    cP[0] == cPo, cI[0] == cIo}, {cA, cE, cEA, cP, cI}, {t, 0, 300}];
```

```
Solve[cEA'[t] == ka * cE[t] * cA[t] - (kb + kc) * cEA[t] /. cEA'[t] → 0, cEA[t]]
```

$$\left\{\left\{cEA[t] \rightarrow \frac{ka\, cA[t] \times cE[t]}{kb + kc}\right\}\right\}$$

$$\text{Simplify}\left[-cE'[t] == (ka + ki) * cE[t] * cA[t] - (kb + kc) * cEA[t] \;/.\; cEA[t] \rightarrow \frac{ka\, cA[t] \times cE[t]}{kb + kc}\right]$$

Out[∘]= $ki\, cA[t] \times cE[t] + cE'[t] == 0$

$$\text{Simplify}\left[-cA'[t] == (ka + ki) * cE[t] * cA[t] - kb * cEA[t] \;/.\; cEA[t] \rightarrow \frac{ka\, cA[t] \times cE[t]}{kb + kc}\right] \;/.\; \left(\frac{ka\, kc}{kb + kc} + ki\right) \rightarrow ks$$

Out[∘]= $ks\, cA[t] \times cE[t] + cA'[t] == 0$

```
DSolve[{ki cA[t] × cE[t] + cE'[t] == 0, ks cA[t] × cE[t] + cA'[t] == 0}, {cA[t], cE[t]}, t]
```

Out[∘]= $$\left\{\left\{cE[t] \rightarrow c_1 - \frac{e^{ks\, c_1 c_2}\, ki\, c_1}{-e^{ks\, t\, c_1} + e^{ks\, c_1 c_2}\, ki},\; cA[t] \rightarrow -\frac{e^{ks\, c_1 c_2}\, ks\, c_1}{-e^{ks\, t\, c_1} + e^{ks\, c_1 c_2}\, ki}\right\}\right\}$$

In[ ]:= $\mathbf{DSolve[\{ki\, cA[t] \times cE[t] + cE'[t] == 0,\ ks\, cA[t] \times cE[t] + cA'[t] == 0\},\ \{cA[t],\ cE[t]\},\ t]\ /.\ t \to 0}$

Out[ ]= $\left\{\left\{cE[0] \to c_1 - \frac{e^{ks\, c_1 c_2}\, ki\, c_1}{-1 + e^{ks\, c_1 c_2}\, ki},\ cA[0] \to -\frac{e^{ks\, c_1 c_2}\, ks\, c_1}{-1 + e^{ks\, c_1 c_2}\, ki}\right\}\right\}$

In[ ]:= $\mathbf{Simplify\left[Reduce\left[\left\{cEo == c_1 - \frac{e^{ks\, c_1 c_2}\, ki\, c_1}{-1 + e^{ks\, c_1 c_2}\, ki},\ cAo == -\frac{e^{ks\, c_1 c_2}\, ks\, c_1}{-1 + e^{ks\, c_1 c_2}\, ki}\right\},\ \{c_1, c_2\},\ Rationals\right],\ cAo > 0\, \&\&\, cEo > 0\, \&\&\, ki > 0\, \&\&\, ks > 0\right]}$

Out[ ]= $(cAo \mid cEo \mid ki \mid ks \mid c_2 \mid c_1) \in \mathbb{Q}\ \&\&\ \frac{cAo\, ki}{ks} + c_1 == cEo\ \&\&\ c_2 == \frac{\mathrm{Log}\left[\frac{cAo}{cEo\, ks}\right]}{-cAo\, ki + cEo\, ks}\ \&\&\ cAo\, ki \neq cEo\, ks$

In[ ]:= $\mathbf{Simplify\left[cE[t] == c_1 - \frac{e^{ks\, c_1 c_2}\, ki\, c_1}{-e^{ks\, t\, c_1} + e^{ks\, c_1 c_2}\, ki}\ /.\ \left\{c_1 \to \frac{-cAo\, ki + cEo\, ks}{ks},\ c_2 \to \frac{\mathrm{Log}\left[\frac{cAo}{cEo\, ks}\right]}{-cAo\, ki + cEo\, ks}\right\}\right]\ /.\ ks \to \frac{ka\, kc}{kb + kc} + ki}$

Out[ ]= $cE[t] == \frac{cEo\, e^{cEo\left(\frac{ka\, kc}{kb+kc}+ki\right)t}\left(-cAo\, ki + cEo\left(\frac{ka\, kc}{kb+kc} + ki\right)\right)}{-cAo\, e^{cAo\, ki\, t}\, ki + cEo\, e^{cEo\left(\frac{ka\, kc}{kb+kc}+ki\right)t}\left(\frac{ka\, kc}{kb+kc} + ki\right)}$

k_c approaches infinity

In[ ]:= $\mathbf{Simplify\left[Limit\left[\frac{cEo\, e^{cEo\left(\frac{ka\, kc}{kb+kc}+ki\right)t}\left(-cAo\, ki + cEo\left(\frac{ka\, kc}{kb+kc} + ki\right)\right)}{-cAo\, e^{cAo\, ki\, t}\, ki + cEo\, e^{cEo\left(\frac{ka\, kc}{kb+kc}+ki\right)t}\left(\frac{ka\, kc}{kb+kc} + ki\right)},\ kc \to Infinity\right],\ cAo > 0\, \&\&\, cEo > 0\, \&\&\, ka > 0\, \&\&\, ki > 0\right]}$

Out[ ]= $\frac{cEo\, e^{cEo\,(ka+ki)\,t}\,(-cAo\, ki + cEo\,(ka + ki))}{-cAo\, e^{cAo\, ki\, t}\, ki + cEo\, e^{cEo\,(ka+ki)\,t}\,(ka + ki)}$

$\mathbf{cE[t] == \frac{cEo\, e^{cEo\,(ka+ki)\,t}\,(-cAo\, ki + cEo\,(ka + ki))}{-cAo\, e^{cAo\, ki\, t}\, ki + cEo\, e^{cEo\,(ka+ki)\,t}\,(ka + ki)}}$

In[ ]:= $\mathbf{Simplify\left[cA[t] == -\frac{e^{ks\, c_1 c_2}\, ks\, c_1}{-e^{ks\, t\, c_1} + e^{ks\, c_1 c_2}\, ki}\ /.\ \left\{c_1 \to \frac{-cAo\, ki + cEo\, ks}{ks},\ c_2 \to \frac{\mathrm{Log}\left[\frac{cAo}{cEo\, ks}\right]}{-cAo\, ki + cEo\, ks}\right\}\right]\ /.\ ks \to \frac{ka\, kc}{kb + kc} + ki}$

Out[ ]= $cA[t] == \frac{cAo\left(cAo\, ki - cEo\left(\frac{ka\, kc}{kb+kc} + ki\right)\right)}{cAo\, ki - cEo\, e^{-cAo\, ki\, t + cEo\left(\frac{ka\, kc}{kb+kc}+ki\right)t}\left(\frac{ka\, kc}{kb+kc} + ki\right)}$

In[•]:= $\text{Simplify}\left[\text{Limit}\left[\frac{\text{cAo}\left(\text{cAo ki} - \text{cEo}\left(\frac{\text{ka kc}}{\text{kb+kc}} + \text{ki}\right)\right)}{\text{cAo ki} - \text{cEo}\, e^{-\text{cAo ki t}+\text{cEo}\left(\frac{\text{ka kc}}{\text{kb+kc}}+\text{ki}\right)\text{t}}\left(\frac{\text{ka kc}}{\text{kb+kc}} + \text{ki}\right)}, \text{kc} \to \text{Infinity}\right],\right.$

$\left.\text{cAo} > 0\ \&\&\ \text{cEo} > 0\ \&\&\ \text{ka} > 0\ \&\&\ \text{ki} > 0\right]$

Out[•]= $\frac{\text{cAo}\,(\text{cAo ki} - \text{cEo}\,(\text{ka} + \text{ki}))}{\text{cAo ki} - \text{cEo}\, e^{(-\text{cAo ki}+\text{cEo}\,(\text{ka}+\text{ki}))\,\text{t}}\,(\text{ka} + \text{ki})}$

$\text{cA[t]} == \frac{\text{cAo}\,(\text{cAo ki} - \text{cEo}\,(\text{ka} + \text{ki}))}{\text{cAo ki} - \text{cEo}\, e^{(-\text{cAo ki}+\text{cEo}\,(\text{ka}+\text{ki}))\,\text{t}}\,(\text{ka} + \text{ki})}$

In[•]:= $\text{Simplify}\Big[$

$\text{cP[t]} == \text{cAo} - \text{cA[t]} - (\text{cEo} - \text{cE[t]})\ /.\ \Big\{\text{cA[t]} \to \frac{\text{cAo}\,(\text{cAo ki} - \text{cEo}\,(\text{ka} + \text{ki}))}{\text{cAo ki} - \text{cEo}\, e^{(-\text{cAo ki}+\text{cEo}\,(\text{ka}+\text{ki}))\,\text{t}}\,(\text{ka} + \text{ki})},$

$\text{cE[t]} \to \frac{\text{cEo}\, e^{\text{cEo}\,(\text{ka+ki})\,\text{t}}\,(-\text{cAo ki} + \text{cEo}\,(\text{ka} + \text{ki}))}{-\text{cAo}\, e^{\text{cAo ki t}}\,\text{ki} + \text{cEo}\, e^{\text{cEo}\,(\text{ka+ki})\,\text{t}}\,(\text{ka} + \text{ki})}\Big\}\Big]$

Out[•]= $\text{cP[t]} == \frac{\text{cAo cEo}\left(e^{\text{cAo ki t}} - e^{\text{cEo}\,(\text{ka+ki})\,\text{t}}\right)\text{ka}}{\text{cAo}\, e^{\text{cAo ki t}}\,\text{ki} - \text{cEo}\, e^{\text{cEo}\,(\text{ka+ki})\,\text{t}}\,(\text{ka} + \text{ki})}$

In[•]:= $\text{Simplify}\left[\text{cI[t]} == \text{cEo} - \text{cE[t]}\ /.\ \text{cE[t]} \to \frac{\text{cEo}\, e^{\text{cEo}\,(\text{ka+ki})\,\text{t}}\,(-\text{cAo ki} + \text{cEo}\,(\text{ka} + \text{ki}))}{-\text{cAo}\, e^{\text{cAo ki t}}\,\text{ki} + \text{cEo}\, e^{\text{cEo}\,(\text{ka+ki})\,\text{t}}\,(\text{ka} + \text{ki})}\right]$

Out[•]= $\text{cI[t]} == \frac{\text{cAo cEo}\left(-e^{\text{cAo ki t}} + e^{\text{cEo}\,(\text{ka+ki})\,\text{t}}\right)\text{ki}}{-\text{cAo}\, e^{\text{cAo ki t}}\,\text{ki} + \text{cEo}\, e^{\text{cEo}\,(\text{ka+ki})\,\text{t}}\,(\text{ka} + \text{ki})}$

2. In the absence of inactivation

In[•]:= $\text{cE[t]} == \frac{\text{cEo}\, e^{\text{cEo}\,(\text{ka+ki})\,\text{t}}\,(-\text{cAo ki} + \text{cEo}\,(\text{ka} + \text{ki}))}{-\text{cAo}\, e^{\text{cAo ki t}}\,\text{ki} + \text{cEo}\, e^{\text{cEo}\,(\text{ka+ki})\,\text{t}}\,(\text{ka} + \text{ki})}\ /.\ \text{ki} \to 0$

Out[•]= $\text{cE[t]} == \text{cEo}$

In[•]:= $\text{cA[t]} == \frac{\text{cAo}\,(\text{cAo ki} - \text{cEo}\,(\text{ka} + \text{ki}))}{\text{cAo ki} - \text{cEo}\, e^{(-\text{cAo ki}+\text{cEo}\,(\text{ka}+\text{ki}))\,\text{t}}\,(\text{ka} + \text{ki})}\ /.\ \text{ki} \to 0$

Out[•]= $\text{cA[t]} == \text{cAo}\, e^{-\text{cEo ka t}}$

In[•]:= $\text{cP[t]} == \text{cAo} - \text{cA[t]}\ /.\ \text{cA[t]} \text{ -> } \text{cAo}\, e^{-\text{cEo ka t}}$

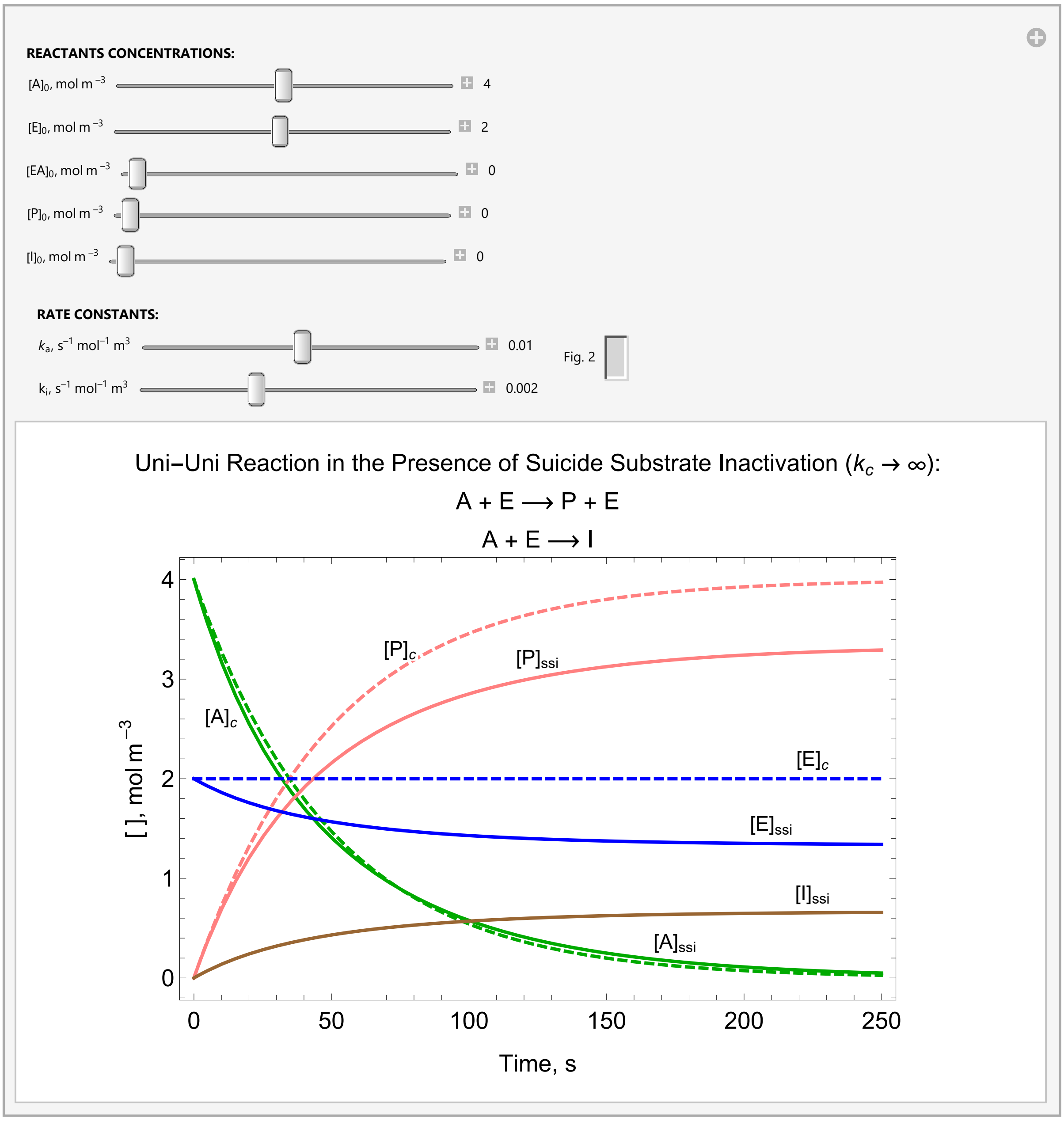
Out[•]= $\text{cP[t]} == \text{cAo} - \text{cAo}\, e^{-\text{cEo ka t}}$

In[5]:=
```
Manipulate[
 Module[{StandardModel1, eqAc, eqAssi, eqPc, eqPssi, eqEc, eqEssi, eqIssi, plot1},
  StandardModel1 = Sequence[
    PlotRange → Automatic,
    PlotLabel → Style[
      "Uni-Uni Reaction in the Presence of Suicide Substrate Inactivation (kc → ∞):
A + E ⟶ P + E
A + E ⟶ I", FontSize → 14],
    Frame → True,
    FrameLabel → {"Time, s", "[ ], mol m^-3"},
```

```
    LabelStyle → {FontSize → 14},
    ImageSize → 1.2 {480, 310}];
  eqAc = cAo e^(-cEo ka t);
  eqAssi = (cAo (cAo ki - cEo (ka + ki)))/(cAo ki - cEo e^((-cAo ki+cEo (ka+ki)) t) (ka + ki));
  eqPc = cAo (1 - e^(-cEo ka t));
  eqPssi = (cAo cEo (e^(cAo ki t) - e^(cEo (ka+ki) t)) ka)/(cAo e^(cAo ki t) ki - cEo e^(cEo (ka+ki) t) (ka + ki));
  eqEc = cEo;
  eqEssi = (cEo e^(cEo (ka+ki) t) (-cAo ki + cEo (ka + ki)))/(-cAo e^(cAo ki t) ki + cEo e^(cEo (ka+ki) t) (ka + ki));
  eqIssi = (cAo cEo (e^(cAo ki t) - e^(cEo (ka+ki) t)) ki)/(cAo e^(cAo ki t) ki - cEo e^(cEo (ka+ki) t) (ka + ki));
  plot1 = Plot[{eqAc, eqAssi, eqPc, eqPssi, eqEc, eqEssi, eqIssi}, {t, 0.0, 250},
    Evaluate@StandardModel1,
    PlotStyle → {{Thick, Darker[Green], Dashed}, {Thick, Darker[Green]}, {Thick, Pink,
       Dashed}, {Thick, Pink}, {Thick, Blue, Dashed}, {Thick, Blue}, {Thick, Brown}},
    Epilog → {Inset[Style["[A]_c", 12, Background → White], {10, 0.2 + eqAc /. t → 25}],
      Inset[Style["[A]_ssi", 12, Background → White], {175, 0.2 + eqAssi /. t → 175}],
      Inset[Style["[P]_c", 12, Background → White], {75, 0.2 + eqPc /. t → 75}],
      Inset[Style["[P]_ssi", 12, Background → White], {125, 0.2 + eqPssi /. t → 125}],
      Inset[Style["[E]_c", 12, Background → White], {225, 0.2 + eqEc /. t → 225}],
      Inset[Style["[E]_ssi", 12, Background → White], {210, 0.2 + eqEssi /. t → 210}],
      Inset[Style["[I]_ssi", 12, Background → White], {225, 0.2 + eqIssi /. t → 225}]
     }];
  Pane[
   Switch[StandardModel,
    1, Show[plot1]
   ], ImageSize → 1.2 {480, 310}]],
 Row[{
   Column[{

     Style["REACTANTS CONCENTRATIONS:", Bold],
     Control@{{cAo, 4, "[A]_0, mol m^-3"}, 0.1, 8, Appearance → "Labeled"},
     Control@{{cEo, 2, "[E]_0, mol m^-3"}, 0.1, 4, Appearance → "Labeled"},
     Control@{{cEAo, 0, "[EA]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
     Control@{{cPo, 0, "[P]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
     Control@{{cIo, 0, "[I]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"}
    }],
   Column[{

     Style["RATE CONSTANTS:", Bold],
     Control@{{ka, 0.01, "k_a, s^-1 mol^-1 m^3"}, 0.001, 0.02, Appearance → "Labeled"},
     Control@{{ki, 0.002, "k_i, s^-1 mol^-1 m^3"}, 0.001, 0.004, Appearance → "Labeled"}
    }],
   Control@{{StandardModel, 1, "Fig. 2"}, {
      1 → ""
```

```
}, ControlType → Setter}}]
]
```

Out[5]=



Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation

$$A + E \underset{k_b}{\overset{k_a}{\rightleftarrows}} EA \xrightarrow{k_c} F + P$$

$$A + F \underset{k_e}{\overset{k_d}{\rightleftarrows}} FA \xrightarrow{k_f} E + Q$$

Quasi-steady-state approximation

```
-cA'[t] == ka * cA[t] * cE[t] - kb * cEA[t] + (kd * cA[t] * cF[t] - ke * cFA[t])
-cE'[t] == ka * cA[t] * cE[t] - (kb * cEA[t] + kf * cFA[t])
cEA'[t] == ka * cA[t] * cE[t] - (kb + kc) * cEA[t]
-cF'[t] == kd * cA[t] * cF[t] - (ke * cFA[t] + kc * cEA[t])
cFA'[t] == kd * cA[t] * cF[t] - (ke + kf) * cFA[t]
cP'[t] == kc * cEA[t]
cQ'[t] == kf * cFA[t]
```

```
-cA′[t] == -kb cEA[t] - ke cFA[t] + ka cA[t] × cE[t] + kd cA[t] × cF[t]

-cE′[t] == -kb cEA[t] - kf cFA[t] + ka cA[t] × cE[t]

cEA′[t] == -((kb + kc) cEA[t]) + ka cA[t] × cE[t]

-cF′[t] == -kc cEA[t] - ke cFA[t] + kd cA[t] × cF[t]

cFA′[t] == -((ke + kf) cFA[t]) + kd cA[t] × cF[t]

cP′[t] == kc cEA[t]

cQ′[t] == kf cFA[t]

Solve[kc cEA[t] == kf cFA[t], cFA[t]]
```

$$\left\{\left\{cFA[t] \to \frac{kc\ cEA[t]}{kf}\right\}\right\}$$

```
Solve[cEA′[t] == -((kb + kc) cEA[t]) + ka cA[t] × cE[t] /. cEA'[t] -> 0, cEA[t]]
```

$$\left\{\left\{cEA[t] \to \frac{ka\ cA[t] \times cE[t]}{kb + kc}\right\}\right\}$$

