CATALYSIS

$$A + E \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} I \underset{k_2^+}{\overset{k_2^-}{\rightleftharpoons}} P + E$$

$$\frac{dI}{dt} = k_1^+[E][A] + k_2^+[E][P] - (k_1^- + k_2^-)[I]$$

$$E_0 = [E] + [I]$$

$$\left(k_1^+[A] + k_2^+[P]\right)\left(E_0 - [I]\right) = (k_1^- + k_2^-)[I]$$

$$[I] = \frac{(k_1^+[A] + k_2^+[P])E_0}{(k_1^- + k_2^-) + k_1^+[A] + k_2^+[P]}$$

$$\text{rate} = \frac{d[P]}{dt} = k_2^-[I] - k_2^+[E][P]$$

$$[E] = \frac{(k_1^- + k_2^-)E_0}{(k_1^- + k_2^-) + k_1^+[A] + k_2^+[P]}$$

$$\text{rate} = \frac{k_2^-(k_1^+[A] + k_2^+[P])E_0 - k_2^+(k_1^- + k_2^-)E_0[P]}{(k_1^- + k_2^-) + k_1^+[A] + k_2^+[P]}$$

$$\text{rate} = \frac{(k_1^+k_2^-[A] - k_2^+k_1^-[P])E_0}{(k_1^- + k_2^-) + k_1^+[A] + k_2^+[P]}$$

AS LONG AS ($[P] \simeq 0$)

$$k_1^+ k_2^- [A] >> k_2^+ k_1^- [P]$$

$$\text{rate}_0 = \frac{(k_2^- E_0)\,[A]_0}{K_M + [A]_0} = R_0$$

$$K_M = \frac{k_1^- + k_2^-}{k_1^+}$$

$$\frac{1}{R_0} = \frac{1}{V_m} + \left(\frac{K_M}{V_M}\right)\frac{1}{[A]_0}$$

$$V_m = k_2^- E_0$$

2 variables E ES

$$\begin{pmatrix} k_1[S] + k_{-2}[P] & ; & -k_1 - k_2 \\ 1 & ; & 1 \end{pmatrix} \begin{pmatrix} E \\ ES \end{pmatrix} = \begin{pmatrix} 0 \\ E_0 \end{pmatrix}$$

$$\underset{\sim}{\underset{\sim}{M}} \, \underset{\sim}{v} = \underset{\sim}{v_0}$$

$$\underset{\sim}{v_0}^T = (0, 0, \dots, 0, E_0)$$

$$A + B \xrightarrow{E} P_1 + P_2$$

$A + E$	$\rightleftharpoons$	I_1	$k_1^+ \; k_1^-$
$B + E$	$\rightleftharpoons$	I_2	$k_2^+ \; k_2^-$
$A + I_2$	$\rightleftharpoons$	J	$k_4^+ \; k_4^-$
$B + J_1$	$\rightleftharpoons$	J	$k_3^+ \; k_3^-$
J	$\longrightarrow$	$P_1 + P_2$	k_r

Matrix from the left hand side of steady state (SS) approximation of the differential equations (rate of change) of the intermediates

```
In[1284]:= ma = {{-k1m - k3p B, 0, k3m, k1p A}, {0, -k2m - k4p A, k4m, k2p B},
     {k3p B, k4p A, -k3m - k4m - kr, 0}, {1, 1, 1, 1}};

   MatrixForm[ma]
```

$$\begin{pmatrix} -k1m - B\,k3p & 0 & k3m & A\,k1p \\ 0 & -k2m - A\,k4p & k4m & B\,k2