```
Solve[cFA′[t] == -((ke + kf) cFA[t]) + kd cA[t] × cF[t] /. cFA'[t] → 0, cF[t]]
```

$$\left\{\left\{cF[t] \to \frac{(ke + kf)\ cFA[t]}{kd\ cA[t]}\right\}\right\}$$

$$\text{Solve}\left[\text{cEo} == \text{cE}[t] + \text{cF}[t] + \text{cEA}[t] + \text{cFA}[t] \;/.\; \text{cF}[t] \to \frac{(\text{ke}+\text{kf})\,\text{cFA}[t]}{\text{kd}\,\text{cA}[t]} \;/.\; \text{cFA}[t] \to \frac{\text{kc}\,\text{cEA}[t]}{\text{kf}} \;/.\; \text{cEA}[t] \to \frac{\text{ka}\,\text{cA}[t] \times \text{cE}[t]}{\text{kb}+\text{kc}},\ \text{cE}[t]\right]$$

Out[∘]= $$\left\{\left\{\text{cE}[t] \to \frac{\text{cEo}\,(\text{kb}+\text{kc})\,\text{kd}\,\text{kf}}{\text{ka}\,\text{kc}\,\text{ke} + \text{ka}\,\text{kc}\,\text{kf} + \text{kb}\,\text{kd}\,\text{kf} + \text{kc}\,\text{kd}\,\text{kf} + \text{ka}\,\text{kc}\,\text{kd}\,\text{cA}[t] + \text{ka}\,\text{kd}\,\text{kf}\,\text{cA}[t]}\right\}\right\}$$

$$\text{Expand}\left[-\text{cA}'[t] == 2 * (\text{ka} * \text{cA}[t] * \text{cE}[t] - \text{kb} * \text{cEA}[t]) \;/.\; \text{cEA}[t] \to \frac{\text{ka}\,\text{cA}[t] \times \text{cE}[t]}{\text{kb}+\text{kc}} \;/.\; \text{cE}[t] \to \frac{\text{cEo}\,(\text{kb}+\text{kc})\,\text{kd}\,\text{kf}}{\text{ka}\,\text{kc}\,\text{ke} + \text{ka}\,\text{kc}\,\text{kf} + \text{kb}\,\text{kd}\,\text{kf} + \text{kc}\,\text{kd}\,\text{kf} + \text{ka}\,\text{kc}\,\text{kd}\,\text{cA}[t] + \text{ka}\,\text{kd}\,\text{kf}\,\text{cA}[t]}\right]$$

Out[∘]= $$-\text{cA}'[t] == \frac{2\,\text{cEo}\,\text{ka}\,\text{kc}\,\text{kd}\,\text{kf}\,\text{cA}[t]}{\text{ka}\,\text{kc}\,\text{ke} + \text{ka}\,\text{kc}\,\text{kf} + \text{kb}\,\text{kd}\,\text{kf} + \text{kc}\,\text{kd}\,\text{kf} + \text{ka}\,\text{kc}\,\text{kd}\,\text{cA}[t] + \text{ka}\,\text{kd}\,\text{kf}\,\text{cA}[t]}$$

$$-\text{cA}'[t] == \frac{2\,\text{cEo}\,\text{ka}\,\text{kc}\,\text{kd}\,\text{kf}\,\text{cA}[t]}{\text{ka}\,\text{kc}\,\text{ke} + \text{ka}\,\text{kc}\,\text{kf} + \text{kb}\,\text{kd}\,\text{kf} + \text{kc}\,\text{kd}\,\text{kf} + \text{ka}\,\text{kc}\,\text{kd}\,\text{cA}[t] + \text{ka}\,\text{kd}\,\text{kf}\,\text{cA}[t]}$$

In[∘]:= $$-\text{cA}'[t] == (2\,\text{cEo} * \text{kc} * \text{kf} / (\text{kc}+\text{kf}))\,\frac{\text{cA}[t]}{\text{kf}\,(\text{kb}+\text{kc}) / (\text{ka}\,(\text{kc}+\text{kf})) + \text{kc}\,(\text{ke}+\text{kf}) / (\text{kd}\,(\text{kc}+\text{kf})) + \text{cA}[t]} \;/.\; \left\{\frac{(\text{kb}+\text{kc})\,\text{kf}}{\text{ka}\,(\text{kc}+\text{kf})} \to \text{kmE},\ \frac{\text{kc}\,(\text{ke}+\text{kf})}{\text{kd}\,(\text{kc}+\text{kf})} \text{ -> } \text{kmF}\right\} \;/.\; \text{kc} * \text{kf} / (\text{kc}+\text{kf}) \to \text{kcf} \;/.\; \text{kmE} + \text{kmF} \to \text{kmEF}$$

Out[∘]= $$-\text{cA}'[t] == \frac{2\,\text{cEo}\,\text{kcf}\,\text{cA}[t]}{\text{kmEF} + \text{cA}[t]}$$

Closed-form solution for the time-dependent variation of [A] (Lambert function)

In[∘]:= $$\text{DSolve}\left[\left\{-\text{cA}'[t] == \frac{2\,\text{cEo}\,\text{kcf}\,\text{cA}[t]}{\text{kmEF} + \text{cA}[t]},\ \text{cA}[0] == \text{cAo}\right\},\ \{\text{cA}[t]\},\ t\right]$$

••• Solve: Inverse functions are being used by Solve, so some solutions may not be found; use Reduce for complete solution information.

••• Solve: Inverse functions are being used by Solve, so some solutions may not be found; use Reduce for complete solution information.

Out[∘]= $$\left\{\left\{\text{cA}[t] \to \text{kmEF}\ \text{ProductLog}\left[\frac{\text{cAo}\,e^{\frac{\text{cAo}}{\text{kmEF}} - \frac{2\,\text{cEo}\,\text{kcf}\,t}{\text{kmEF}}}}{\text{kmEF}}\right]\right\}\right\}$$

In[∘]:= $$\text{cA}[t] \to \text{kmEF}\ \text{ProductLog}\left[\frac{\text{cAo}\,e^{\frac{\text{cAo}}{\text{kmEF}} - \frac{2\,\text{cEo}\,\text{kcf}\,t}{\text{kmEF}}}}{\text{kmEF}}\right] \;/.\; \text{kmEF} \text{ -> } \text{kmE} + \text{kmF} \;/.\; \text{kcf} \text{ -> } \text{kc} * \text{kf} / (\text{kc}+\text{kf})$$

Out[∘]= $$\text{cA}[t] \to (\text{kmE}+\text{kmF})\ \text{ProductLog}\left[\frac{\text{cAo}\,e^{\frac{\text{cAo}}{\text{kmE}+\text{kmF}} - \frac{2\,\text{cEo}\,\text{kc}\,\text{kf}\,t}{(\text{kc}+\text{kf})\,(\text{kmE}+\text{kmF})}}}{\text{kmE}+\text{kmF}}\right]$$

Figure 3A (Mathematics-1964681). Representative numerical solutions of the time-dependent variation of the reaction rate for the substrate A, and the products P and Q of an enzyme-catalyzed ping-pong reaction with one substrate undergoing disproportionation under non-steady-state conditions.

```
In[6]:= Manipulate[Module[{PingPongModel1, soln, plot1},
    PingPongModel1 = Sequence[
      PlotRange → {{0, 250}, {0, 0.0305}},
      PlotLabel →
       Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation:
A + E ⟺ EA → P + F
A + F ⟺ FA → Q + E", FontSize → 14],
      Frame → True,
      FrameLabel → {"Time, s", "d[ ]/dt, mol m^-3 s^-1"},
      LabelStyle → {FontSize → 14},
      ImageSize → 1.2 {480, 310}];
    soln = NDSolve[{-cA'[t] == (ka * cE[t] + kd * cF[t]) * cA[t] - (kb * cEA[t] + ke * cFA[t]),
       -cE'[t] == ka * cA[t] * cE[t] - (kb * cEA[t] + kf * cFA[t]),
       -cF'[t] == kd * cA[t] * cF[t] - (ke * cFA[t] + kc * cEA[t]),
       cEA'[t] == ka * cA[t] * cE[t] - (kb + kc) * cEA[t],
       cFA'[t] == kd * cA[t] * cF[t] - (ke + kf) * cFA[t], cP'[t] == kc * cEA[t],
       cQ'[t] == kf * cFA[t], cA[0] == cAo, cE[0] == cEo, cF[0] == cFo,
       cEA[0] == cEAo, cFA[0] == cFAo, cP[0] == cPo, cQ[0] == cQo},
      {cA, cE, cF, cEA, cFA, cP, cQ}, {t, 0.0, 250}];
    plot1 = Plot[{-cA'[t] /. soln,
       cP'[t] + cQ'[t] /. soln,
       cP'[t] /. soln,
       cQ'[t] /. soln}, {t, 0.02, 250},
      GridLines → {{
         {t /. Last[FindMaximum[cEA[t] + cFA[t] /. soln, {t, 0}]], {Black, Thick, Dashed}},
         {t /. Last[FindMaximum[kc * cEA[t] + kf * cFA[t] /. soln, {t, 0}]],
          {Black, Thick, Dotted}}}, {}},
      Evaluate@PingPongModel1,
      PlotStyle → {{Thick, Darker[Green]},
        {Thick, Pink}, {Thick, Pink, Dashed}, {Thick, Pink, Dotted}},
      Epilog → {Inset[Style["-[A]'", 12, Background → White],
         {25, -cA'[40] /. soln[[1]]}],
        Inset[Style["[P]'+ [Q]'", 12, Background → White],
         {175, 0.005 + cP'[175] + cQ'[175] /. soln[[1]]}], Inset[
         Style["[P]'", 12, Background → White], {30, -0.0025 + cP'[30] /. soln[[1]]}],
        Inset[Style["[Q]'", 12, Background → White], {30, -0.004 + cQ'[30] /. soln[[1]]}]
       }];
    Pane[
     Switch[PingPong,
      1, Show[plot1]
     ], ImageSize → 1.2 {480, 310}]],
   Row[{
     Column[{

       Style["REACTANTS CONCENTRATIONS:", Bold],
       Control@{{cAo, 4, "[A]_0, mol m^-3"}, 0.1, 8, Appearance → "Labeled"},
       Control@{{cEo, 2, "[E]_0, mol m^-3"}, 0.1, 4, Appearance → "Labeled"},
       Control@{{cFo, 0, "[F]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
       Control@{{cEAo, 0, "[EA]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
       Control@{{cFAo, 0, "[FA]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
```

```
      Control@{{cPo, 0, "[P]₀, mol m^-3"}, 0, 0, Appearance → "Labeled"},
      Control@{{cQo, 0, "[Q]₀, mol m^-3"}, 0, 0, Appearance → "Labeled"}
     }],
    Column[{

      Style["RATE CONSTANTS:", Bold],
      Control@{{ka, 0.01, "ka, s^-1 mol^-1 m^3"}, 0.001, 0.02, Appearance → "Labeled"},
      Control@{{kb, 0.005, "kb, s^-1"}, 0.001, 0.01, Appearance → "Labeled"},
      Control@{{kc, 0.02, "kc, s^-1"}, 0.001, 0.04, Appearance → "Labeled"},
      Control@{{kd, 0.05, "kd, s^-1 mol^-1 m^3"}, 0.01, 0.1, Appearance → "Labeled"},
      Control@{{ke, 0.004, "ke, s^-1"}, 0.001, 0.008, Appearance → "Labeled"},
      Control@{{kf, 0.04, "kf, s^-1"}, 0.001, 0.08, Appearance → "Labeled"}
     }],
    Control@{{PingPong, 1, "Panel"}, {
       1 → "A"
      }, ControlType → Setter}}]
]
```

REACTANTS CONCENTRATIONS:

$[A]_0$, mol m^{-3} 4

$[E]_0$, mol m^{-3} 2

$[F]_0$, mol m^{-3} 0

$[EA]_0$, mol m^{-3} 0

$[FA]_0$, mol m^{-3} 0

$[P]_0$, mol m^{-3} 0

$[Q]_0$, mol m^{-3} 0

RATE CONSTANTS:

k_a, s^{-1} mol^{-1} m^3 0.01

k_b, s^{-1} 0.005

k_c, s^{-1} 0.02

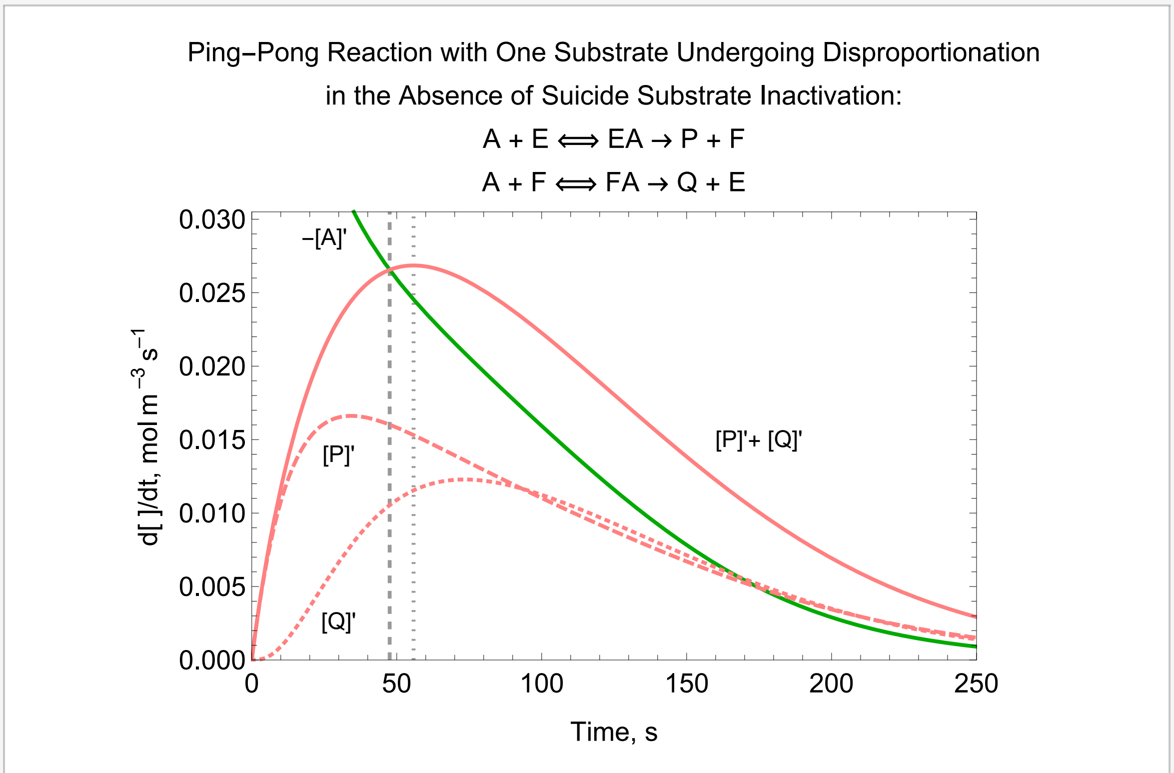
k_d, s^{-1} mol^{-1} m^3 0.05

k_e, s^{-1} 0.004

k_f, s^{-1} 0.04

Panel A

Out[6]=



In[•]:=
```
Module[{soln, cAEcAF, kccAEkfcAF}, soln = soln = ParametricNDSolve[
    {-cA'[t] == (ka * cE[t] + kd * cF[t]) * cA[t] - (kb * cEA[t] + ke * cFA[t]),
     -cE'[t] == ka * cA[t] * cE[t] - (kb * cEA[t] + kf * cFA[t]),
     -cF'[t] == kd * cA[t] * cF[t] - (ke * cFA[t] + kc * cEA[t]),
     cEA'[t] == ka * cA[t] * cE[t] - (kb + kc) * cEA[t],
     cFA'[t] == kd * cA[t] * cF[t] - (ke + kf) * cFA[t], cP'[t] == kc * cEA[t],
     cQ'[t] == kf * cFA[t], cA[0] == cAo, cE[0] == cEo, cF[0] == cFo, cEA[0] == cEAo,
     cFA[0] == cFAo, cP[0] == cPo, cQ[0] == cQo}, {cA, cP, cQ, cE, cF, cEA, cFA},
    {t, 0.0, 300}, {cAo, cPo, cQo, cEo, cFo, cEAo, cFAo, ka, kb, kc, kd, ke, kf}];
  cAEcAF = NMaximize[{cEA[cAo, cPo, cQo, cEo, cFo, cEAo, cFAo, ka, kb, kc, kd, ke, kf][t] +
       cFA[cAo, cPo, cQo, cEo, cFo, cEAo, cFAo, ka, kb, kc, kd, ke, kf][t] /. soln /.
      {cAo → 4, cEo → 2, cFo → 0, cPo -> 0, cQo -> 0, cEAo -> 0, cFAo -> 0, ka -> 0.01,
       kb → 0.005, kc → 0.02, kd -> 0.05, ke → 0.004, kf → 0.04}, 0.1 < t < 100}, t];
  kccAEkfcAF = NMaximize[{kc * cEA[cAo, cPo, cQo, cEo, cFo,
          cEAo, cFAo, ka, kb, kc, kd, ke, kf][t] +
       kf * cFA[cAo, cPo, cQo, cEo, cFo, cEAo, cFAo, ka, kb, kc, kd, ke, kf][t] /. soln /.
      {cAo → 4, cEo → 2, cFo → 0, cPo -> 0, cQo -> 0, cEAo -> 0, cFAo -> 0, ka -> 0.01,
       kb → 0.005, kc → 0.02, kd -> 0.05, ke → 0.004, kf → 0.04}, 0.1 < t < 100}, t];
  {cAEcAF, kccAEkfcAF}]
```

Out[•]=
```
{{1.06424, {t → 47.5648}}, {0.0268526, {t → 55.812}}}
```

Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation

$$A + E \underset{k_b}{\overset{k_a}{\rightleftarrows}} EA \xrightarrow{k_c} F + P$$

$$A + F \underset{k_e}{\overset{k_d}{\rightleftarrows}} FA \xrightarrow{k_f} E + Q$$

Figure 3B (Mathematics-1964681). Representative numerical solutions of the time-dependent variation of the reaction rate for the enzyme states E and F, and the substrate-enzyme complexes EA and FA of an enzyme-catalyzed ping-pong reaction with one substrate undergoing disproportionation under non-steady-state conditions.

In[34]:=
```
Manipulate[Module[{PingPongModel1, soln, plot1},
  PingPongModel1 = Sequence[
    PlotRange → {{0, 250}, {-0.009, 0.009}},
    PlotLabel →
     Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation:
A + E ⟺ EA → P + F
A + F ⟺ FA → Q + E", FontSize → 14],
    Frame → True,
    FrameLabel → {"Time, s", "d[ ]/dt, mol m^-3 s^-1"},
    LabelStyle → {FontSize → 14},
    ImageSize → 1.2 {480, 310}];
  soln = NDSolve[{-cA'[t] == (ka * cE[t] + kd * cF[t]) * cA[t] - (kb * cEA[t] + ke * cFA[t]),
     -cE'[t] == ka * cA[t] * cE[t] - (kb * cEA[t] + kf * cFA[t]),
     -cF'[t] == kd * cA[t] * cF[t] - (ke * cFA[t] + kc * cEA[t]),
     cEA'[t] == ka * cA[t] * cE[t] - (kb + kc) * cEA[t],
     cFA'[t] == kd * cA[t] * cF[t] - (ke + kf) * cFA[t], cP'[t] == kc * cEA[t],
     cQ'[t] == kf * cFA[t], cA[0] == cAo, cE[0] == cEo, cF[0] == cFo,
     cEA[0] == cEAo, cFA[0] == cFAo, cP[0] == cPo, cQ[0] == cQo},
    {cA, cE, cF, cEA, cFA, cP, cQ}, {t, 0.0, 250}];
  plot1 = Plot[{
     cE'[t] + cF'[t] /. soln,
     cE'[t] /. soln,
     cF'[t] /. soln,
     cEA'[t] + cFA'[t] /. soln,
     cEA'[t] /. soln,
     cFA'[t] /. soln}, {t, 0.02, 250},
    GridLines → {{
       {t /. Last[FindMaximum[cEA[t] + cFA[t] /. soln, {t, 0}]], {Black, Thick, Dashed}}},
      {}},
```

```
    Evaluate@PingPongModel1,
    PlotStyle → {{Thick, Blue}, {Thick, Blue, Dashed}, {Thick, Blue, Dotted},
      {Thick, Brown}, {Thick, Brown, Dashed}, {Thick, Brown, Dotted}},
    Epilog → {Inset[Style["[E]'+[F]'", 12, Background → White],
       {125, 0.001 + cE'[125] + cF'[125] /. soln[[1]]}],
      Inset[Style["[E]'", 12, Background → White],
       {100, -0.001 + cE'[100] /. soln[[1]]}], Inset[
       Style["[F]'", 12, Background → White], {150, -0.001 + cF'[150] /. soln[[1]]}],
      Inset[Style["[EA]'+[FA]'", 12, Background → White],
       {125, -0.001 + cEA'[125] + cFA'[125] /. soln[[1]]}],
      Inset[Style["[EA]'", 12, Background → White],
       {100, 0.001 + cEA'[100] /. soln[[1]]}], Inset[
       Style["[FA]'", 12, Background → White], {125, 0.001 + cFA'[125] /. soln[[1]]}]
     }];
  Pane[
   Switch[PingPong,
    1, Show[plot1]
   ], ImageSize → 1.2 {480, 310}]],
 Row[{
   Column[{

     Style["REACTANTS CONCENTRATIONS:", Bold],
     Control@{{cAo, 4, "[A]0, mol m^-3"}, 0.1, 8, Appearance → "Labeled"},
     Control@{{cEo, 2, "[E]0, mol m^-3"}, 0.1, 4, Appearance → "Labeled"},
     Control@{{cFo, 0, "[F]0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
     Control@{{cEAo, 0, "[EA]0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
     Control@{{cFAo, 0, "[FA]0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
     Control@{{cPo, 0, "[P]0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
     Control@{{cQo, 0, "[Q]0, mol m^-3"}, 0, 0, Appearance → "Labeled"}
    }],
   Column[{

     Style["RATE CONSTANTS:", Bold],
     Control@{{ka, 0.01, "ka, s^-1 mol^-1 m^3"}, 0.001, 0.02, Appearance → "Labeled"},
     Control@{{kb, 0.005, "kb, s^-1"}, 0.001, 0.01, Appearance → "Labeled"},
     Control@{{kc, 0.02, "kc, s^-1"}, 0.001, 0.04, Appearance → "Labeled"},
     Control@{{kd, 0.05, "kd, s^-1 mol^-1 m^3"}, 0.01, 0.1, Appearance → "Labeled"},
     Control@{{ke, 0.004, "ke, s^-1"}, 0.001, 0.008, Appearance → "Labeled"},
     Control@{{kf, 0.04, "kf, s^-1"}, 0.001, 0.08, Appearance → "Labeled"}
    }],
   Control@{{PingPong, 1, "Panel"}, {
      1 → "B"
     }, ControlType → Setter}}]
]
```

REACTANTS CONCENTRATIONS:

$[A]_0$, mol m^{-3} 4

$[E]_0$, mol m^{-3} 2

$[F]_0$, mol m^{-3} 0

$[EA]_0$, mol m^{-3} 0

$[FA]_0$, mol m^{-3} 0

$[P]_0$, mol m^{-3} 0

$[Q]_0$, mol m^{-3} 0

RATE CONSTANTS:

k_a, s^{-1} mol^{-1} m^3 0.01

k_b, s^{-1} 0.005

k_c, s^{-1} 0.02

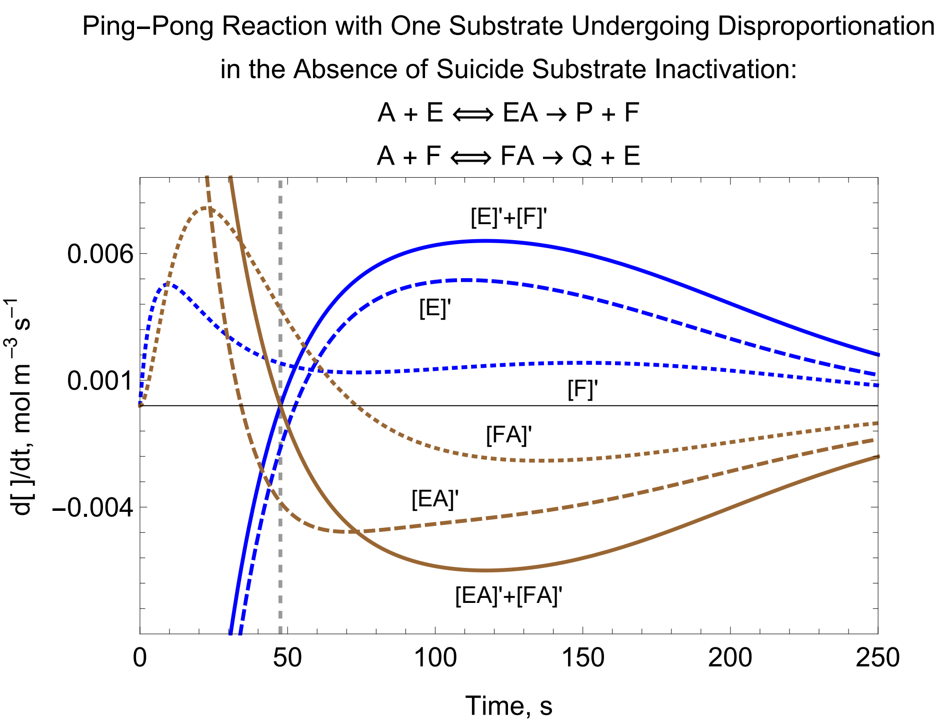
k_d, s^{-1} mol^{-1} m^3 0.05

k_e, s^{-1} 0.004

k_f, s^{-1} 0.04

Panel B

Out[∘]=



In[ ]:=
```
Module[{soln, cAEcAF}, soln = soln = ParametricNDSolve[
    {-cA'[t] == (ka * cE[t] + kd * cF[t]) * cA[t] - (kb * cEA[t] + ke * cFA[t]),
     -cE'[t] == ka * cA[t] * cE[t] - (kb * cEA[t] + kf * cFA[t]),
     -cF'[t] == kd * cA[t] * cF[t] - (ke * cFA[t] + kc * cEA[t]),
     cEA'[t] == ka * cA[t] * cE[t] - (kb + kc) * cEA[t],
     cFA'[t] == kd * cA[t] * cF[t] - (ke + kf) * cFA[t], cP'[t] == kc * cEA[t],
     cQ'[t] == kf * cFA[t], cA[0] == cAo, cE[0] == cEo, cF[0] == cFo, cEA[0] == cEAo,
     cFA[0] == cFAo, cP[0] == cPo, cQ[0] == cQo}, {cA, cP, cQ, cE, cF, cEA, cFA},
    {t, 0.0, 300}, {cAo, cPo, cQo, cEo, cFo, cEAo, cFAo, ka, kb, kc, kd, ke, kf}];
  cAEcAF = NMaximize[{cEA[cAo, cPo, cQo, cEo, cFo, cEAo, cFAo, ka, kb, kc, kd, ke, kf][t] +
       cFA[cAo, cPo, cQo, cEo, cFo, cEAo, cFAo, ka, kb, kc, kd, ke, kf][t] /. soln /.
     {cAo → 4, cEo → 2, cFo → 0, cPo -> 0, cQo -> 0, cEAo -> 0, cFAo -> 0, ka -> 0.01,
      kb → 0.005, kc → 0.02, kd -> 0.05, ke → 0.004, kf → 0.04}, 0.1 < t < 100}, t];
  cAEcAF]
```

Out[ ]= {1.06424, {t → 47.5648}}

Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation

$$A + E \xrightarrow{k_a} F + P$$

$$A + F \xrightarrow{k_d} E + Q$$

$k_c \rightarrow \infty$ and $k_f \rightarrow \infty$

Figure 4 (Mathematics-1964681). Representative numerical (subscript ns) and approximate analytical (subscript n = 2) solutions of the time-dependent variation of the reaction rate for the substrate A undergoing disproportionation and one of the active enzymes states, E, of an enzyme-catalyzed ping-pong reaction in which the substrate-enzyme complexes do not accumulate.

1. Solution around t = 0

```
In[ ]:= -cA'[t] == ka * cA[t] * cE[t] + kd * cA[t] * cF[t] /. cF[t] → cEo - cE[t]
        -cE'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t] /. cF[t] → cEo - cE[t]
        -cF'[t] == cE'[t]
```

Out[ ]= $-cA'[t] == kd\, cA[t]\, (cEo - cE[t]) + ka\, cA[t] \times cE[t]$

Out[ ]= $-cE'[t] == -kd\, cA[t]\, (cEo - cE[t]) + ka\, cA[t] \times cE[t]$

Out[ ]= $-cF'[t] == cE'[t]$

Chain rule

dy/dx=(dy/dt) /(dx/dt)

```
In[ ]:= Simplify[-cA'[t] / (-cE'[t]) ==
          (kd cA[t] (cEo - cE[t]) + ka cA[t] × cE[t]) / (-kd cA[t] (cEo - cE[t]) + ka cA[t] × cE[t])]
```

Out[ ]= $\dfrac{cEo\, kd + (ka - kd)\, cE[t]}{cEo\, kd - (ka + kd)\, cE[t]} + \dfrac{cA'[t]}{cE'[t]} == 0$

```
In[ ]:= Collect[Simplify[DSolve[{-cA'[cE] == (cE (ka - kd) + cEo kd)/(cEo kd - cE (ka + kd)), cA[cEo] == cAo}, cA[cE], cE],
          ka > 0 && kd > 0 && cEo > 0 && cAo > 0] /. cE → cE[t], ka + kd]
```

Out[ ]= $\left\{\left\{cA[cE[t]] \to cAo + \dfrac{(ka - kd)\,(-cEo + cE[t])}{ka + kd} + \dfrac{-2\, cEo\, ka\, kd\, Log[cEo\, ka] + 2\, cEo\, ka\, kd\, Log[-cEo\, kd + (ka + kd)\, cE[t]]}{(ka + kd)^2}\right\}\right\}$

In[∘]:=
```
Simplify[-cE'[t] == -kd cA[t] (cEo - cE[t]) + ka cA[t] × cE[t] /.
  cA[t] -> cAo + ((ka - kd) (-cEo + cE[t]))/(ka + kd) +
   (-2 cEo ka kd Log[cEo ka] + 2 cEo ka kd Log[-cEo kd + (ka + kd) cE[t]])/(ka + kd)^2]
```

Out[∘]= $$\frac{1}{(\mathrm{ka}+\mathrm{kd})^2}(\mathrm{cEo\,kd}-(\mathrm{ka}+\mathrm{kd})\,\mathrm{cE}[t])\big(\mathrm{cAo\,ka}^2-\mathrm{cEo\,ka}^2+2\,\mathrm{cAo\,ka\,kd}+\mathrm{cAo\,kd}^2+\mathrm{cEo\,kd}^2+(\mathrm{ka}^2-\mathrm{kd}^2)\,\mathrm{cE}[t]-2\,\mathrm{cEo\,ka\,kd\,Log}[\mathrm{cEo\,ka}]+2\,\mathrm{cEo\,ka\,kd\,Log}[-\mathrm{cEo\,kd}+(\mathrm{ka}+\mathrm{kd})\,\mathrm{cE}[t]]\big)==\mathrm{cE}'[t]$$

Power expansion series

In[∘]:=
```
Series[1/(ka + kd)^2 (cEo kd - (ka + kd) cE[t])
  (cAo ka^2 - cEo ka^2 + 2 cAo ka kd + cAo kd^2 + cEo kd^2 + (ka^2 - kd^2) cE[t] - 2 cEo ka kd
    Log[cEo ka] + 2 cEo ka kd Log[-cEo kd + (ka + kd) cE[t]]) == cE'[t], {cE[t], cEo, 1}]
```

Out[∘]= $$-\mathrm{cAo\,cEo\,ka}+(-\mathrm{cAo\,ka}-\mathrm{cEo\,ka}-\mathrm{cAo\,kd})\,(\mathrm{cE}[t]-\mathrm{cEo})+O[\mathrm{cE}[t]-\mathrm{cEo}]^2==\mathrm{cE}'[t]$$

In[∘]:=
```
Series[1/(ka + kd)^2 (cEo kd - (ka + kd) cE[t])
  (cAo ka^2 - cEo ka^2 + 2 cAo ka kd + cAo kd^2 + cEo kd^2 + (ka^2 - kd^2) cE[t] - 2 cEo ka kd
    Log[cEo ka] + 2 cEo ka kd Log[-cEo kd + (ka + kd) cE[t]]) == cE'[t], {cE[t], cEo, 2}]
```

Out[∘]= $$-\mathrm{cAo\,cEo\,ka}+(-\mathrm{cAo\,ka}-\mathrm{cEo\,ka}-\mathrm{cAo\,kd})\,(\mathrm{cE}[t]-\mathrm{cEo})-\mathrm{ka}\,(\mathrm{cE}[t]-\mathrm{cEo})^2+O[\mathrm{cE}[t]-\mathrm{cEo}]^3==\mathrm{cE}'[t]$$

In[∘]:=
```
cEn1 = Simplify[DSolve[
   {-cAo cEo ka + (-cAo ka - cEo ka - cAo kd) (cE[t] - cEo) == cE'[t], cE[0] == cEo}, cE[t], t]]
```

Out[∘]= $$\left\{\left\{\mathrm{cE}[t]\to\frac{\mathrm{cEo}\left(\mathrm{cEo\,ka}+\mathrm{cAo}\left(e^{-((\mathrm{cEo\,ka}+\mathrm{cAo}\,(\mathrm{ka}+\mathrm{kd}))\,t)}\,\mathrm{ka}+\mathrm{kd}\right)\right)}{\mathrm{cEo\,ka}+\mathrm{cAo}\,(\mathrm{ka}+\mathrm{kd})}\right\}\right\}$$

In[∘]:=
```
cAn1 = Simplify[cA[t] == cAo + ((ka - kd) (-cEo + cE[t]))/(ka + kd) +
    (-2 cEo ka kd Log[cEo ka] + 2 cEo ka kd Log[-cEo kd + (ka + kd) cE[t]])/(ka + kd)^2 /.
   cE[t] → (cEo (cEo ka + cAo (e^-((cEo ka+cAo (ka+kd)) t) ka + kd)))/(cEo ka + cAo (ka + kd)),
   ka > 0 && kd > 0 && cAo > 0 && cEo > 0]
```

Out[∘]= $$\mathrm{cA}[t]==\mathrm{cAo}+\frac{\mathrm{cEo}\,(\mathrm{ka}-\mathrm{kd})\left(-1+\frac{\mathrm{cEo\,ka}+\mathrm{cAo}\left(e^{-((\mathrm{cEo\,ka}+\mathrm{cAo}\,(\mathrm{ka}+\mathrm{kd}))\,t)}\,\mathrm{ka}+\mathrm{kd}\right)}{\mathrm{cEo\,ka}+\mathrm{cAo}\,(\mathrm{ka}+\mathrm{kd})}\right)}{\mathrm{ka}+\mathrm{kd}}+\frac{2\,\mathrm{cEo\,ka\,kd\,Log}\left[\frac{\mathrm{cEo\,ka}+\mathrm{cAo}\,e^{-((\mathrm{cEo\,ka}+\mathrm{cAo}\,(\mathrm{ka}+\mathrm{kd}))\,t)}\,(\mathrm{ka}+\mathrm{kd})}{\mathrm{cEo\,ka}+\mathrm{cAo}\,(\mathrm{ka}+\mathrm{kd})}\right]}{(\mathrm{ka}+\mathrm{kd})^2}$$

In[∘]:=
```
cEn2 = Simplify[
  DSolve[{-cAo cEo ka + (-cAo ka - cEo ka - cAo kd) (cE[t] - cEo) - ka (cE[t] - cEo)^2 == cE'[t],
    cE[0] == cEo}, cE[t], t], ka > 0 && kd > 0 && cAo > 0 && cEo > 0]
```

Solve: Inverse functions are being used by Solve, so some solutions may not be found; use Reduce for complete solution information.

Out[∘]=
$$\left\{\left\{cE[t] \to \frac{1}{2\,ka}\left(cEo\,ka - cAo\,(ka+kd) + \sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}\right.\right.\right.$$
$$\mathrm{Tanh}\left[\frac{1}{2}\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}\;t + \right.$$
$$\left.\left.\left.\left.\mathrm{ArcTanh}\left[\frac{cEo\,ka + cAo\,(ka+kd)}{\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}}\right]\right]\right)\right\}\right\}$$

In[∘]:=
$$\mathbf{cAn2 = Simplify\left[cA[t] == cAo + \frac{(ka-kd)\,(-cEo + cE[t])}{ka+kd} + \right.}$$
$$\mathbf{\frac{-2\,cEo\,ka\,kd\,Log[cEo\,ka] + 2\,cEo\,ka\,kd\,Log[-cEo\,kd + (ka+kd)\,cE[t]]}{(ka+kd)^2}\;/.}$$
$$\mathbf{cE[t] \to \frac{1}{2\,ka}\left(cEo\,ka - cAo\,(ka+kd) + \sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}\right.}$$
$$\mathbf{\mathrm{Tanh}\left[\frac{1}{2}\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}\;t + \right.}$$
$$\mathbf{\left.\left.\mathrm{ArcTanh}\left[\frac{cEo\,ka + cAo\,(ka+kd)}{\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}}\right]\right]\right),}$$
$$\mathbf{\left. ka > 0\;\&\&\;kd > 0\;\&\&\;cAo > 0\;\&\&\;cEo > 0\right]}$$

Out[∘]=
$$cA[t] == cAo +$$
$$\frac{1}{(ka+kd)^2}\,2\,cEo\,ka\,kd\left(-Log[cEo\,ka] + Log\left[-cEo\,kd + \frac{1}{2\,ka}\,(ka+kd)\left(cEo\,ka - cAo\,(ka+kd) + \right.\right.\right.$$
$$\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}\;\mathrm{Tanh}\left[\right.$$
$$\frac{1}{2}\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}\;t + \mathrm{ArcTanh}\left[\right.$$
$$\left.\left.\left.\left.\left.\left.\frac{cEo\,ka + cAo\,(ka+kd)}{\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}}\right]\right]\right)\right]\right) - \frac{1}{2\,ka\,(ka+kd)}$$
$$(ka-kd)\left(cEo\,ka + cAo\,(ka+kd) - \sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}\right.$$
$$\mathrm{Tanh}\left[\frac{1}{2}\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}\;t + \right.$$
$$\left.\left.\mathrm{ArcTanh}\left[\frac{cEo\,ka + cAo\,(ka+kd)}{\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}}\right]\right]\right)$$

In[◦]:= **cEn1D = D[cE[t] == $\frac{\text{cEo} \left(\text{cEo ka} + \text{cAo} \left(e^{-((\text{cEo ka}+\text{cAo (ka+kd)}) t)} \text{ ka} + \text{kd}\right)\right)}{\text{cEo ka} + \text{cAo (ka + kd)}}$, t]**

Out[◦]= $\text{cE}'[t] == \frac{\text{cAo cEo } e^{-((\text{cEo ka}+\text{cAo (ka+kd)}) t)} \text{ ka } (-\text{cEo ka} - \text{cAo (ka + kd)})}{\text{cEo ka} + \text{cAo (ka + kd)}}$

In[◦]:= **cAn1D = D[cA[t] == cAo + $\frac{\text{cEo (ka} - \text{kd)} \left(-1 + \frac{\text{cEo ka}+\text{cAo} \left(e^{-((\text{cEo ka}+\text{cAo (ka+kd)}) t)} \text{ ka+kd}\right)}{\text{cEo ka+cAo (ka+kd)}}\right)}{\text{ka} + \text{kd}}$ + $\frac{2 \text{ cEo ka kd Log}\left[\frac{\text{cEo ka+cAo } e^{-((\text{cEo ka+cAo (ka+kd)}) t)} \text{ (ka+kd)}}{\text{cEo ka+cAo (ka+kd)}}\right]}{(\text{ka} + \text{kd})^2}$, t]**

Out[◦]= $\text{cA}'[t] == \frac{\text{cAo cEo } e^{-((\text{cEo ka}+\text{cAo (ka+kd)}) t)} \text{ ka (ka} - \text{kd) } (-\text{cEo ka} - \text{cAo (ka + kd)})}{(\text{ka} + \text{kd}) (\text{cEo ka} + \text{cAo (ka + kd)})} + \frac{2 \text{ cAo cEo } e^{-((\text{cEo ka}+\text{cAo (ka+kd)}) t)} \text{ ka kd } (-\text{cEo ka} - \text{cAo (ka + kd)})}{(\text{ka} + \text{kd}) \left(\text{cEo ka} + \text{cAo } e^{-((\text{cEo ka}+\text{cAo (ka+kd)}) t)} \text{ (ka + kd)}\right)}$

In[◦]:= **cEn2D =**

D[cE[t] == $\frac{1}{2 \text{ ka}} \left(\text{cEo ka} - \text{cAo (ka + kd)} + \sqrt{\text{cEo}^2 \text{ ka}^2 + 2 \text{ cAo cEo ka } (-\text{ka} + \text{kd}) + \text{cAo}^2 (\text{ka} + \text{kd})^2} \right.$ $\text{Tanh}\left[\frac{1}{2} \sqrt{\text{cEo}^2 \text{ ka}^2 + 2 \text{ cAo cEo ka } (-\text{ka} + \text{kd}) + \text{cAo}^2 (\text{ka} + \text{kd})^2} \text{ t} + \right.$ $\left.\left.\text{ArcTanh}\left[\frac{\text{cEo ka} + \text{cAo (ka + kd)}}{\sqrt{\text{cEo}^2 \text{ ka}^2 + 2 \text{ cAo cEo ka } (-\text{ka} + \text{kd}) + \text{cAo}^2 (\text{ka} + \text{kd})^2}}\right]\right]\right)$, t]

Out[◦]= $\text{cE}'[t] == \frac{1}{4 \text{ ka}} \left(\text{cEo}^2 \text{ ka}^2 + 2 \text{ cAo cEo ka } (-\text{ka} + \text{kd}) + \text{cAo}^2 (\text{ka} + \text{kd})^2\right)$ $\text{Sech}\left[\frac{1}{2} \sqrt{\text{cEo}^2 \text{ ka}^2 + 2 \text{ cAo cEo ka } (-\text{ka} + \text{kd}) + \text{cAo}^2 (\text{ka} + \text{kd})^2} \text{ t} + \right.$ $\left.\text{ArcTanh}\left[\frac{\text{cEo ka} + \text{cAo (ka + kd)}}{\sqrt{\text{cEo}^2 \text{ ka}^2 + 2 \text{ cAo cEo ka } (-\text{ka} + \text{kd}) + \text{cAo}^2 (\text{ka} + \text{kd})^2}}\right]\right]^2$

In[∘]:= **cAn2D =**

$$D\left[cA[t] == cAo + \frac{1}{(ka+kd)^2} 2\, cEo\, ka\, kd \left(-Log[cEo\, ka] + Log\left[-cEo\, kd + \frac{1}{2\, ka} (ka+kd) \left(cEo\, ka - cAo\, (ka+kd) + \sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2}\; Tanh\left[\frac{1}{2} \sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2}\; t + ArcTanh\left[\frac{cEo\, ka + cAo\, (ka+kd)}{\sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2}}\right]\right]\right)\right]\right) - \frac{1}{2\, ka\, (ka+kd)} (ka-kd) \left(cEo\, ka + cAo\, (ka+kd) - \sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2}\; Tanh\left[\frac{1}{2} \sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2}\; t + ArcTanh\left[\frac{cEo\, ka + cAo\, (ka+kd)}{\sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2}}\right]\right]\right), t\right]$$

Out[∘]=

$$cA'[t] == \frac{1}{4\, ka\, (ka+kd)} (ka-kd) \left(cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2\right) Sech\left[\frac{1}{2} \sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2}\; t + ArcTanh\left[\frac{cEo\, ka + cAo\, (ka+kd)}{\sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2}}\right]\right]^2 + \left(cEo\, kd \left(cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2\right) Sech\left[\frac{1}{2} \sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2}\; t + ArcTanh\left[\frac{cEo\, ka + cAo\, (ka+kd)}{\sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2}}\right]\right]^2\right) \Big/ \left(2\, (ka+kd) \left(-cEo\, kd + \frac{1}{2\, ka} (ka+kd) \left(cEo\, ka - cAo\, (ka+kd) + \sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2}\; Tanh\left[\frac{1}{2} \sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2}\; t + ArcTanh\left[\frac{cEo\, ka + cAo\, (ka+kd)}{\sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\, (-ka+kd) + cAo^2 (ka+kd)^2}}\right]\right]\right)\right)\right)$$

2. Steady-state approximation

In[•]:=
```
-cA'[t] == ka*cA[t]*cE[t] + kd*cA[t]*cF[t] /. cF[t] → cEo - cE[t]
-cE'[t] == ka*cA[t]*cE[t] - kd*cA[t]*cF[t] /. cF[t] → cEo - cE[t]
-cF'[t] == cE'[t]
```

Out[•]= $-cA'[t] == kd\,cA[t]\,(cEo - cE[t]) + ka\,cA[t] \times cE[t]$

Out[•]= $-cE'[t] == -kd\,cA[t]\,(cEo - cE[t]) + ka\,cA[t] \times cE[t]$

Out[•]= $-cF'[t] == cE'[t]$

In[•]:=
```
Solve[-cE'[t] == -kd cA[t] (cEo - cE[t]) + ka cA[t] × cE[t] /. cE'[t] → 0, cE[t]]
```

Out[•]= $\left\{\left\{cE[t] \to \frac{cEo\,kd}{ka + kd}\right\}\right\}$

In[•]:= $D\left[DSolve\left[\left\{-cA'[t] == kd\,cA[t]\,(cEo - cE[t]) + ka\,cA[t] \times cE[t] \;/.\; cE[t] \to \frac{cEo\,kd}{ka + kd},\; cA[0] == cAo\right\}, cA[t], t\right], t\right]$

Out[•]= $\left\{\left\{cA'[t] \to -\frac{2\,cAo\,cEo\,e^{-\frac{2\,cEo\,ka\,kd\,t}{ka+kd}}\,ka\,kd}{ka + kd}\right\}\right\}$

In[1]:=
```
Manipulate[
 Module[{PingPongModel1, soln, eqAns, eqAn2, eqAss, eqEns, eqEn2, eqEss, plot1},
  PingPongModel1 = Sequence[
    PlotRange → Full,
    PlotLabel →
     Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation (kc → ∞ and kf → ∞):
A + E ⟶ P + F
A + F ⟶ Q + E", FontSize → 14],
    Frame → True,
    FrameLabel → {"Time, s", "d[ ]/dt, mol m^-3 s^-1"},
    LabelStyle → {FontSize → 14},
    ImageSize → 1.2 {480, 310}];
  soln = NDSolve[{-cA'[t] == ka*cA[t]*cE[t] + kd*cA[t]*cF[t],
     -cE'[t] == ka*cA[t]*cE[t] - kd*cA[t]*cF[t],
     cF'[t] == ka*cA[t]*cE[t] - kd*cA[t]*cF[t], cP'[t] == ka*cA[t]*cE[t],
     cQ'[t] == kd*cA[t]*cF[t], cA[0] == cAo, cE[0] == cEo, cF[0] == cFo,
     cP[0] == cPo, cQ[0] == cQo}, {cA, cE, cF, cP, cQ}, {t, 0.0, 250}];
  eqAns = -cA'[t] /. soln;
```

$$eqAn2 = -\left(\frac{1}{4\,ka\,(ka + kd)}\,(ka - kd)\,\left(cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka + kd) + cAo^2\,(ka + kd)^2\right)\right.$$
$$Sech\left[\frac{1}{2}\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka + kd) + cAo^2\,(ka + kd)^2}\;t +\right.$$
$$\left.ArcTanh\left[\frac{cEo\,ka + cAo\,(ka + kd)}{\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka + kd) + cAo^2\,(ka + kd)^2}}\right]\right]^2 +$$
$$\left(cEo\,ka\,kd\,\left(cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka + kd) + cAo^2\,(ka + kd)^2\right)\right.$$

$$\mathrm{Sech}\left[\frac{1}{2}\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}\;t + \mathrm{ArcTanh}\left[\frac{cEo\,ka + cAo\,(ka+kd)}{\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}}\right]\right]^2\Bigg)\Bigg/$$

$$\Bigg((ka+kd)\Bigg(cEo\,ka\,(ka-kd) - cAo\,(ka+kd)^2 + (ka+kd)\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}\;\mathrm{Tanh}\left[\frac{1}{2}\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}\;t + \mathrm{ArcTanh}\left[\frac{cEo\,ka + cAo\,(ka+kd)}{\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}}\right]\right]\Bigg)\Bigg);$$

$$eqAss = \frac{2\,cAo\,cEo\,e^{-\frac{2\,cEo\,ka\,kd\,t}{ka+kd}}\,ka\,kd}{ka+kd};$$

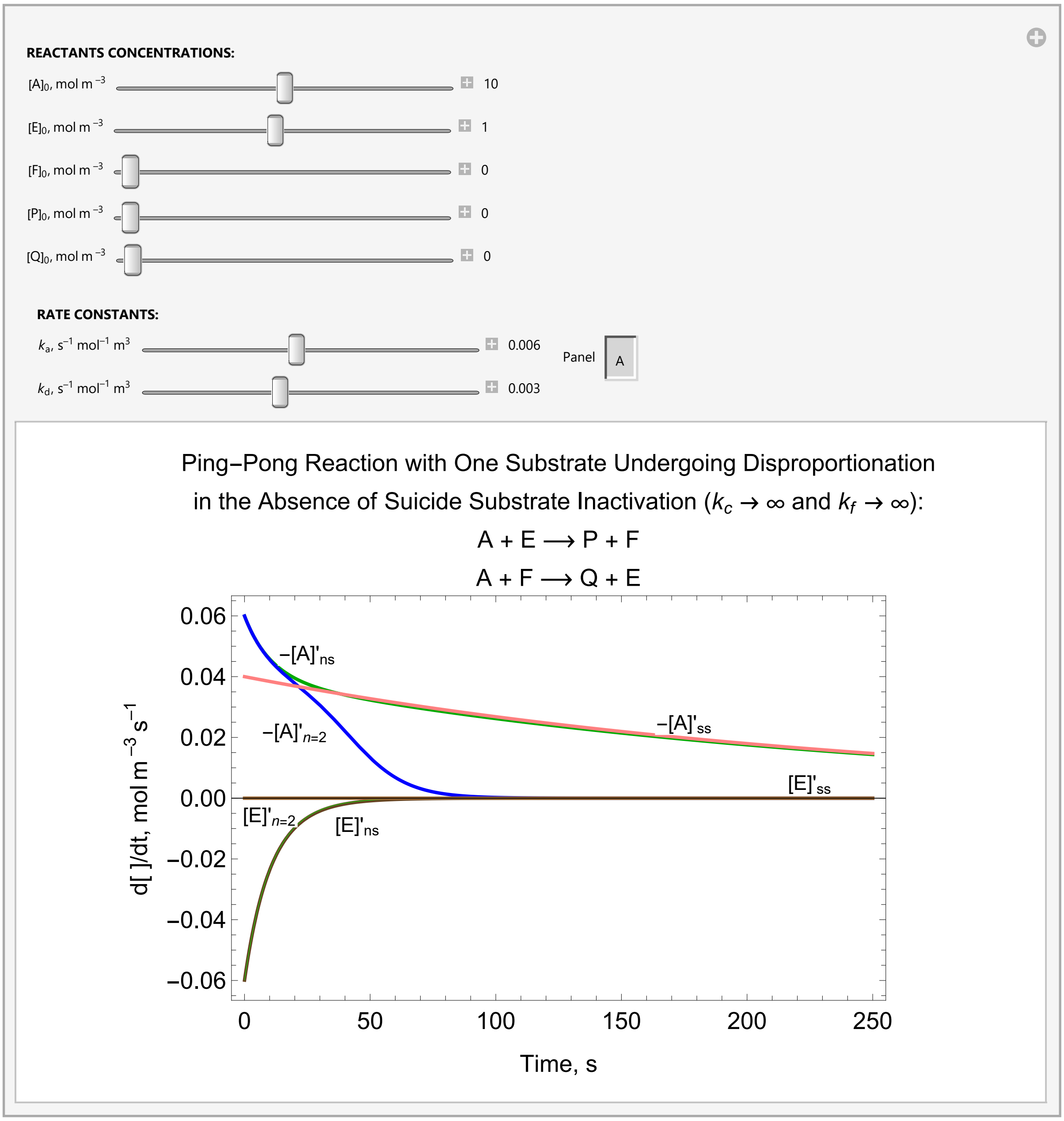
```
eqEns = cE'[t] /. soln;
```

$$eqEn2 = \frac{1}{4\,ka}\left(cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2\right)\mathrm{Sech}\left[\frac{1}{2}\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}\;t + \mathrm{ArcTanh}\left[\frac{cEo\,ka + cAo\,(ka+kd)}{\sqrt{cEo^2\,ka^2 + 2\,cAo\,cEo\,ka\,(-ka+kd) + cAo^2\,(ka+kd)^2}}\right]\right]^2;$$

```
eqEss = 0;
plot1 = Plot[{eqAns, eqAn2, eqAss, eqEns, eqEn2, eqEss}, {t, 0.02, 250},
  Evaluate@PingPongModel1,
  PlotStyle → {{Thick, Darker[Green]}, {Thick, Blue},
    {Thick, Pink}, {Thick, Darker[Brown]}, {Thin, Green}, {Thick, Brown}},
  Epilog → {Inset[Style["-[A]'ns", 12, Background → White],
      {25, 0.01 - cA'[25] /. soln[[1]]}],
    Inset[Style["-[A]'n=2", 12, Background → White], {20, eqAn2 /. t → 40}],
    Inset[Style["-[A]'ss", 12, Background → White], {175, 0.005 + eqAss /. t → 175}],
    Inset[Style["[E]'ns", 12, Background → White],
      {45, -0.01 - cE'[45] /. soln[[1]]}],
    Inset[Style["[E]'n=2", 12, Background → White], {10, 0.004 + eqEn2 /. t → 20}],
    Inset[Style["[E]'ss", 12, Background → White], {225, 0.005 + eqEss /. t → 225}]}];
Pane[
 Switch[PingPong,
  1, Show[plot1]
 ], ImageSize → 1.2 {480, 310}]],
Row[{
  Column[{

    Style["REACTANTS CONCENTRATIONS:", Bold],
    Control@{{cAo, 10, "[A]0, mol m^-3"}, 0.1, 20, Appearance → "Labeled"},
    Control@{{cEo, 1, "[E]0, mol m^-3"}, 0.1, 2, Appearance → "Labeled"},
    Control@{{cFo, 0, "[F]0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
```

```
      Control@{{cPo, 0, "[P]₀, mol m⁻³"}, 0, 0, Appearance → "Labeled"},
      Control@{{cQo, 0, "[Q]₀, mol m⁻³"}, 0, 0, Appearance → "Labeled"}
    }],
   Column[{

      Style["RATE CONSTANTS:", Bold],
      Control@{{ka, 0.006, "ka, s⁻¹ mol⁻¹ m³"}, 0.001, 0.012, Appearance → "Labeled"},
      Control@{{kd, 0.003, "kd, s⁻¹ mol⁻¹ m³"}, 0.001, 0.006, Appearance → "Labeled"}
    }],
   Control@{{PingPong, 1, "Panel"}, {
      1 → "A"
     }, ControlType → Setter}}]
]
```

Out[1]=



Ping-Pong Reaction with One Substrate Undergoing Disproportionation in the Presence of Suicide Substrate Inactivation

$A + E \xrightarrow{k_a} F + P$

$A + F \xrightarrow{k_d} E + Q$

$A + E\ (\text{or } F) \xrightarrow{k_i} I$

$k_c \to \infty$ and $k_f \to \infty$

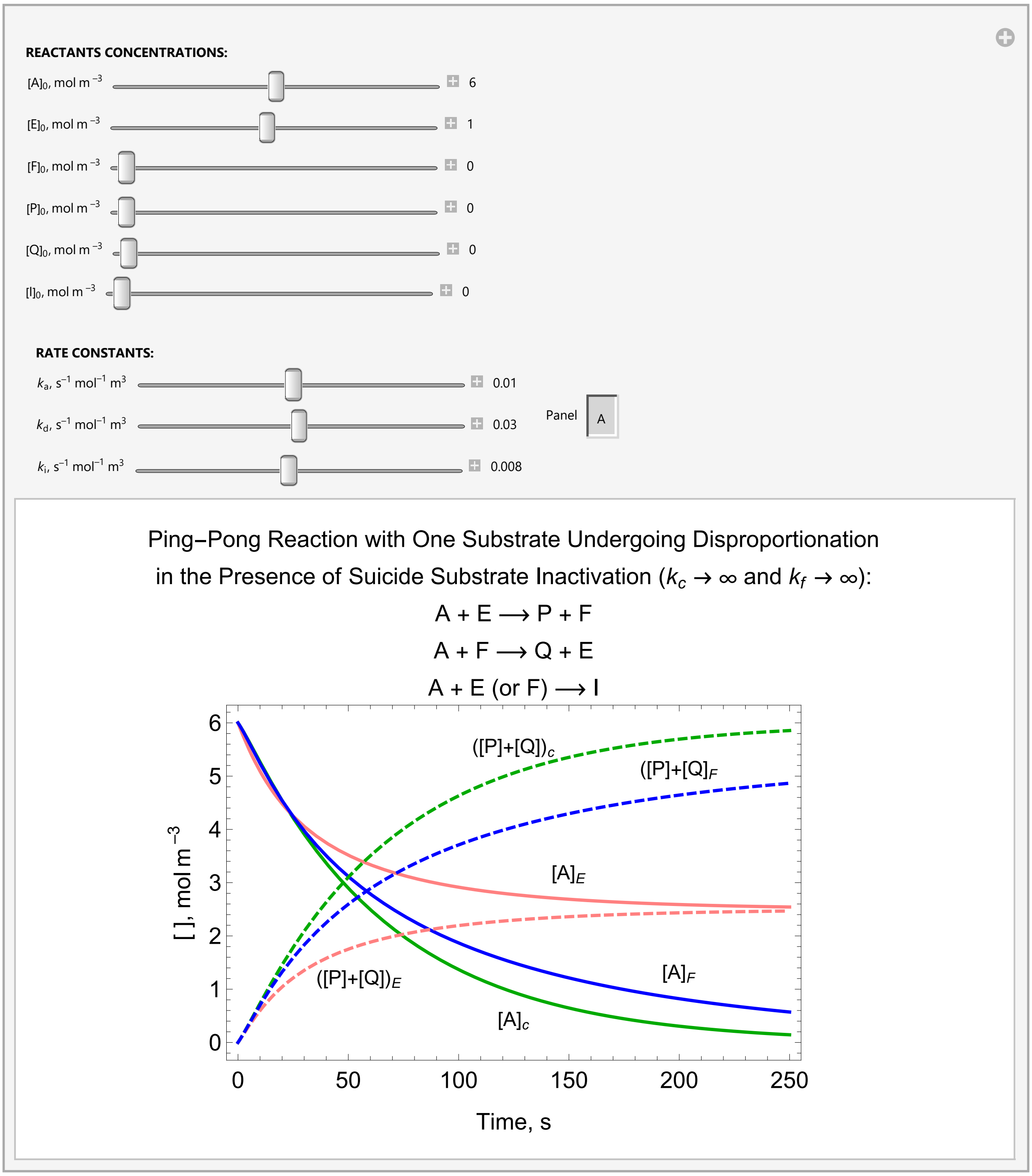
Figure 5 (Mathematics-1964681). Representative numerically integrated solutions of the time-dependent variation of the concentration for the substrate A undergoing disproportionation and the sum of products P and Q of an enzyme-catalyzed ping-pong reaction in which suicide substrate inactivation by A occurs when the enzyme is in the active state E (subscript E) or F (subscript F).

```
In[2]:= Manipulate[Module[{PingPongModel1, soln, solne, solnf, plot1},
  PingPongModel1 = Sequence[
    PlotRange → Full,
    PlotLabel →
     Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Presence of Suicide Substrate Inactivation (kc → ∞ and kf → ∞):
A + E ⟶ P + F
A + F ⟶ Q + E
A + E (or F) ⟶ I", FontSize → 14],
    Frame → True,
    FrameLabel → {"Time, s", "[ ], mol m^-3"},
    LabelStyle → {FontSize → 14},
    ImageSize → 1.2 {480, 310}];
  soln = NDSolve[{-cA'[t] == ka * cA[t] * cE[t] + kd * cA[t] * cF[t],
     -cE'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t],
     cF'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t],
     cP'[t] == ka * cA[t] * cE[t],
     cQ'[t] == kd * cA[t] * cF[t],
     cA[0] == cAo, cE[0] == cEo, cF[0] == cFo, cP[0] == cPo, cQ[0] == cQo},
    {cA, cE, cF, cP, cQ}, {t, 0.0, 250}];
  solne = NDSolve[{-cA'[t] == (ka + ki) * cA[t] * cE[t] + kd * cA[t] * cF[t],
     -cE'[t] == (ka + ki) * cA[t] * cE[t] - kd * cA[t] * cF[t],
     cF'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t],
     cP'[t] == ka * cA[t] * cE[t],
     cQ'[t] == kd * cA[t] * cF[t],
     cI'[t] == ki * cA[t] * cE[t],
```

```
    cA[0] == cAo, cE[0] == cEo, cF[0] == cFo, cI[0] == cIo, cP[0] == cPo, cQ[0] == cQo},
   {cA, cE, cF, cP, cQ, cI}, {t, 0.0, 250}];
 solnf = NDSolve[{-cA'[t] == ka * cA[t] * cE[t] + (kd + ki) * cA[t] * cF[t],
    -cE'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t],
    cF'[t] == ka * cA[t] * cE[t] - (kd + ki) * cA[t] * cF[t],
    cP'[t] == ka * cA[t] * cE[t],
    cQ'[t] == kd * cA[t] * cF[t],
    cI'[t] == ki * cA[t] * cF[t],
    cA[0] == cAo, cE[0] == cEo, cF[0] == cFo, cI[0] == cIo, cP[0] == cPo, cQ[0] == cQo},
   {cA, cE, cF, cP, cQ, cI}, {t, 0.0, 250}];

 plot1 = Plot[{cA[t] /. soln,
    cA[t] /. solne,
    cA[t] /. solnf,
    cP[t] + cQ[t] /. soln,
    cP[t] + cQ[t] /. solne,
    cP[t] + cQ[t] /. solnf}, {t, 0.0, 250},
   Evaluate@PingPongModel1,
   PlotStyle → {{Thick, Darker[Green]}, {Thick, Pink}, {Thick, Blue},
     {Thick, Darker[Green], Dashed}, {Thick, Pink, Dashed}, {Thick, Blue, Dashed}},
   Epilog → {Inset[Style["[A]_c", 12, Background → White],
      {125, -0.5 + cA[125] /. soln[[1]]}],
     Inset[Style["[A]_E", 12, Background → White], {150, 0.5 + cA[150] /. solne[[1]]}],
     Inset[Style["[A]_F", 12, Background → White], {200, 0.5 + cA[200] /. solnf[[1]]}],
     Inset[Style["([P]+[Q])_c", 12, Background → White],
      {125, 0.5 + cP[125] + cQ[125] /. soln[[1]]}],
     Inset[Style["([P]+[Q])_E", 12, Background → White],
      {55, -0.6 + cP[55] + cQ[55] /. solne[[1]]}], Inset[Style["([P]+[Q]_F",
       12, Background → White], {200, 0.5 + cP[200] + cQ[200] /. solnf[[1]]}]
    }];
 Pane[
  Switch[PingPong,
   1, Show[plot1]
  ], ImageSize → 1.2 {480, 310}]],
Row[{
  Column[{

    Style["REACTANTS CONCENTRATIONS:", Bold],
    Control@{{cAo, 6, "[A]_0, mol m^-3"}, 0.1, 12, Appearance → "Labeled"},
    Control@{{cEo, 1, "[E]_0, mol m^-3"}, 0.1, 2, Appearance → "Labeled"},
    Control@{{cFo, 0, "[F]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
    Control@{{cPo, 0, "[P]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
    Control@{{cQo, 0, "[Q]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
    Control@{{cIo, 0, "[I]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"}
   }],
  Column[{

    Style["RATE CONSTANTS:", Bold],
    Control@{{ka, 0.01, "k_a, s^-1 mol^-1 m^3"}, 0.001, 0.02, Appearance → "Labeled"},
    Control@{{kd, 0.03, "k_d, s^-1 mol^-1 m^3"}, 0.001, 0.06, Appearance → "Labeled"},
    Control@{{ki, 0.008, "k_i, s^-1 mol^-1 m^3"}, 0.001, 0.016, Appearance → "Labeled"}
```

```
    }],
   Control@{{PingPong, 1, "Panel"}, {
      1 → "A"
     }, ControlType → Setter}}]
]
```

Out[2]=



Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Presence of Suicide Substrate Inactivation

$$A + E \xrightarrow{k_a} F + P$$

$$A + F \xrightarrow{k_d} E + Q$$

$$A + E \xrightarrow{k_i} I$$

$k_c \to \infty$, $k_f \to \infty$, [A] remains constant and inactivates E.

Figure 6A&C (Mathematics-1964681). Representative approximate analytically integrated solutions of the time-dependent variation of the concentration for (A) the products P and Q and (C) the two active enzyme states E and F, together with the inactivate state I, of a ping-pong reaction under non-steady-state conditions, in which the suicide substrate A undergoes disproportionation and inactivates (A, C) E , while its concentration remains constant

```
In[•]:= -cA'[t] == (ka + ki) cA[t] × cE[t] + kd cA[t] × cF[t] /. cA[t] → cAo
        -cF'[t] == -ka cA[t] × cE[t] + kd cA[t] × cF[t] /. cA[t] → cAo
        -cE'[t] == (ka + ki) cA[t] × cE[t] - kd cA[t] × cF[t] /. cA[t] → cAo
        cP'[t] == ka * cA[t] * cE[t] /. cA[t] → cAo
        cQ'[t] == kd * cA[t] * cF[t] /. cA[t] → cAo
        cI'[t] == ki * cA[t] * cE[t] /. cA[t] → cAo
Out[•]= -cA'[t] == cAo (ka + ki) cE[t] + cAo kd cF[t]
Out[•]= -cF'[t] == -cAo ka cE[t] + cAo kd cF[t]
Out[•]= -cE'[t] == cAo (ka + ki) cE[t] - cAo kd cF[t]
Out[•]= cP'[t] == cAo ka cE[t]
Out[•]= cQ'[t] == cAo kd cF[t]
Out[•]= cI'[t] == cAo ki cE[t]
```

In[•]:=
$$\mathbf{Simplify}\Big[\mathbf{DSolve}[\{-cF'[t] == -cAo\,ka\,cE[t] + cAo\,kd\,cF[t],\ -cE'[t] == cAo\,(ka+ki)\,cE[t] - cAo\,kd\,cF[t],\ cE[0] == cEo,\ cF[0] == 0\},\ \{cE[t], cF[t]\},\ t],\ ka > 0\ \&\&\ kd > 0\ \&\&\ ki > 0\ \&\&\ cAo > 0\ \&\&\ cEo > 0\ \&\&\ \sqrt{-4\,kd\,ki + (ka+kd+ki)^2} > 0\Big]$$

Out[•]=
$$\Big\{\Big\{cE[t] \to \frac{1}{2\sqrt{-4\,kd\,ki + (ka+kd+ki)^2}}\, cEo\, e^{-\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\right) t} \Big(ka - e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\,ka - kd + e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\,kd + ki - e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\,ki + \sqrt{-4\,kd\,ki + (ka+kd+ki)^2} + e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\sqrt{-4\,kd\,ki + (ka+kd+ki)^2}\Big),$$
$$cF[t] \to \frac{cEo\, e^{-\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\right) t}\left(-1 + e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\right) ka}{\sqrt{-4\,kd\,ki + (ka+kd+ki)^2}}\Big\}\Big\}$$

In[•]:=
$$\mathbf{Factor}\Big[\mathbf{DSolve}\Big[\Big\{cP'[t] == cAo\,ka\,cE[t]\ /.\ cE[t] \to \frac{1}{2\sqrt{-4\,kd\,ki + (ka+kd+ki)^2}}\, cEo\, e^{-\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\right) t} \Big(ka - e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\,ka - kd + e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\,kd + ki - e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\,ki + \sqrt{-4\,kd\,ki + (ka+kd+ki)^2} + e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\sqrt{-4\,kd\,ki + (ka+kd+ki)^2}\Big),\ cP[0] == 0\Big\},\ cP[t],\ t\Big]\Big]$$

Out[•]=
$$\Big\{\Big\{cP[t] \to \Big(cEo\, e^{-\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\right) t}\,ka\,\Big(ka - e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\,ka + kd - e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\,kd - ki + e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\,ki - \sqrt{-4\,kd\,ki + (ka+kd+ki)^2} - e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\sqrt{-4\,kd\,ki + (ka+kd+ki)^2} + 2\,e^{\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\right) t}\sqrt{-4\,kd\,ki + (ka+kd+ki)^2}\Big)\Big) \Big/ \Big(2\,ki\,\sqrt{-4\,kd\,ki + (ka+kd+ki)^2}\Big)\Big\}\Big\}$$

In[•]:=
$$\mathbf{Simplify}\Big[\mathbf{Limit}\Big[\Big(cEo\, e^{-\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\right) t}\,ka\,\Big(ka - e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\,ka + kd - e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\,kd - ki + e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\,ki - \sqrt{-4\,kd\,ki + (ka+kd+ki)^2} - e^{cAo\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\,t}\sqrt{-4\,kd\,ki + (ka+kd+ki)^2} + 2\,e^{\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\,kd\,ki+(ka+kd+ki)^2}\right) t}\sqrt{-4\,kd\,ki + (ka+kd+ki)^2}\Big)\Big) \Big/ \Big(2\,ki\,\sqrt{-4\,kd\,ki + (ka+kd+ki)^2}\Big),\ t \to \mathrm{Infinity}\Big],\ ka > 0\ \&\&\ kd > 0\ \&\&\ ki > 0\ \&\&\ cAo > 0\ \&\&\ cEo > 0\Big]$$

Out[•]=
$$\frac{cEo\,ka}{ki}$$

In[∘]:=
$$\mathrm{Simplify}\Big[\mathrm{Factor}\Big[\mathrm{DSolve}\Big[\Big\{\mathrm{cQ}'[t] == \mathrm{cAo}\,\mathrm{kd}\,\mathrm{cF}[t]\ /.\ \mathrm{cF}[t] \rightarrow \frac{\mathrm{cEo}\, e^{-\frac{1}{2}\mathrm{cAo}\left(\mathrm{ka}+\mathrm{kd}+\mathrm{ki}+\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\right)t}\left(-1+e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\right)\mathrm{ka}}{\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}},\ \mathrm{cQ}[0] == 0\Big\},\ \mathrm{cQ}[t],\ t\Big]\Big]\Big]$$

Out[∘]=
$$\Big\{\Big\{\mathrm{cQ}[t] \rightarrow \Big(\mathrm{cEo}\, e^{-\frac{1}{2}\mathrm{cAo}\left(\mathrm{ka}+\mathrm{kd}+\mathrm{ki}+\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\right)t}\,\mathrm{ka}\Big(\mathrm{ka}-e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\,\mathrm{ka}+\mathrm{kd}-e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\,\mathrm{kd}+\mathrm{ki}-e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\,\mathrm{ki}-\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}-e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}+2\,e^{\frac{1}{2}\mathrm{cAo}\left(\mathrm{ka}+\mathrm{kd}+\mathrm{ki}+\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\right)t}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\Big)\Big)\Big/\Big(2\,\mathrm{ki}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\Big)\Big\}\Big\}$$

In[∘]:=
$$\mathrm{Simplify}\Big[\mathrm{Limit}\Big[\Big(\mathrm{cEo}\, e^{-\frac{1}{2}\mathrm{cAo}\left(\mathrm{ka}+\mathrm{kd}+\mathrm{ki}+\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\right)t}\,\mathrm{ka}\Big(\mathrm{ka}-e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\,\mathrm{ka}+\mathrm{kd}-e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\,\mathrm{kd}+\mathrm{ki}-e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\,\mathrm{ki}-\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}-e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}+2\,e^{\frac{1}{2}\mathrm{cAo}\left(\mathrm{ka}+\mathrm{kd}+\mathrm{ki}+\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\right)t}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\Big)\Big)\Big/\Big(2\,\mathrm{ki}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\Big),\ t\rightarrow \mathrm{Infinity}\Big],\ \mathrm{ka}>0\,\&\&\,\mathrm{kd}>0\,\&\&\,\mathrm{ki}>0\,\&\&\,\mathrm{cAo}>0\,\&\&\,\mathrm{cEo}>0\Big]$$

Out[∘]=
$$\frac{\mathrm{cEo}\,\mathrm{ka}}{\mathrm{ki}}$$

In[∘]:=
$$\mathrm{Factor}\Big[\mathrm{DSolve}\Big[\Big\{\mathrm{cI}'[t] == \mathrm{cAo}\,\mathrm{ki}\,\mathrm{cE}[t]\ /.\ \mathrm{cE}[t] \rightarrow \frac{1}{2\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}}\,\mathrm{cEo}\, e^{-\frac{1}{2}\mathrm{cAo}\left(\mathrm{ka}+\mathrm{kd}+\mathrm{ki}+\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\right)t}\Big(\mathrm{ka}-e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\,\mathrm{ka}-\mathrm{kd}+e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\,\mathrm{kd}+\mathrm{ki}-e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\,\mathrm{ki}+\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}+e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\Big),\ \mathrm{cI}[0] == 0\Big\},\ \mathrm{cI}[t],\ t\Big]\Big]$$

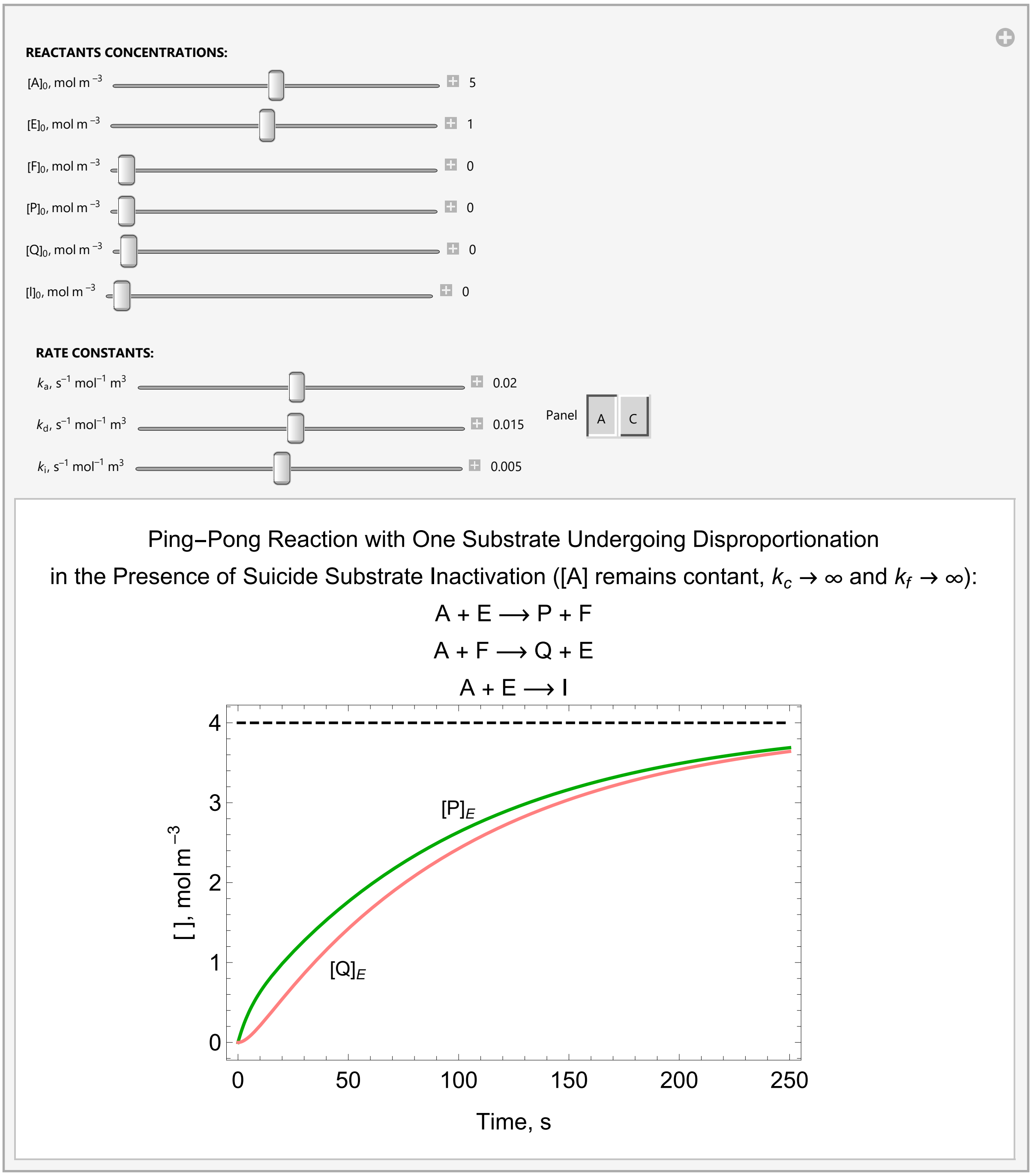
Out[∘]=
$$\Big\{\Big\{\mathrm{cI}[t] \rightarrow \frac{1}{2\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}}\,\mathrm{cEo}\, e^{-\frac{1}{2}\mathrm{cAo}\left(\mathrm{ka}+\mathrm{kd}+\mathrm{ki}+\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\right)t}\Big(\mathrm{ka}-e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\,\mathrm{ka}+\mathrm{kd}-e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\,\mathrm{kd}-\mathrm{ki}+e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\,\mathrm{ki}-\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}-e^{\mathrm{cAo}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\,t}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}+2\,e^{\frac{1}{2}\mathrm{cAo}\left(\mathrm{ka}+\mathrm{kd}+\mathrm{ki}+\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\right)t}\sqrt{-4\,\mathrm{kd}\,\mathrm{ki}+(\mathrm{ka}+\mathrm{kd}+\mathrm{ki})^2}\Big)\Big\}\Big\}$$

```
In[ ]:= Simplify[Limit[1/(2 Sqrt[-4 kd ki + (ka + kd + ki)^2]) cEo E^(-1/2 cAo (ka+kd+ki+ Sqrt[-4 kd ki+ (ka+kd+ki)^2]) t)
        (ka - E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t) ka + kd - E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t) kd - ki + E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t)
           ki - Sqrt[-4 kd ki + (ka + kd + ki)^2] - E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t) Sqrt[-4 kd ki + (ka + kd + ki)^2] +
          2 E^(1/2 cAo (ka+kd+ki+ Sqrt[-4 kd ki+ (ka+kd+ki)^2]) t) Sqrt[-4 kd ki + (ka + kd + ki)^2]),
      t → Infinity], ka > 0 && kd > 0 && ki > 0 && cAo > 0 && cEo > 0]

Out[ ]= cEo

In[3]:= Manipulate[Module[{PingPongModel1, eqPe, eqPeL,
         eqQe, eqQeL, eqEe, eqFe, eqIe, eqIeL, soln, plot1, plot2},
       PingPongModel1 = Sequence[
         PlotRange → Full,
         PlotLabel →
          Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Presence of Suicide Substrate Inactivation ([A]
             remains contant, kc → ∞ and kf → ∞):
A + E ⟶ P + F
A + F ⟶ Q + E
A + E ⟶ I", FontSize → 14],
         Frame → True,
         FrameLabel → {"Time, s", "[ ], mol m^-3"},
         LabelStyle → {FontSize → 14},
         ImageSize → 1.2 {480, 310}];
       eqPe = (cEo E^(-1/2 cAo (ka+kd+ki+ Sqrt[-4 kd ki+ (ka+kd+ki)^2]) t) ka
           (ka - E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t) ka + kd - E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t) kd - ki +
             E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t) ki - Sqrt[-4 kd ki + (ka + kd + ki)^2] - E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t)
              Sqrt[-4 kd ki + (ka + kd + ki)^2] + 2 E^(1/2 cAo (ka+kd+ki+ Sqrt[-4 kd ki+ (ka+kd+ki)^2]) t)
              Sqrt[-4 kd ki + (ka + kd + ki)^2])) / (2 ki Sqrt[-4 kd ki + (ka + kd + ki)^2]);
       eqPeL = Limit[eqPe, t → Infinity];
       eqQe = (cEo E^(-1/2 cAo (ka+kd+ki+ Sqrt[-4 kd ki+ (ka+kd+ki)^2]) t) ka
           (ka - E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t) ka + kd - E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t) kd + ki -
             E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t) ki - Sqrt[-4 kd ki + (ka + kd + ki)^2] - E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t)
              Sqrt[-4 kd ki + (ka + kd + ki)^2] + 2 E^(1/2 cAo (ka+kd+ki+ Sqrt[-4 kd ki+ (ka+kd+ki)^2]) t)
              Sqrt[-4 kd ki + (ka + kd + ki)^2])) / (2 ki Sqrt[-4 kd ki + (ka + kd + ki)^2]);
       eqQeL = Limit[eqQe, t → Infinity];
       eqIe = -1/(2 Sqrt[-4 kd ki + (ka + kd + ki)^2]) cEo
         E^(-1/2 cAo (ka+kd+ki+ Sqrt[-4 kd ki+ (ka+kd+ki)^2]) t) (-ka + E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t) ka -
           kd + E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t) kd + ki - E^(cAo Sqrt[-4 kd ki+ (ka+kd+ki)^2] t) ki +
```

```
    Sqrt[-4 kd ki + (ka + kd + ki)^2] + E^(cAo Sqrt[-4 kd ki+(ka+kd+ki)^2] t) Sqrt[-4 kd ki + (ka + kd + ki)^2] -
     2 E^(1/2 cAo (ka+kd+ki+Sqrt[-4 kd ki+(ka+kd+ki)^2]) t) Sqrt[-4 kd ki + (ka + kd + ki)^2]);
 eqIeL = Limit[eqIe, t → Infinity];
 eqEe = 1/(2 Sqrt[-4 kd ki + (ka + kd + ki)^2]) cEo E^(-1/2 cAo (ka+kd+ki+Sqrt[-4 kd ki+(ka+kd+ki)^2]) t)
   (ka - E^(cAo Sqrt[-4 kd ki+(ka+kd+ki)^2] t) ka - kd + E^(cAo Sqrt[-4 kd ki+(ka+kd+ki)^2] t) kd + ki - E^(cAo Sqrt[-4 kd ki+(ka+kd+ki)^2] t)
     ki + Sqrt[-4 kd ki + (ka + kd + ki)^2] + E^(cAo Sqrt[-4 kd ki+(ka+kd+ki)^2] t) Sqrt[-4 kd ki + (ka + kd + ki)^2]);
 eqFe = (cEo E^(-1/2 cAo (ka+kd+ki+Sqrt[-4 kd ki+(ka+kd+ki)^2]) t) (-1 + E^(cAo Sqrt[-4 kd ki+(ka+kd+ki)^2] t)) ka)/
   Sqrt[-4 kd ki + (ka + kd + ki)^2];
 plot1 = Plot[{eqPe, eqPeL; eqQe, eqQeL}, {t, 0.0, 250},
   Evaluate@PingPongModel1,
   PlotStyle → {{Thick, Darker[Green]}, {Thick, Pink}, {Black, Dashed}},
   Epilog → {Inset[Style["[P]_E", 12, Background → White], {100, 0.3 + eqPe /. t → 100}],
     Inset[Style["[Q]_E", 12, Background → White], {50, -0.5 + eqQe /. t → 50}]
    }];
 plot2 = Plot[{eqEe, eqFe, eqIe, eqIeL}, {t, 0, 250},
   Evaluate@PingPongModel1,
   PlotStyle →
    {{Thick, Blue}, {Thick, Brown}, {Thick, Green}, {Thick, Black, Dashed}},
   Epilog → {Inset[Style["[E]_E", 12, Background → White], {20, eqEe /. t → 3}],
     Inset[Style["[F]_E", 12, Background → White], {100, 0.1 + eqFe /. t → 100}],
     Inset[Style["[I]_E", 12, Background → White], {150, 0.08 + eqIe /. t → 150}]
    }];
 Pane[
  Switch[PingPong,
   1, Show[plot1],
   2, Show[plot2]
  ], ImageSize → 1.2 {480, 310}]],
Row[{
  Column[{

    Style["REACTANTS CONCENTRATIONS:", Bold],
    Control@{{cAo, 5, "[A]_0, mol m^-3"}, 0.1, 10, Appearance → "Labeled"},
    Control@{{cEo, 1, "[E]_0, mol m^-3"}, 0.1, 2, Appearance → "Labeled"},
    Control@{{cFo, 0, "[F]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
    Control@{{cPo, 0, "[P]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
    Control@{{cQo, 0, "[Q]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
    Control@{{cIo, 0, "[I]_0, mol m^-3"}, 0, 0, Appearance → "Labeled"}
   }],
  Column[{

    Style["RATE CONSTANTS:", Bold],
    Control@{{ka, 0.02, "k_a, s^-1 mol^-1 m^3"}, 0.001, 0.04, Appearance → "Labeled"},
    Control@{{kd, 0.015, "k_d, s^-1 mol^-1 m^3"}, 0.001, 0.03, Appearance → "Labeled"},
    Control@{{ki, 0.005, "k_i, s^-1 mol^-1 m^3"}, 0.001, 0.01, Appearance → "Labeled"}
```

```
    }],
   Control@{{PingPong, 1, "Panel"}, {
      1 → "A",
      2 → "C"
     }, ControlType → Setter}}]
]
```

Out[3]=



Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Presence of Suicide Substrate Inactivation

$$A + E \xrightarrow{k_a} F + P$$

$$A + F \xrightarrow{k_d} E + Q$$

$$A + F \xrightarrow{k_i} I$$

$k_c \to \infty$, $k_f \to \infty$, [A] remains constant and inactivates F.

Figure 6B&D (Mathematics-1964681). Representative approximate analytically integrated solutions of the time-dependent variation of the concentration for (B) the products P and Q and (D) the two active enzyme states E and F, together with the inactivate state I, of a ping-pong reaction under non-steady-state conditions, in which the suicide substrate A undergoes disproportionation and inactivates (B, D) F, while its concentration remains constant

```
In[•]:= -cA'[t] == ka cA[t] × cE[t] + (kd + ki) cA[t] × cF[t] /. cA[t] → cAo
        -cF'[t] == -ka cA[t] × cE[t] + (kd + ki) cA[t] × cF[t] /. cA[t] → cAo
        -cE'[t] == ka cA[t] × cE[t] - kd cA[t] × cF[t] /. cA[t] → cAo
        cP'[t] == ka * cA[t] * cE[t] /. cA[t] → cAo
        cQ'[t] == kd * cA[t] * cF[t] /. cA[t] → cAo
        cI'[t] == ki * cA[t] * cF[t] /. cA[t] → cAo

Out[•]= -cA'[t] == cAo ka cE[t] + cAo (kd + ki) cF[t]

Out[•]= -cF'[t] == -cAo ka cE[t] + cAo (kd + ki) cF[t]

Out[•]= -cE'[t] == cAo ka cE[t] - cAo kd cF[t]

Out[•]= cP'[t] == cAo ka cE[t]

Out[•]= cQ'[t] == cAo kd cF[t]

Out[•]= cI'[t] == cAo ki cF[t]
```

In[•]:=
```
Simplify[DSolve[{-cF'[t] == -cAo ka cE[t] + cAo (kd + ki) cF[t],
    -cE'[t] == cAo ka cE[t] - cAo kd cF[t], cE[0] == cEo, cF[0] == 0}, {cE[t], cF[t]}, t],
  ka > 0 && kd > 0 && ki > 0 && cAo > 0 && cEo > 0 && Sqrt[-4 ka ki + (ka + kd + ki)^2] > 0]
```

Out[•]=

$$\left\{\left\{cE[t] \to \frac{1}{2\sqrt{-4\,ka\,ki + (ka+kd+ki)^2}}\, cEo\, e^{-\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\right) t} \left(ka - e^{cAo\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\, t}\, ka - kd + e^{cAo\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\, t}\, kd - ki + e^{cAo\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\, t}\, ki + \sqrt{-4\,ka\,ki + (ka+kd+ki)^2} + e^{cAo\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\, t} \sqrt{-4\,ka\,ki + (ka+kd+ki)^2}\right), cF[t] \to \frac{cEo\, e^{-\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\right) t} \left(-1 + e^{cAo\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\, t}\right) ka}{\sqrt{-4\,ka\,ki + (ka+kd+ki)^2}}\right\}\right\}$$

In[•]:=
```
Simplify[Factor[DSolve[{cP'[t] == cAo ka cE[t] /.
     cE[t] -> 1/(2 Sqrt[-4 ka ki + (ka + kd + ki)^2]) cEo E^(-1/2 cAo (ka+kd+ki+Sqrt[-4 ka ki+(ka+kd+ki)^2]) t)
      (ka - E^(cAo Sqrt[-4 ka ki+(ka+kd+ki)^2] t) ka - kd + E^(cAo Sqrt[-4 ka ki+(ka+kd+ki)^2] t) kd -
       ki + E^(cAo Sqrt[-4 ka ki+(ka+kd+ki)^2] t) ki + Sqrt[-4 ka ki + (ka + kd + ki)^2] +
       E^(cAo Sqrt[-4 ka ki+(ka+kd+ki)^2] t) Sqrt[-4 ka ki + (ka + kd + ki)^2]), cP[0] == 0}, cP[t], t]]]
```

Out[•]=

$$\left\{\left\{cP[t] \to -\left(\left(cEo\, e^{-\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{ka^2+2\,ka\,(kd-ki)+(kd+ki)^2}\right) t} \left(\left(-1 + e^{cAo\sqrt{ka^2+2\,ka\,(kd-ki)+(kd+ki)^2}\, t}\right) ka\,(kd-ki) + (kd+ki) \left(\left(-1 + e^{cAo\sqrt{ka^2+2\,ka\,(kd-ki)+(kd+ki)^2}\, t}\right) kd + \left(-1 + e^{cAo\sqrt{ka^2+2\,ka\,(kd-ki)+(kd+ki)^2}\, t}\right) ki + \left(1 + e^{cAo\sqrt{ka^2+2\,ka\,(kd-ki)+(kd+ki)^2}\, t} - 2\, e^{\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{ka^2+2\,ka\,(kd-ki)+(kd+ki)^2}\right) t}\right) \sqrt{ka^2 + 2\,ka\,(kd-ki) + (kd+ki)^2}\right)\right)\right) \Big/ \left(2\,ki\,\sqrt{ka^2+2\,ka\,(kd-ki)+(kd+ki)^2}\right)\right)\right\}\right\}$$

In[∘]:=
```
Simplify[Limit[-((cEo E^(-1/2 cAo (ka+kd+ki+Sqrt[ka^2+2 ka (kd-ki)+(kd+ki)^2]) t)
    ((-1 + E^(cAo Sqrt[ka^2+2 ka (kd-ki)+(kd+ki)^2] t)) ka (kd - ki) + (kd + ki)
      ((-1 + E^(cAo Sqrt[ka^2+2 ka (kd-ki)+(kd+ki)^2] t)) kd + (-1 + E^(cAo Sqrt[ka^2+2 ka (kd-ki)+(kd+ki)^2] t)) ki +
       (1 + E^(cAo Sqrt[ka^2+2 ka (kd-ki)+(kd+ki)^2] t) - 2 E^(1/2 cAo (ka+kd+ki+Sqrt[ka^2+2 ka (kd-ki)+(kd+ki)^2]) t))
        Sqrt[ka^2 + 2 ka (kd - ki) + (kd + ki)^2]))) /
    (2 ki Sqrt[ka^2 + 2 ka (kd - ki) + (kd + ki)^2])), t -> Infinity], ka >
  0 && kd > 0 && ki > 0 && cAo >
  0 && cEo >
  0]
```

Out[∘]=
$$\frac{cEo\,(kd+ki)}{ki}$$

In[∘]:=
```
Simplify[Factor[DSolve[{cQ'[t] == cAo kd cF[t] /.
    cF[t] -> (cEo E^(-1/2 cAo (ka+kd+ki+Sqrt[-4 ka ki+(ka+kd+ki)^2]) t) (-1 + E^(cAo Sqrt[-4 ka ki+(ka+kd+ki)^2] t)) ka) /
      Sqrt[-4 ka ki + (ka + kd + ki)^2],
   cQ[0] == 0}, cQ[t], t]]]
```

Out[∘]=
```
{{cQ[t] -> (cEo E^(-1/2 cAo (ka+kd+ki+Sqrt[-4 ka ki+(ka+kd+ki)^2]) t) kd (ka - E^(cAo Sqrt[-4 ka ki+(ka+kd+ki)^2] t) ka + kd -
      E^(cAo Sqrt[-4 ka ki+(ka+kd+ki)^2] t) kd + ki - E^(cAo Sqrt[-4 ka ki+(ka+kd+ki)^2] t) ki - Sqrt[-4 ka ki + (ka + kd + ki)^2] -
      E^(cAo Sqrt[-4 ka ki+(ka+kd+ki)^2] t) Sqrt[-4 ka ki + (ka + kd + ki)^2] + 2 E^(1/2 cAo (ka+kd+ki+Sqrt[-4 ka ki+(ka+kd+ki)^2]) t)
      Sqrt[-4 ka ki + (ka + kd + ki)^2])) / (2 ki Sqrt[-4 ka ki + (ka + kd + ki)^2])}}
```

In[∘]:=
```
Simplify[Limit[(cEo E^(-1/2 cAo (ka+kd+ki+Sqrt[-4 ka ki+(ka+kd+ki)^2]) t) kd (ka - E^(cAo Sqrt[-4 ka ki+(ka+kd+ki)^2] t) ka +
      kd - E^(cAo Sqrt[-4 ka ki+(ka+kd+ki)^2] t) kd + ki - E^(cAo Sqrt[-4 ka ki+(ka+kd+ki)^2] t) ki -
      Sqrt[-4 ka ki + (ka + kd + ki)^2] - E^(cAo Sqrt[-4 ka ki+(ka+kd+ki)^2] t) Sqrt[-4 ka ki + (ka + kd + ki)^2] +
      2 E^(1/2 cAo (ka+kd+ki+Sqrt[-4 ka ki+(ka+kd+ki)^2]) t) Sqrt[-4 ka ki + (ka + kd + ki)^2])) /
    (2 ki Sqrt[-4 ka ki + (ka + kd + ki)^2]), t -> Infinity],
  ka > 0 && kd > 0 && ki > 0 && cAo > 0 && cEo > 0]
```

Out[∘]=
$$\frac{cEo\,kd}{ki}$$

In[ ]:= Simplify[Factor[DSolve[{cI′[t] == cAo ki cF[t] /.

$$cF[t] \to \frac{cEo\, e^{-\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\right) t} \left(-1 + e^{cAo \sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\, t}\right) ka}{\sqrt{-4\, ka\, ki + (ka + kd + ki)^2}},$$

cI[0] == 0}, cI[t], t]]]

Out[ ]=

$$\left\{\left\{cI[t] \to \frac{1}{2 \sqrt{-4\, ka\, ki + (ka + kd + ki)^2}} cEo\, e^{-\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\right) t} \left(ka - e^{cAo \sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\, t} ka + kd - e^{cAo \sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\, t} kd + ki - e^{cAo \sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\, t} ki - \sqrt{-4\, ka\, ki + (ka + kd + ki)^2} - e^{cAo \sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\, t} \sqrt{-4\, ka\, ki + (ka + kd + ki)^2} + 2\, e^{\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\right) t} \sqrt{-4\, ka\, ki + (ka + kd + ki)^2}\right)\right\}\right\}$$

In[ ]:=

$$\text{Simplify}\left[\text{Limit}\left[\frac{1}{2 \sqrt{-4\, ka\, ki + (ka + kd + ki)^2}} cEo\, e^{-\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\right) t} \left(ka - e^{cAo \sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\, t} ka + kd - e^{cAo \sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\, t} kd + ki - e^{cAo \sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\, t} ki - \sqrt{-4\, ka\, ki + (ka + kd + ki)^2} - e^{cAo \sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\, t} \sqrt{-4\, ka\, ki + (ka + kd + ki)^2} + 2\, e^{\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{-4\, ka\, ki+(ka+kd+ki)^2}\right) t} \sqrt{-4\, ka\, ki + (ka + kd + ki)^2}\right),\right.\right.$$

t → Infinity], ka > 0 && kd > 0 && ki > 0 && cAo > 0 && cEo > 0]

Out[ ]= cEo

```
In[4]:= Manipulate[Module[{PingPongModel1, eqPf, eqPfL,
    eqQf, eqQfL, eqEf, eqFf, eqIf, eqIfL, soln, plot1, plot2},
   PingPongModel1 = Sequence[
     PlotRange → Full,
     PlotLabel →
      Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Presence of Suicide Substrate Inactivation (A
        remains contant, kc → ∞ and kf → ∞):
A + E ⟶ P + F
A + F ⟶ Q + E
A + F ⟶ I", FontSize → 14],
     Frame → True,
     FrameLabel → {"Time, s", "[ ], mol m^-3"},
     LabelStyle → {FontSize → 14},
     ImageSize → 1.2 {480, 310}];
```

$$eqPf = -\frac{1}{2\, ki \sqrt{ka^2 + 2\, ka\, (kd - ki) + (kd + ki)^2}} cEo\, e^{-\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{ka^2+2\, ka\, (kd-ki)+(kd+ki)^2}\right) t} \left(\left(-1 + e^{cAo \sqrt{ka^2+2\, ka\, (kd-ki)+(kd+ki)^2}\, t}\right) ka\, (kd - ki) + (kd + ki) \left(\left(-1 + e^{cAo \sqrt{ka^2+2\, ka\, (kd-ki)+(kd+ki)^2}\, t}\right) kd + \left(-1 + e^{cAo \sqrt{ka^2+2\, ka\, (kd-ki)+(kd+ki)^2}\, t}\right) ki + \left(1 + e^{cAo \sqrt{ka^2+2\, ka\, (kd-ki)+(kd+ki)^2}\, t} - 2\, e^{\frac{1}{2} cAo \left(ka+kd+ki+\sqrt{ka^2+2\, ka\, (kd-ki)+(kd+ki)^2}\right) t}\right)\right.\right.$$

```
      Sqrt[ka^2 + 2 ka (kd - ki) + (kd + ki)^2]));
eqPfL = Limit[eqPf, t → Infinity];
```

$$eqQf = \frac{1}{2\,ki\,\sqrt{-4\,ka\,ki + (ka + kd + ki)^2}}\,cEo\,e^{-\frac{1}{2}\,cAo\,\left(ka+kd+ki+\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\right)\,t}\,kd\left(ka - e^{cAo\,\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\,t}\,ka + kd - e^{cAo\,\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\,t}\,kd + ki - e^{cAo\,\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\,t}\,ki - \sqrt{-4\,ka\,ki + (ka + kd + ki)^2} - e^{cAo\,\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\,t}\,\sqrt{-4\,ka\,ki + (ka + kd + ki)^2} + 2\,e^{\frac{1}{2}\,cAo\,\left(ka+kd+ki+\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\right)\,t}\,\sqrt{-4\,ka\,ki + (ka + kd + ki)^2}\right);$$

```
eqQfL = Limit[eqQf, t → Infinity];
```

$$eqIf = \frac{1}{2\,\sqrt{-4\,ka\,ki + (ka + kd + ki)^2}}\,cEo\,e^{-\frac{1}{2}\,cAo\,\left(ka+kd+ki+\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\right)\,t}\left(ka - e^{cAo\,\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\,t}\,ka + kd - e^{cAo\,\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\,t}\,kd + ki - e^{cAo\,\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\,t}\,ki - \sqrt{-4\,ka\,ki + (ka + kd + ki)^2} - e^{cAo\,\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\,t}\,\sqrt{-4\,ka\,ki + (ka + kd + ki)^2} + 2\,e^{\frac{1}{2}\,cAo\,\left(ka+kd+ki+\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\right)\,t}\,\sqrt{-4\,ka\,ki + (ka + kd + ki)^2}\right);$$

```
eqIfL = Limit[eqIf, t → Infinity];
```

$$eqEf = \frac{1}{2\,\sqrt{-4\,ka\,ki + (ka + kd + ki)^2}}\,cEo\,e^{-\frac{1}{2}\,cAo\,\left(ka+kd+ki+\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\right)\,t}\left(ka - e^{cAo\,\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\,t}\,ka - kd + e^{cAo\,\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\,t}\,kd - ki + e^{cAo\,\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\,t}\,ki + \sqrt{-4\,ka\,ki + (ka + kd + ki)^2} + e^{cAo\,\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\,t}\,\sqrt{-4\,ka\,ki + (ka + kd + ki)^2}\right);$$

$$eqFf = \frac{cEo\,e^{-\frac{1}{2}\,cAo\,\left(ka+kd+ki+\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\right)\,t}\left(-1 + e^{cAo\,\sqrt{-4\,ka\,ki+(ka+kd+ki)^2}\,t}\right)\,ka}{\sqrt{-4\,ka\,ki + (ka + kd + ki)^2}};$$

```
plot1 = Plot[{eqPf, eqPfL, eqQf, eqQfL}, {t, 0.0, 250},
   Evaluate@PingPongModel1,
   PlotStyle → {{Thick, Darker[Blue]},
     {Thick, Black, Dashed}, {Thick, Pink}, {Thick, Black, Dotted}},
   Epilog → {Inset[Style["[P]F", 12, Background → White], {125, 0.3 + eqPf /. t → 125}],
     Inset[Style["[Q]F", 12, Background → White], {75, -0.5 + eqQf /. t → 75}]
    }];
plot2 = Plot[{eqEf, eqFf, eqIf, eqIfL}, {t, 0, 250},
   Evaluate@PingPongModel1,
   PlotStyle →
    {{Thick, Blue}, {Thick, Brown}, {Thick, Green}, {Thick, Black, Dashed}},
   Epilog → {Inset[Style["[E]F", 12, Background → White], {20, eqEf /. t → 3}],
     Inset[Style["[F]F", 12, Background → White], {75, 0.1 + eqFf /. t → 75}],
     Inset[Style["[I]F", 12, Background → White], {125, 0.08 + eqIf /. t → 125}]}];
Pane[
  Switch[PingPong,
   1, Show[plot1],
   2, Show[plot2]
  ], ImageSize → 1.2 {480, 310}]],
Row[{
  Column[{
```

```
    Style["REACTANTS CONCENTRATIONS:", Bold],
    Control@{{cAo, 5, "[A]0, mol m-3"}, 0.1, 10, Appearance → "Labeled"},
    Control@{{cEo, 1, "[E]0, mol m-3"}, 0.1, 2, Appearance → "Labeled"},
    Control@{{cFo, 0, "[F]0, mol m-3"}, 0, 0, Appearance → "Labeled"},
    Control@{{cPo, 0, "[P]0, mol m-3"}, 0, 0, Appearance → "Labeled"},
    Control@{{cQo, 0, "[Q]0, mol m-3"}, 0, 0, Appearance → "Labeled"},
    Control@{{cIo, 0, "[I]0, mol m-3"}, 0, 0, Appearance → "Labeled"}
   }],
  Column[{

    Style["RATE CONSTANTS:", Bold],
    Control@{{ka, 0.02, "ka, s-1 mol-1 m3"}, 0.001, 0.04, Appearance → "Labeled"},
    Control@{{kd, 0.015, "kd, s-1 mol-1 m3"}, 0.001, 0.03, Appearance → "Labeled"},
    Control@{{ki, 0.005, "ki, s-1 mol-1 m3"}, 0.001, 0.01, Appearance → "Labeled"}
   }],
  Control@{{PingPong, 1, "Panels"}, {
     1 → "B",
     2 → "D"
    }, ControlType → Setter}}]
]
```

Out[4]=

REACTANTS CONCENTRATIONS:

$[A]_0$, mol m^{-3} 5

$[E]_0$, mol m^{-3} 1

$[F]_0$, mol m^{-3} 0

$[P]_0$, mol m^{-3} 0

$[Q]_0$, mol m^{-3} 0

$[I]_0$, mol m^{-3} 0

RATE CONSTANTS:

k_a, s^{-1} mol^{-1} m^3 0.02

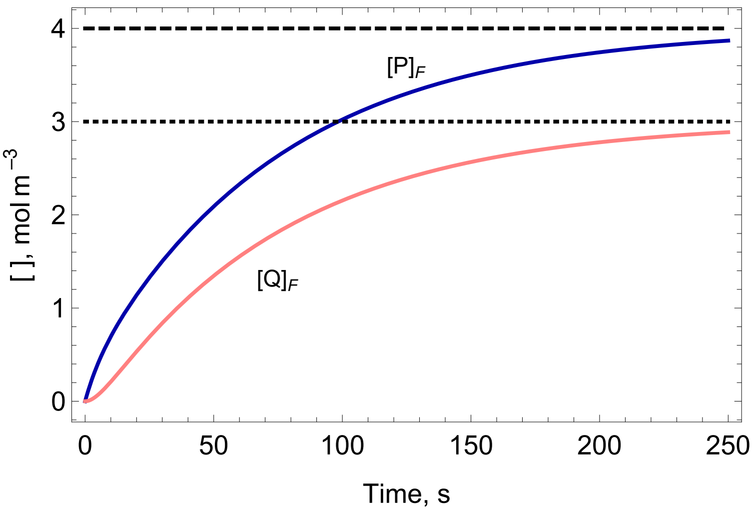
k_d, s^{-1} mol^{-1} m^3 0.015

k_i, s^{-1} mol^{-1} m^3 0.005

Panels B D

Ping–Pong Reaction with One Substrate Undergoing Disproportionation
in the Presence of Suicide Substrate Inactivation (A remains contant, $k_c \to \infty$ and $k_f \to \infty$):

$$A + E \longrightarrow P + F$$
$$A + F \longrightarrow Q + E$$
$$A + F \longrightarrow I$$



Ping-Pong Reaction with One Substrate Undergoing Disproportionation in the Absence of Suicide Substrate Inactivation

$$A + E \xrightarrow{k_a} F + P$$

$$A + F \xrightarrow{k_d} E + Q$$

$k_a < k_d$, $k_c \to \infty$ and $k_f \to \infty$.

Figure S1A, C & E (Mathematics-1964681). Representative numerical (dashed lines, subscript ns) and analytical (solid lines, subscript ss) solutions of the time-dependent variation of (A & C) the concentration for the substrate A, the products P and Q, and the two active enzyme states E and F and (E) the reaction rate for A, P and Q of an enzyme-catalyzed ping-pong reaction. The substrate A follows disproportionation and the accumulation of the intermediate substrate-enzyme complexes EA and FA is negligible. For the analytical solution, E and F were assumed to be in steady-state.

```
In[•]:= -cA'[t] == ka * cA[t] * cE[t] + kd * cA[t] * cF[t] /. cF[t] → cEo - cE[t]
        -cE'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t] /. cF[t] → cEo - cE[t]
        cF'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t] /.
         {cF'[t] → -cE'[t], cF[t] → cEo - cE[t]}
Out[•]= -cA′[t] == kd cA[t] (cEo - cE[t]) + ka cA[t] × cE[t]
Out[•]= -cE′[t] == -kd cA[t] (cEo - cE[t]) + ka cA[t] × cE[t]
Out[•]= -cE′[t] == -kd cA[t] (cEo - cE[t]) + ka cA[t] × cE[t]
In[•]:= Solve[-kd cA[t] (cEo - cE[t]) + ka cA[t] × cE[t] == 0, cE[t]]
```

Out[•]= $\left\{\left\{cE[t] \to \frac{cEo\ kd}{ka + kd}\right\}\right\}$

In[•]:= DSolve$\left[\left\{-cA'[t] == kd\ cA[t]\ (cEo - cE[t]) + ka\ cA[t] \times cE[t]\ /.\ cE[t] \to \frac{cEo\ kd}{ka + kd},\ cA[0] == cAo\right\},\ cA[t],\ t\right]$

Out[•]= $\left\{\left\{cA[t] \to cAo\ e^{-\frac{2\ cEo\ ka\ kd\ t}{ka+kd}}\right\}\right\}$

In[∘]:= Simplify[
DSolve[{cP'[t] == ka * cA[t] * cE[t] /. cE[t] → $\frac{\text{cEo kd}}{\text{ka + kd}}$ /. cA[t] → cAo $e^{-\frac{2\,\text{cEo ka kd t}}{\text{ka+kd}}}$, cP[0] == 0},
cP[t], t]]

Out[∘]= $\left\{\left\{\text{cP}[t] \to \frac{1}{2}\,\text{cAo}\left(1 - e^{-\frac{2\,\text{cEo ka kd t}}{\text{ka+kd}}}\right)\right\}\right\}$

In[∘]:= Solve[cEo == cE[t] + cF[t] /. cE[t] → $\frac{\text{cEo kd}}{\text{ka + kd}}$, cF[t]]

Out[∘]= $\left\{\left\{\text{cF}[t] \to \frac{\text{cEo ka}}{\text{ka + kd}}\right\}\right\}$

In[∘]:= Simplify[
DSolve[{cQ'[t] == kd * cA[t] * cF[t] /. cF[t] → $\frac{\text{cEo ka}}{\text{ka + kd}}$ /. cA[t] → cAo $e^{-\frac{2\,\text{cEo ka kd t}}{\text{ka+kd}}}$, cQ[0] == 0},
cQ[t], t]]

Out[∘]= $\left\{\left\{\text{cQ}[t] \to \frac{1}{2}\,\text{cAo}\left(1 - e^{-\frac{2\,\text{cEo ka kd t}}{\text{ka+kd}}}\right)\right\}\right\}$

In[6]:=
```
Manipulate[Module[{PingPongModel1, PingPongModel2, PingPongModel3, soln, eqAns,
    eqAss, eqPns, eqPss, eqQns, eqQss, eqPQns, eqPQss, eqEns, eqEss, eqFns, eqFss,
    eqAnsD, eqAssD, eqPnsD, eqPssD, eqQnsD, eqQssD, plot1, plot2, plot3},
   PingPongModel1 = Sequence[
     PlotRange → Full,
     PlotLabel →
      Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation (kc → ∞ and kf → ∞):
A + E ⟶ P + F
A + F ⟶ Q + E
", FontSize → 14],
     Frame → True,
     FrameLabel → {"Time, s", "[ ], mol m^-3"},
     LabelStyle → {FontSize → 14},
     ImageSize → 1.2 {480, 310}];
   PingPongModel2 = Sequence[
     PlotRange → {{0, 50}, {0, 0.069}},
     PlotLabel →
      Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation (kc → ∞ and kf → ∞):
A + E ⟶ P + F
A + F ⟶ Q + E", FontSize → 14],
     Frame → True,
     FrameLabel → {"Time, s", "[ ], mol m^-3 s^-1"},
     LabelStyle → {FontSize → 14},
     ImageSize → 1.2 {480, 310}];
   PingPongModel3 = Sequence[
     PlotRange → {{0, 50}, {-0.05, 1.05}},
     PlotLabel →
      Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
```

```
in the Absence of Suicide Substrate Inactivation (kc → ∞ and kf → ∞):
A + E ⟶ P + F
A + F ⟶ Q + E
", FontSize → 14],
    Frame → True,
    FrameLabel → {"Time, s", "[ ], mol m^-3"},
    LabelStyle → {FontSize → 14},
    ImageSize → 1.2 {480, 310}];
  soln = NDSolve[{-cA'[t] == ka * cA[t] * cE[t] + kd * cA[t] * cF[t],
     -cE'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t],
     cF'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t], cP'[t] == ka * cA[t] * cE[t],
     cQ'[t] == kd * cA[t] * cF[t], cA[0] == cAo, cE[0] == cEo, cF[0] == cFo,
     cP[0] == cPo, cQ[0] == cQo}, {cA, cE, cF, cP, cQ}, {t, 0.0, 250}];
  eqAns = cA[t] /. soln;
  eqAss = cAo E^(-(2 cEo ka kd t)/(ka+kd));
  eqPns = cP[t] /. soln;
  eqPss = 1/2 cAo (1 - E^(-(2 cEo ka kd t)/(ka+kd)));
  eqQns = cQ[t] /. soln;
  eqQss = 1/2 cAo (1 - E^(-(2 cEo ka kd t)/(ka+kd)));
  eqPQns = cP[t] + cQ[t] /. soln;
  eqPQss = cAo (1 - E^(-(2 cEo ka kd t)/(ka+kd)));
  eqEns = cE[t] /. soln;
  eqEss = (cEo kd)/(ka + kd);
  eqFns = cF[t] /. soln;
  eqFss = (cEo ka)/(ka + kd);
  eqAnsD = -cA'[t] /. soln;
  eqAssD = -D[cAo E^(-(2 cEo ka kd t)/(ka+kd)), t];
  eqPnsD = cP'[t] /. soln;
  eqPssD = D[1/2 cAo (1 - E^(-(2 cEo ka kd t)/(ka+kd))), t];
  eqQnsD = cQ'[t] /. soln;
  eqQssD = D[1/2 cAo (1 - E^(-(2 cEo ka kd t)/(ka+kd))), t];
  plot1 = Plot[{eqAns, eqAss, eqPns, eqPss, eqQns, eqQss;
     eqPQns, eqPQss}, {t, 0.0, 250},
    Evaluate@PingPongModel1,
    PlotStyle → {{Thick, Pink}, {Thick, Darker[Blue], Dashed}, {Thick, Brown}, {Thick,
       Dashed, Red}, {Thick, Darker[Green]}, {Thick, Blue}, {Thick, Green, Dashed}},
    Epilog → {Inset[Style["[A]ns", 12, Background → White],
       {50, 0.5 + cA[50] /. soln[[1]]}],
      Inset[Style["[A]ss", 12, Background → White], {25, -0.5 + eqAss /. t → 25}],
      Inset[Style["[P]ns", 12, Background → White], {75, 0.4 + cP[75] /. soln[[1]]}],
      Inset[
       Style["[P]ss or [Q]ss", 12, Background → White], {200, 0.5 + eqPss /. t → 200}],
      Inset[Style["[Q]ns", 12, Background → White], {110, -0.5 + cQ[110] /. soln[[1]]}],
      Inset[Style["([P]+[Q])ns", 12, Background → White],
```

```
      {225, -0.5 + cP[225] + cQ[225] /. soln[[1]]}],
     Inset[Style["([P]+[Q])ss", 12, Background → White], {125, 0.5 + eqPQss /. t → 125}]
    }];
 plot2 = Plot[{eqAnsD, eqAssD, eqPnsD, eqPssD, eqQnsD, eqQssD;}, {t, 0, 250},
   Evaluate@PingPongModel2,
   PlotStyle → {{Thick, Pink}, {Thick, Darker[Cyan], Dashed},
     {Thick, Brown}, {Thick, Dashed, Red}, {Thick, Darker[Green]}},
   Epilog → {Inset[Style["[A]'ns", 12, Background → White],
      {5, -0.005 - cA'[5] /. soln[[1]]}],
     Inset[Style["[A]'ss", 12, Background → White], {5, 0.005 + eqAssD /. t → 5}],
     Inset[Style["[P]'ns", 12, Background → White], {7, 0.005 + cP'[7] /. soln[[1]]}],
     Inset[Style["[P]'ss or [Q]'ss", 12, Background → White],
      {40, -0.01 + eqPssD /. t → 40}], Inset[Style["[Q]'ns", 12, Background → White],
      {5, -0.01 + cQ'[5] /. soln[[1]]}]}];
 plot3 = Plot[{eqEns, eqEss, eqFns, eqFss}, {t, 0.02, 250},
   Evaluate@PingPongModel3,
   PlotStyle → {{Thick, Pink}, {Thick, Darker[Blue], Dashed},
     {Thick, Darker[Green]}, {Thick, Dashed, Darker[Cyan]}},
   Epilog → {Inset[Style["[E]ns", 12, Background → White],
      {5, 0.05 + cE[5] /. soln[[1]]}],
     Inset[Style["[E]ss", 12, Background → White], {3, -0.05 + eqEss /. t → 3}],
     Inset[Style["[F]ns", 12, Background → White], {5, -0.05 + cF[5] /. soln[[1]]}],
     Inset[Style["[F]ss", 12, Background → White], {3, 0.05 + eqFss /. t → 3}]}];
 Pane[
  Switch[PingPong,
   1, Show[plot1],
   2, Show[plot2],
   3, Show[plot3]
  ], ImageSize → 1.2 {480, 310}]],
Row[{
  Column[{

    Style["REACTANTS CONCENTRATIONS:", Bold],
    Control@{{cAo, 5, "[A]0, mol m-3"}, 0.1, 10, Appearance → "Labeled"},
    Control@{{cEo, 1, "[E]0, mol m-3"}, 0.1, 2, Appearance → "Labeled"},
    Control@{{cFo, 0, "[F]0, mol m-3"}, 0, 0, Appearance → "Labeled"},
    Control@{{cPo, 0, "[P]0, mol m-3"}, 0, 0, Appearance → "Labeled"},
    Control@{{cQo, 0, "[Q]0, mol m-3"}, 0, 0, Appearance → "Labeled"},
    Control@{{cIo, 0, "[I]0, mol m-3"}, 0, 0, Appearance → "Labeled"}
   }],
  Column[{

    Style["RATE CONSTANTS:", Bold],
    Control@{{ka, 0.005, "ka, s-1 mol-1 m3"}, 0.001, 0.01, Appearance → "Labeled"},
    Control@{{kd, 0.05, "kd, s-1 mol-1 m3"}, 0.001, 0.1, Appearance → "Labeled"}
   }],
  Control@{{PingPong, 1, "Panels"}, {
     1 → "A",
     2 → "B",
     3 → "C"
    }, ControlType → Setter}}]
```

]

REACTANTS CONCENTRATIONS:

$[A]_0$, mol m^{-3} 5

$[E]_0$, mol m^{-3} 1

$[F]_0$, mol m^{-3} 0

$[P]_0$, mol m^{-3} 0

$[Q]_0$, mol m^{-3} 0

$[I]_0$, mol m^{-3} 0

RATE CONSTANTS:

k_a, s^{-1} mol^{-1} m^3 0.005

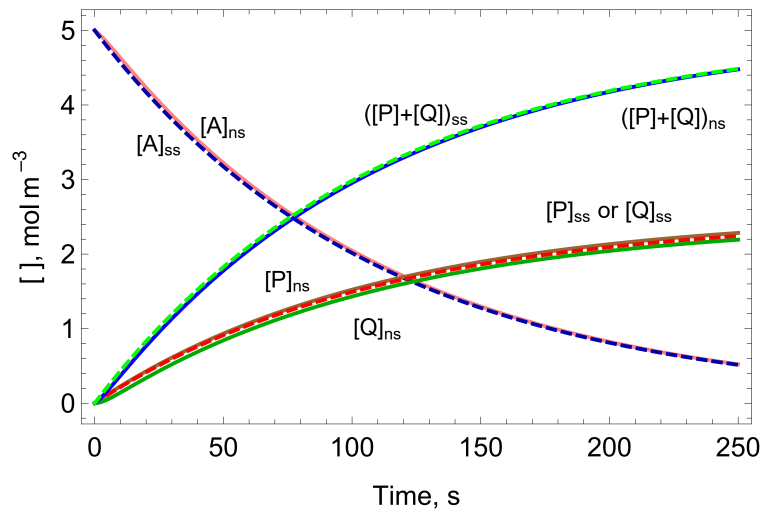
k_d, s^{-1} mol^{-1} m^3 0.05

Panels A B C

Out[6]=

Ping−Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation ($k_c \to \infty$ and $k_f \to \infty$):

$$A + E \longrightarrow P + F$$
$$A + F \longrightarrow Q + E$$



Ping-Pong Reaction with One Substrate Undergoing Disproportionation in the Absence of Suicide Substrate Inactivation

$$A + E \xrightarrow{k_a} F + P$$

$$A + F \xrightarrow{k_d} E + Q$$

$k_a > k_d, k_c \rightarrow \infty$ and $k_f \rightarrow \infty$.

Figure S1D–F (Mathematics-1964681). Representative numerical (dashed lines, subscript ns) and analytical (solid lines, subscript ss) solutions of the time-dependent variation of (B & D) the concentration for the substrate A, the products P and Q, and the two active enzyme states E and F and (F) the reaction rate for A, P and Q of an enzyme-catalyzed ping-pong reaction. The substrate A follows disproportionation and the accumulation of the intermediate substrate-enzyme complexes EA and FA is negligible. For the analytical solution, E and F were assumed to be in steady-state.

```
In[∘]:= -cA'[t] == ka * cA[t] * cE[t] + kd * cA[t] * cF[t] /. cF[t] → cEo - cE[t]
        -cE'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t] /. cF[t] → cEo - cE[t]
        cF'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t] /.
         {cF'[t] → -cE'[t], cF[t] → cEo - cE[t]}
```

Out[∘]= $-cA'[t] == kd\, cA[t]\, (cEo - cE[t]) + ka\, cA[t] \times cE[t]$

Out[∘]= $-cE'[t] == -kd\, cA[t]\, (cEo - cE[t]) + ka\, cA[t] \times cE[t]$

Out[∘]= $-cE'[t] == -kd\, cA[t]\, (cEo - cE[t]) + ka\, cA[t] \times cE[t]$

```
In[∘]:= Solve[-kd cA[t] (cEo - cE[t]) + ka cA[t] × cE[t] == 0, cE[t]]
```

Out[∘]= $\left\{\left\{cE[t] \rightarrow \frac{cEo\ kd}{ka + kd}\right\}\right\}$

In[∘]:= $\text{DSolve}\left[\left\{-cA'[t] == kd\, cA[t]\, (cEo - cE[t]) + ka\, cA[t] \times cE[t]\ /.\ cE[t] \rightarrow \frac{cEo\ kd}{ka + kd},\ cA[0] == cAo\right\},\ cA[t],\ t\right]$

Out[∘]= $\left\{\left\{cA[t] \rightarrow cAo\, e^{-\frac{2\, cEo\, ka\, kd\, t}{ka+kd}}\right\}\right\}$

In[∘]:=
```
Simplify[
  DSolve[{cP'[t] == ka * cA[t] * cE[t] /. cE[t] → (cEo kd)/(ka + kd) /. cA[t] → cAo ⅇ^(-(2 cEo ka kd t)/(ka+kd)), cP[0] == 0},
   cP[t], t]]
```

Out[∘]=

$$\left\{\left\{cP[t] \to \frac{1}{2} cAo \left(1 - e^{-\frac{2\,cEo\,ka\,kd\,t}{ka+kd}}\right)\right\}\right\}$$

In[∘]:=
```
Solve[cEo == cE[t] + cF[t] /. cE[t] → (cEo kd)/(ka + kd), cF[t ]]
```

Out[∘]=

$$\left\{\left\{cF[t] \to \frac{cEo\,ka}{ka + kd}\right\}\right\}$$

In[∘]:=
```
Simplify[
  DSolve[{cQ'[t] == kd * cA[t] * cF[t] /. cF[t] → (cEo ka)/(ka + kd) /. cA[t] → cAo ⅇ^(-(2 cEo ka kd t)/(ka+kd)), cQ[0] == 0},
   cQ[t], t]]
```

Out[∘]=

$$\left\{\left\{cQ[t] \to \frac{1}{2} cAo \left(1 - e^{-\frac{2\,cEo\,ka\,kd\,t}{ka+kd}}\right)\right\}\right\}$$

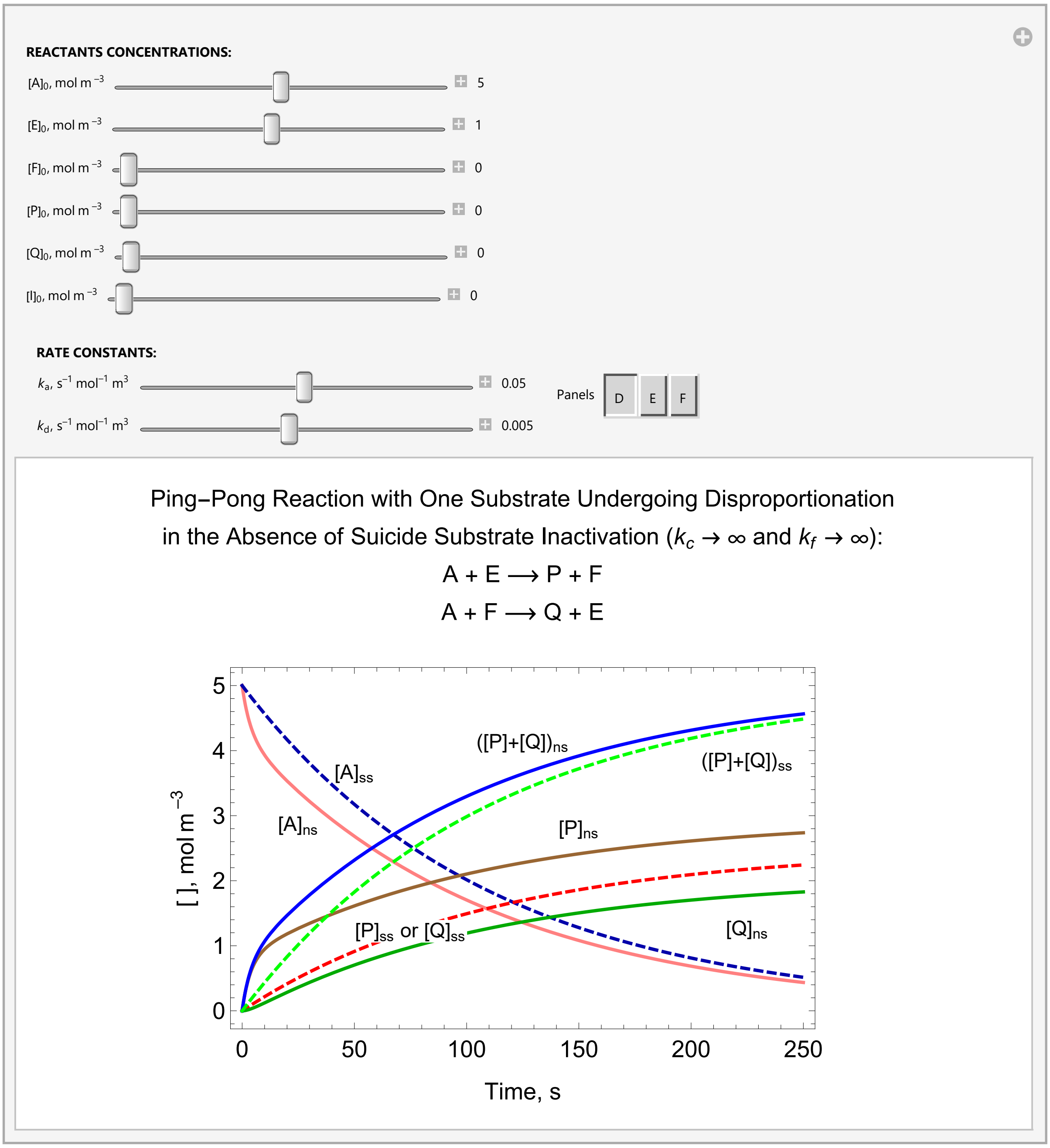
In[7]:=
```
Manipulate[Module[{PingPongModel1, PingPongModel2, PingPongModel3, soln, eqAns,
    eqAss, eqPns, eqPss, eqQns, eqQss, eqPQns, eqPQss, eqEns, eqEss, eqFns, eqFss,
    eqAnsD, eqAssD, eqPnsD, eqPssD, eqQnsD, eqQssD, plot1, plot2, plot3},
   PingPongModel1 = Sequence[
     PlotRange → Full,
     PlotLabel →
      Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation (kc → ∞ and kf → ∞):
A + E ⟶ P + F
A + F ⟶ Q + E
", FontSize → 14],
     Frame → True,
     FrameLabel → {"Time, s", "[ ], mol m^-3"},
     LabelStyle → {FontSize → 14},
     ImageSize → 1.2 {480, 310}];
   PingPongModel2 = Sequence[
     PlotRange → {{0, 50}, {0, 0.069}},
     PlotLabel →
      Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation (kc → ∞ and kf → ∞):
A + E ⟶ P + F
A + F ⟶ Q + E", FontSize → 14],
     Frame → True,
     FrameLabel → {"Time, s", "[ ], mol m^-3 s^-1"},
     LabelStyle → {FontSize → 14},
     ImageSize → 1.2 {480, 310}];
   PingPongModel3 = Sequence[
     PlotRange → {{0, 50}, {-0.05, 1.05}},
     PlotLabel →
      Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
```

```
in the Absence of Suicide Substrate Inactivation (kc → ∞ and kf → ∞):
A + E ⟶ P + F
A + F ⟶ Q + E
", FontSize → 14],
    Frame → True,
    FrameLabel → {"Time, s", "[ ], mol m^-3"},
    LabelStyle → {FontSize → 14},
    ImageSize → 1.2 {480, 310}];
  soln = NDSolve[{-cA'[t] == ka * cA[t] * cE[t] + kd * cA[t] * cF[t],
     -cE'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t],
     cF'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t], cP'[t] == ka * cA[t] * cE[t],
     cQ'[t] == kd * cA[t] * cF[t], cA[0] == cAo, cE[0] == cEo, cF[0] == cFo,
     cP[0] == cPo, cQ[0] == cQo}, {cA, cE, cF, cP, cQ}, {t, 0.0, 250}];
  eqAns = cA[t] /. soln;
  eqAss = cAo e^(-2 cEo ka kd t/(ka+kd));
  eqPns = cP[t] /. soln;
  eqPss = 1/2 cAo (1 - e^(-2 cEo ka kd t/(ka+kd)));
  eqQns = cQ[t] /. soln;
  eqQss = 1/2 cAo (1 - e^(-2 cEo ka kd t/(ka+kd)));
  eqPQns = cP[t] + cQ[t] /. soln;
  eqPQss = cAo (1 - e^(-2 cEo ka kd t/(ka+kd)));
  eqEns = cE[t] /. soln;
  eqEss = cEo kd/(ka + kd);
  eqFns = cF[t] /. soln;
  eqFss = cEo ka/(ka + kd);
  eqAnsD = -cA'[t] /. soln;
  eqAssD = -D[cAo e^(-2 cEo ka kd t/(ka+kd)), t];
  eqPnsD = cP'[t] /. soln;
  eqPssD = D[1/2 cAo (1 - e^(-2 cEo ka kd t/(ka+kd))), t];
  eqQnsD = cQ'[t] /. soln;
  eqQssD = D[1/2 cAo (1 - e^(-2 cEo ka kd t/(ka+kd))), t];
  plot1 = Plot[{eqAns, eqAss, eqPns, eqPss, eqQns, eqQss;
     eqPQns, eqPQss}, {t, 0.0, 250},
    Evaluate@PingPongModel1,
    PlotStyle → {{Thick, Pink}, {Thick, Darker[Blue], Dashed}, {Thick, Brown}, {Thick,
       Dashed, Red}, {Thick, Darker[Green]}, {Thick, Blue}, {Thick, Green, Dashed}},
    Epilog → {Inset[Style["[A]ns", 12, Background → White],
       {25, -0.5 + cA[25] /. soln[[1]]}],
      Inset[Style["[A]ss", 12, Background → White], {50, 0.5 + eqAss /. t → 50}],
      Inset[Style["[P]ns", 12, Background → White], {150, 0.4 + cP[150] /. soln[[1]]}],
      Inset[Style["[P]ss or [Q]ss", 12, Background → White], {75, eqPss /. t → 75}],
      Inset[Style["[Q]ns", 12, Background → White], {225, -0.5 + cQ[225] /. soln[[1]]}],
      Inset[Style["([P]+[Q])ns", 12, Background → White],
       {125, 0.5 + cP[125] + cQ[125] /. soln[[1]]}],
```

```
      Inset[Style["([P]+[Q])ss", 12, Background → White],
       {225, -0.5 + eqPQss /. t → 225}]
     }];
  plot2 = Plot[{eqAnsD, eqAssD, eqPnsD, eqPssD, eqQnsD, eqQssD;}, {t, 0, 250},
    Evaluate@PingPongModel2,
    PlotStyle → {{Thick, Pink}, {Thick, Darker[Cyan], Dashed},
      {Thick, Brown}, {Thick, Dashed, Red}, {Thick, Darker[Green]}},
    Epilog → {Inset[Style["-[A]'ns", 12, Background → White],
       {25, -0.005 - cA'[25] /. soln[[1]]}],
      Inset[Style["-[A]'ss", 12, Background → White], {40, 0.005 + eqAssD /. t → 40}],
      Inset[Style["[P]'ns", 12, Background → White], {4, cP'[6] /. soln[[1]]}],
      Inset[Style["[P]'ss or [Q]'ss", 12, Background → White],
       {6, 0.005 + eqPssD /. t → 6}], Inset[Style["[Q]'ns", 12, Background → White],
       {5, -0.007 + cQ'[5] /. soln[[1]]}]}];
  plot3 = Plot[{eqEns, eqEss, eqFns, eqFss}, {t, 0.02, 250},
    Evaluate@PingPongModel3,
    PlotStyle → {{Thick, Pink}, {Thick, Darker[Blue], Dashed},
      {Thick, Darker[Green]}, {Thick, Dashed, Darker[Cyan]}},
    Epilog → {Inset[Style["[E]ns", 12, Background → White],
       {10, 0.1 + cE[10] /. soln[[1]]}],
      Inset[Style["[E]ss", 12, Background → White], {7, -0.05 + eqEss /. t → 7}],
      Inset[Style["[F]ns", 12, Background → White], {10, -0.1 + cF[10] /. soln[[1]]}],
      Inset[Style["[F]ss", 12, Background → White], {7, 0.05 + eqFss /. t → 7}]}];
  Pane[
   Switch[PingPong,
    1, Show[plot1],
    2, Show[plot2],
    3, Show[plot3]
   ], ImageSize → 1.2 {480, 310}]],
 Row[{
   Column[{

     Style["REACTANTS CONCENTRATIONS:", Bold],
     Control@{{cAo, 5, "[A]0, mol m-3"}, 0.1, 10, Appearance → "Labeled"},
     Control@{{cEo, 1, "[E]0, mol m-3"}, 0.1, 2, Appearance → "Labeled"},
     Control@{{cFo, 0, "[F]0, mol m-3"}, 0, 0, Appearance → "Labeled"},
     Control@{{cPo, 0, "[P]0, mol m-3"}, 0, 0, Appearance → "Labeled"},
     Control@{{cQo, 0, "[Q]0, mol m-3"}, 0, 0, Appearance → "Labeled"},
     Control@{{cIo, 0, "[I]0, mol m-3"}, 0, 0, Appearance → "Labeled"}
    }],
   Column[{

     Style["RATE CONSTANTS:", Bold],
     Control@{{ka, 0.05, "ka, s-1 mol-1 m3"}, 0.001, 0.1, Appearance → "Labeled"},
     Control@{{kd, 0.005, "kd, s-1 mol-1 m3"}, 0.001, 0.01, Appearance → "Labeled"}
    }],
   Control@{{PingPong, 1, "Panels"}, {
      1 → "D",
      2 → "E",
      3 → "F"
     }, ControlType → Setter}}]
```

]

Out[7]=


REACTANTS CONCENTRATIONS:
$[A]_0$, mol m^{-3} 5
$[E]_0$, mol m^{-3} 1
$[F]_0$, mol m^{-3} 0
$[P]_0$, mol m^{-3} 0
$[Q]_0$, mol m^{-3} 0
$[I]_0$, mol m^{-3} 0
RATE CONSTANTS:
k_a, s^{-1} mol^{-1} m^3 0.05
k_d, s^{-1} mol^{-1} m^3 0.005
Panels D E F
Ping–Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation ($k_c \to \infty$ and $k_f \to \infty$):
$A + E \longrightarrow P + F$
$A + F \longrightarrow Q + E$
$[A]_{ss}$
$[A]_{ns}$
$([P]+[Q])_{ns}$
$([P]+[Q])_{ss}$
$[P]_{ns}$
$[P]_{ss}$ or $[Q]_{ss}$
$[Q]_{ns}$
[ ], mol m^{-3}
Time, s
0
1
2
3
4
5
50
100
150
200
250

Ping-Pong Reaction with One Substrate Undergoing Disproportionation in the Absence of Suicide Substrate Inactivation

$$A + E \xrightarrow{k_a} F + P$$

$$A + F \xrightarrow{k_d} E + Q$$

$k_c \rightarrow \infty$ and $k_f \rightarrow \infty$

Figure S2A&B (Mathematics-1964681). Representative numerically (subscript ns) and analytically (subscript n = 1 or n = 2) integrated solutions of the temporal variation of the concentration for (A) the substrate A and (B) the two active enzyme states E and F of an enzyme catalyzed ping-pong reaction under non-steady-state conditions. The substrate A undergoes disproportionation and the substrate-enzyme complexes AE and AF do not accumulate. The numerical solutions (ns) for and are shown together with two approximate integrated solutions around obtained using the first terms () of the power expansion series of the enzyme-dependent function of [E]' . Horizontal solid and dashed lines are the limit values of the analytical solution for [E] and [F] (i.e., $[E]_\infty$ and $[F]_\infty$) when the times goes forward and [A] becomes exhausted.

1. Solution around t = 0

```
In[•]:= -cA'[t] == ka * cA[t] * cE[t] + kd * cA[t] * cF[t] /. cF[t] → cEo - cE[t]
        -cE'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t] /. cF[t] → cEo - cE[t]
        -cF'[t] == cE'[t]
Out[•]= -cA′[t] == kd cA[t] (cEo - cE[t]) + ka cA[t] × cE[t]
Out[•]= -cE′[t] == -kd cA[t] (cEo - cE[t]) + ka cA[t] × cE[t]
Out[•]= -cF′[t] == cE′[t]
```

Chain rule

dy/dx=(dy/dt) /(dx/dt)

```
In[•]:= Simplify[-cA′[t] / (-cE′[t]) ==
          (kd cA[t] (cEo - cE[t]) + ka cA[t] × cE[t]) / (-kd cA[t] (cEo - cE[t]) + ka cA[t] × cE[t])]
```

$$\text{Out}[\circ]= \frac{\text{cEo kd} + (\text{ka} - \text{kd})\ \text{cE}[t]}{\text{cEo kd} - (\text{ka} + \text{kd})\ \text{cE}[t]} + \frac{\text{cA}'[t]}{\text{cE}'[t]} == 0$$

[A(t)]=Function([E](t))

In[∘]:=
$$\text{Collect}\left[\text{Simplify}\left[\text{DSolve}\left[\left\{-\text{cA}'[\text{cE}] == \frac{\text{cE}\ (\text{ka}-\text{kd}) + \text{cEo kd}}{\text{cEo kd} - \text{cE}\ (\text{ka}+\text{kd})},\ \text{cA}[\text{cEo}] == \text{cAo}\right\},\ \text{cA}[\text{cE}],\ \text{cE}\right],\ \text{ka} > 0\ \&\&\ \text{kd} > 0\ \&\&\ \text{cEo} > 0\ \&\&\ \text{cAo} > 0\right]\ /.\ \text{cE} \to \text{cE}[t],\ \text{ka}+\text{kd}\right]$$

Out[∘]=
$$\left\{\left\{\text{cA}[\text{cE}[t]] \to \text{cAo} + \frac{(\text{ka}-\text{kd})\ (-\text{cEo}+\text{cE}[t])}{\text{ka}+\text{kd}} + \frac{-2\ \text{cEo ka kd Log}[\text{cEo ka}] + 2\ \text{cEo ka kd Log}[-\text{cEo kd} + (\text{ka}+\text{kd})\ \text{cE}[t]]}{(\text{ka}+\text{kd})^2}\right\}\right\}$$

$[A(t)]=0$, $[E]_\infty$ and $[F]_\infty$

In[∘]:=
$$\text{Solve}\left[\text{cA}[\text{cE}[t]] == \text{cAo} + \frac{(\text{ka}-\text{kd})\ (-\text{cEo}+\text{cE}[t])}{\text{ka}+\text{kd}} + \frac{-2\ \text{cEo ka kd Log}[\text{cEo ka}] + 2\ \text{cEo ka kd Log}[-\text{cEo kd} + (\text{ka}+\text{kd})\ \text{cE}[t]]}{(\text{ka}+\text{kd})^2}\ /.\ \text{cA}[\text{cE}[t]] \to 0,\ \text{cE}[t]\right]$$

⋯ Solve: Inverse functions are being used by Solve, so some solutions may not be found; use Reduce for complete solution information.

Out[∘]=
$$\left\{\left\{\text{cE}[t] \to \frac{\text{cEo kd}\left(-\text{ka}+\text{kd}-2\ \text{ka ProductLog}\left[\frac{e^{-\frac{\text{cAo}}{\text{cEo}}+\frac{\text{ka}}{2\ \text{kd}}-\frac{\text{cAo ka}}{2\ \text{cEo kd}}-\frac{\text{kd}}{2\ \text{ka}}-\frac{\text{cAo kd}}{2\ \text{cEo ka}}-\frac{\text{ka}}{2\ (\text{ka}+\text{kd})}+\frac{\text{kd}^2}{2\ \text{ka}\ (\text{ka}+\text{kd})}}\ (\text{ka}-\text{kd})}{2\ \text{kd}}\right]\right)}{(-\text{ka}+\text{kd})\ (\text{ka}+\text{kd})}\right\}\right\}$$

$$\text{cF}[t] = \text{cEo} - \text{cE}[t]\ /.\ \text{cE}[t] \to \frac{\text{cEo kd}\left(-\text{ka}+\text{kd}-2\ \text{ka ProductLog}\left[\frac{e^{-\frac{\text{cAo}}{\text{cEo}}+\frac{\text{ka}}{2\ \text{kd}}-\frac{\text{cAo ka}}{2\ \text{cEo kd}}-\frac{\text{kd}}{2\ \text{ka}}-\frac{\text{cAo kd}}{2\ \text{cEo ka}}-\frac{\text{ka}}{2\ (\text{ka}+\text{kd})}+\frac{\text{kd}^2}{2\ \text{ka}\ (\text{ka}+\text{kd})}}\ (\text{ka}-\text{kd})}{2\ \text{kd}}\right]\right)}{(-\text{ka}+\text{kd})\ (\text{ka}+\text{kd})};$$

Power expansion series

In[∘]:=
$$\text{Simplify}\left[-\text{cE}'[t] == -\text{kd cA}[t]\ (\text{cEo}-\text{cE}[t]) + \text{ka cA}[t] \times \text{cE}[t]\ /.\ \text{cA}[t] \text{->} \text{cAo} + \frac{(\text{ka}-\text{kd})\ (-\text{cEo}+\text{cE}[t])}{\text{ka}+\text{kd}} + \frac{-2\ \text{cEo ka kd Log}[\text{cEo ka}] + 2\ \text{cEo ka kd Log}[-\text{cEo kd} + (\text{ka}+\text{kd})\ \text{cE}[t]]}{(\text{ka}+\text{kd})^2}\right]$$

Out[∘]=
$$\frac{1}{(\text{ka}+\text{kd})^2}\ (\text{cEo kd} - (\text{ka}+\text{kd})\ \text{cE}[t])\ \left(\text{cAo ka}^2 - \text{cEo ka}^2 + 2\ \text{cAo ka kd} + \text{cAo kd}^2 + \text{cEo kd}^2 + \left(\text{ka}^2-\text{kd}^2\right)\ \text{cE}[t] - 2\ \text{cEo ka kd Log}[\text{cEo ka}] + 2\ \text{cEo ka kd Log}[-\text{cEo kd} + (\text{ka}+\text{kd})\ \text{cE}[t]]\right) == \text{cE}'[t]$$

In[∘]:=
$$\text{Series}\left[\frac{1}{(\text{ka}+\text{kd})^2}\ (\text{cEo kd} - (\text{ka}+\text{kd})\ \text{cE}[t])\ \left(\text{cAo ka}^2 - \text{cEo ka}^2 + 2\ \text{cAo ka kd} + \text{cAo kd}^2 + \text{cEo kd}^2 + \left(\text{ka}^2-\text{kd}^2\right)\ \text{cE}[t] - 2\ \text{cEo ka kd Log}[\text{cEo ka}] + 2\ \text{cEo ka kd Log}[-\text{cEo kd} + (\text{ka}+\text{kd})\ \text{cE}[t]]\right) == \text{cE}'[t],\ \{\text{cE}[t],\ \text{cEo},\ 1\}\right]$$

Out[∘]=
$$-\text{cAo cEo ka} + (-\text{cAo ka} - \text{cEo ka} - \text{cAo kd})\ (\text{cE}[t] - \text{cEo}) + O[\text{cE}[t] - \text{cEo}]^2 == \text{cE}'[t]$$

In[∘]:=
```
Series[1/(ka + kd)^2 (cEo kd - (ka + kd) cE[t])
  (cAo ka^2 - cEo ka^2 + 2 cAo ka kd + cAo kd^2 + cEo kd^2 + (ka^2 - kd^2) cE[t] - 2 cEo ka kd
    Log[cEo ka] + 2 cEo ka kd Log[-cEo kd + (ka + kd) cE[t]]) == cE'[t], {cE[t], cEo, 2}]
```

Out[∘]=
$$-\text{cAo cEo ka} + (-\text{cAo ka} - \text{cEo ka} - \text{cAo kd})\ (\text{cE}[t] - \text{cEo}) - \text{ka}\ (\text{cE}[t] - \text{cEo})^2 + O[\text{cE}[t] - \text{cEo}]^3 == \text{cE}'[t]$$

In[∘]:=
```
cEn1 = Simplify[DSolve[
  {-cAo cEo ka + (-cAo ka - cEo ka - cAo kd) (cE[t] - cEo) == cE'[t], cE[0] == cEo}, cE[t], t]]
```

Out[∘]=
$$\left\{\left\{\text{cE}[t] \to \frac{\text{cEo}\left(\text{cEo ka} + \text{cAo}\left(e^{-((\text{cEo ka}+\text{cAo}(\text{ka}+\text{kd}))\,t)}\ \text{ka} + \text{kd}\right)\right)}{\text{cEo ka} + \text{cAo}\ (\text{ka} + \text{kd})}\right\}\right\}$$

In[∘]:=
```
cAn1 = Simplify[cA[t] == cAo + ((ka - kd) (-cEo + cE[t]))/(ka + kd) +
    (-2 cEo ka kd Log[cEo ka] + 2 cEo ka kd Log[-cEo kd + (ka + kd) cE[t]])/(ka + kd)^2 /.
   cE[t] -> (cEo (cEo ka + cAo (E^(-((cEo ka + cAo (ka + kd)) t)) ka + kd)))/(cEo ka + cAo (ka + kd)),
  ka > 0 && kd > 0 && cAo > 0 && cEo > 0]
```

Out[∘]=
$$\text{cA}[t] == \text{cAo} + \frac{\text{cEo}\ (\text{ka} - \text{kd})\left(-1 + \frac{\text{cEo ka}+\text{cAo}\left(e^{-((\text{cEo ka}+\text{cAo}(\text{ka}+\text{kd}))\,t)}\ \text{ka}+\text{kd}\right)}{\text{cEo ka}+\text{cAo}(\text{ka}+\text{kd})}\right)}{\text{ka} + \text{kd}} + \frac{2\ \text{cEo ka kd Log}\left[\frac{\text{cEo ka}+\text{cAo}\ e^{-((\text{cEo ka}+\text{cAo}(\text{ka}+\text{kd}))\,t)}\ (\text{ka}+\text{kd})}{\text{cEo ka}+\text{cAo}(\text{ka}+\text{kd})}\right]}{(\text{ka} + \text{kd})^2}$$

In[∘]:=
```
cEn2 = Simplify[
  DSolve[{-cAo cEo ka + (-cAo ka - cEo ka - cAo kd) (cE[t] - cEo) - ka (cE[t] - cEo)^2 == cE'[t],
    cE[0] == cEo}, cE[t], t], ka > 0 && kd > 0 && cAo > 0 && cEo > 0]
```

Solve: Inverse functions are being used by Solve, so some solutions may not be found; use Reduce for complete solution information.

Out[∘]=
$$\left\{\left\{\text{cE}[t] \to \frac{1}{2\ \text{ka}}\left(\text{cEo ka} - \text{cAo}\ (\text{ka} + \text{kd}) + \sqrt{\text{cEo}^2\ \text{ka}^2 + 2\ \text{cAo cEo ka}\ (-\text{ka} + \text{kd}) + \text{cAo}^2\ (\text{ka} + \text{kd})^2}\ \text{Tanh}\left[\frac{1}{2}\sqrt{\text{cEo}^2\ \text{ka}^2 + 2\ \text{cAo cEo ka}\ (-\text{ka} + \text{kd}) + \text{cAo}^2\ (\text{ka} + \text{kd})^2}\ t + \text{ArcTanh}\left[\frac{\text{cEo ka} + \text{cAo}\ (\text{ka} + \text{kd})}{\sqrt{\text{cEo}^2\ \text{ka}^2 + 2\ \text{cAo cEo ka}\ (-\text{ka} + \text{kd}) + \text{cAo}^2\ (\text{ka} + \text{kd})^2}}\right]\right]\right)\right\}\right\}$$

In[∘]:=
```
cAn2 = Simplify[cA[t] == cAo + ((ka - kd) (-cEo + cE[t]))/(ka + kd) +
    (-2 cEo ka kd Log[cEo ka] + 2 cEo ka kd Log[-cEo kd + (ka + kd) cE[t]])/(ka + kd)^2 /.
   cE[t] -> 1/(2 ka) (cEo ka - cAo (ka + kd) + Sqrt[cEo^2 ka^2 + 2 cAo cEo ka (-ka + kd) + cAo^2 (ka + kd)^2]
       Tanh[1/2 Sqrt[cEo^2 ka^2 + 2 cAo cEo ka (-ka + kd) + cAo^2 (ka + kd)^2] t +
         ArcTanh[(cEo ka + cAo (ka + kd))/Sqrt[cEo^2 ka^2 + 2 cAo cEo ka (-ka + kd) + cAo^2 (ka + kd)^2]]]),
  ka > 0 && kd > 0 && cAo > 0 && cEo > 0]
```

Out[∘]=

$$cA[t] == cAo + \frac{1}{(ka+kd)^2}\, 2\, cEo\, ka\, kd \left(-Log[cEo\, ka] + Log\left[-cEo\, kd + \frac{1}{2\, ka}(ka+kd)\left(cEo\, ka - cAo\,(ka+kd) + \sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\,(-ka+kd) + cAo^2 (ka+kd)^2}\; Tanh\left[\frac{1}{2}\sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\,(-ka+kd) + cAo^2 (ka+kd)^2}\; t + ArcTanh\left[\frac{cEo\, ka + cAo\,(ka+kd)}{\sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\,(-ka+kd) + cAo^2 (ka+kd)^2}}\right]\right]\right)\right]\right) - \frac{1}{2\, ka\,(ka+kd)}(ka-kd)\left(cEo\, ka + cAo\,(ka+kd) - \sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\,(-ka+kd) + cAo^2 (ka+kd)^2}\; Tanh\left[\frac{1}{2}\sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\,(-ka+kd) + cAo^2 (ka+kd)^2}\; t + ArcTanh\left[\frac{cEo\, ka + cAo\,(ka+kd)}{\sqrt{cEo^2 ka^2 + 2\, cAo\, cEo\, ka\,(-ka+kd) + cAo^2 (ka+kd)^2}}\right]\right]\right)$$

In[10]:=
```
Manipulate[Module[{PingPongModel1, PingPongModel2, soln, eqAns,
    eqAn1, eqAn2, eqEns, eqEn1, eqEn2, eqEnsL, eqFnsL, plot1, plot2},
   PingPongModel1 = Sequence[
     PlotRange -> {{0, 250}, {1, 4}},
     PlotLabel ->
      Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation (kc → ∞ and kf → ∞):
A + E ⟶ P + F
A + F ⟶ Q + E
", FontSize -> 14],
     Frame -> True,
     FrameLabel -> {"Time, s", "d[ ]/dt, mol m^-3"},
     LabelStyle -> {FontSize -> 14},
     ImageSize -> 1.2 {480, 310}];
   PingPongModel2 = Sequence[
     PlotRange -> {{0, 250}, {0, 2}},
```

```
    PlotLabel →
     Style["Ping-Pong Reaction with One Substrate Undergoing Disproportionation
in the Absence of Suicide Substrate Inactivation (kc → ∞ and kf → ∞):
A + E ⟶ P + F
A + F ⟶ Q + E", FontSize → 14],
    Frame → True,
    FrameLabel → {"Time, s", "d[ ]/dt, mol m^-3"},
    LabelStyle → {FontSize → 14},
    ImageSize → 1.2 {480, 310}];
  soln = NDSolve[{-cA'[t] == ka * cA[t] * cE[t] + kd * cA[t] * cF[t],
     -cE'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t],
     cF'[t] == ka * cA[t] * cE[t] - kd * cA[t] * cF[t], cP'[t] == ka * cA[t] * cE[t],
     cQ'[t] == kd * cA[t] * cF[t], cA[0] == cAo, cE[0] == cEo, cF[0] == cFo,
     cP[0] == cPo, cQ[0] == cQo}, {cA, cE, cF, cP, cQ}, {t, 0.0, 250}];

  eqAns = cA[t] /. soln;
```

$$\text{eqAn1} = \text{cAo} + \frac{\text{cEo}\ (\text{ka} - \text{kd})\ \left(-1 + \frac{\text{cEo ka} + \text{cAo}\ \left(e^{-((\text{cEo ka}+\text{cAo}\ (\text{ka}+\text{kd}))\ t)}\ \text{ka}+\text{kd}\right)}{\text{cEo ka}+\text{cAo}\ (\text{ka}+\text{kd})}\right)}{\text{ka} + \text{kd}} + \frac{2\ \text{cEo ka kd Log}\left[\frac{\text{cEo ka}+\text{cAo}\ e^{-((\text{cEo ka}+\text{cAo}\ (\text{ka}+\text{kd}))\ t)}\ (\text{ka}+\text{kd})}{\text{cEo ka}+\text{cAo}\ (\text{ka}+\text{kd})}\right]}{(\text{ka} + \text{kd})^2};$$

$$\text{eqAn2} = \text{cAo} + \frac{1}{(\text{ka} + \text{kd})^2}\ 2\ \text{cEo ka kd Log}\Bigg[\frac{1}{2\ \text{cEo ka}^2}\Bigg(\text{cEo ka}\ (\text{ka} - \text{kd}) - \text{cAo}\ (\text{ka} + \text{kd})^2 + (\text{ka} + \text{kd})\ \sqrt{\text{cEo}^2\ \text{ka}^2 + 2\ \text{cAo cEo ka}\ (-\text{ka} + \text{kd}) + \text{cAo}^2\ (\text{ka} + \text{kd})^2}\ \text{Tanh}\Big[\frac{1}{2}\ \sqrt{\text{cEo}^2\ \text{ka}^2 + 2\ \text{cAo cEo ka}\ (-\text{ka} + \text{kd}) + \text{cAo}^2\ (\text{ka} + \text{kd})^2}\ t + \text{ArcTanh}\Big[\frac{\text{cEo ka} + \text{cAo}\ (\text{ka} + \text{kd})}{\sqrt{\text{cEo}^2\ \text{ka}^2 + 2\ \text{cAo cEo ka}\ (-\text{ka} + \text{kd}) + \text{cAo}^2\ (\text{ka} + \text{kd})^2}}\Big]\Big]\Bigg)\Bigg] - \frac{1}{2\ \text{ka}\ (\text{ka} + \text{kd})}\ (\text{ka} - \text{kd})\ \Bigg(\text{cEo ka} + \text{cAo}\ (\text{ka} + \text{kd}) - \sqrt{\text{cEo}^2\ \text{ka}^2 + 2\ \text{cAo cEo ka}\ (-\text{ka} + \text{kd}) + \text{cAo}^2\ (\text{ka} + \text{kd})^2}\ \text{Tanh}\Big[\frac{1}{2}\ \sqrt{\text{cEo}^2\ \text{ka}^2 + 2\ \text{cAo cEo ka}\ (-\text{ka} + \text{kd}) + \text{cAo}^2\ (\text{ka} + \text{kd})^2}\ t + \text{ArcTanh}\Big[\frac{\text{cEo ka} + \text{cAo}\ (\text{ka} + \text{kd})}{\sqrt{\text{cEo}^2\ \text{ka}^2 + 2\ \text{cAo cEo ka}\ (-\text{ka} + \text{kd}) + \text{cAo}^2\ (\text{ka} + \text{kd})^2}}\Big]\Big]\Bigg);$$

```
  eqEns = cE[t] /. soln;
  eqEnsL =
```

$$\left(\text{cEo kd}\left(-\text{ka} + \text{kd} - 2\ \text{ka ProductLog}\left[\frac{e^{-\frac{\text{cAo}}{\text{cEo}}+\frac{\text{ka}}{2\ \text{kd}}-\frac{\text{cAo ka}}{2\ \text{cEo kd}}-\frac{\text{kd}}{2\ \text{ka}}-\frac{\text{cAo kd}}{2\ \text{cEo ka}}-\frac{\text{ka}}{2\ (\text{ka}+\text{kd})}+\frac{\text{kd}^2}{2\ \text{ka}\ (\text{ka}+\text{kd})}}\ (\text{ka} - \text{kd})}{2\ \text{kd}}\right]\right)\right) \Big/ ((-\text{ka} + \text{kd})\ (\text{ka} + \text{kd}));$$

```
  eqFnsL = cEo - eqEnsL;
```

$$\text{eqEn1} = \frac{\text{cEo}\ \left(\text{cEo ka} + \text{cAo}\ \left(e^{-((\text{cEo ka}+\text{cAo}\ (\text{ka}+\text{kd}))\ t)}\ \text{ka} + \text{kd}\right)\right)}{\text{cEo ka} + \text{cAo}\ (\text{ka} + \text{kd})};$$

```
eqEn2 = 1/(2 ka) (cEo ka - cAo (ka + kd) + Sqrt[cEo^2 ka^2 + 2 cAo cEo ka (-ka + kd) + cAo^2 (ka + kd)^2]
     Tanh[1/2 Sqrt[cEo^2 ka^2 + 2 cAo cEo ka (-ka + kd) + cAo^2 (ka + kd)^2] t +
       ArcTanh[(cEo ka + cAo (ka + kd))/Sqrt[cEo^2 ka^2 + 2 cAo cEo ka (-ka + kd) + cAo^2 (ka + kd)^2]]]);
plot1 = Plot[{eqAns, eqAn1, eqAn2}, {t, 0.0, 250},
  Evaluate@PingPongModel1,
  PlotStyle → {{Thick, Darker[Green]}, {Thick, Pink}, {Thick, Blue}},
  Epilog →
   {Inset[Style["[A]ns", 12, Background → White], {175, -0.2 + cA[175] /. soln[[1]]}],
    Inset[Style["[A]n=1", 12, Background → White], {225, 0.2 + eqAn1 /. t → 225}],
    Inset[Style["[A]n=2", 12, Background → White], {200, 0.2 + eqAn2 /. t → 200}]
   }];
plot2 = Plot[{eqEns, eqEn1, eqEn2, eqEnsL, eqFnsL}, {t, 0, 250},
  Evaluate@PingPongModel2,
  PlotStyle → {{Thick, Darker[Green]}, {Thick, Pink},
    {Thick, Blue}, {Thick, Brown}, {Thick, Brown, Dashed}},
  Epilog → {Inset[Style["[E]ns", 12, Background → White],
      {100, -0.2 + cE[100] /. soln[[1]]}],
    Inset[Style["[E]∞", 12, Background → White], {50, 0.25}],
    Inset[Style["[F]∞", 12, Background → White], {50, 1.75}],
    Inset[Style["[E]n=1", 12, Background → White], {150, 0.1 + eqEn1 /. t → 150}],
    Inset[Style["[E]n=2", 12, Background → White], {225, 0.1 + eqEn2 /. t → 225}]
   }];
Pane[
 Switch[PingPong,
  1, Show[plot1],
  2, Show[plot2]
 ], ImageSize → 1.2 {480, 310}]],
Row[{
 Column[{

   Style["REACTANTS CONCENTRATIONS:", Bold],
   Control@{{cAo, 4, "[A]0, mol m^-3"}, 0.01, 8, Appearance → "Labeled"},
   Control@{{cEo, 2, "[E]0, mol m^-3"}, 0.01, 4, Appearance → "Labeled"},
   Control@{{cFo, 0, "[F]0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
   Control@{{cPo, 0, "[P]0, mol m^-3"}, 0, 0, Appearance → "Labeled"},
   Control@{{cQo, 0, "[Q]0, mol m^-3"}, 0, 0, Appearance → "Labeled"}
  }],
 Column[{

   Style["RATE CONSTANTS:", Bold],
   Control@{{ka, 0.005, "ka, s^-1 mol^-1 m^3"}, 0.001, 0.01, Appearance → "Labeled"},
   Control@{{kd, 0.001, "kd, s^-1 mol^-1 m^3"}, 0.001, 0.002, Appearance → "Labeled"}
  }],
 Control@{{PingPong, 1, "Panels"}, {
    1 → "A",
```

```
      2 → "B"
     }, ControlType → Setter}}]
]
```

Out[10]=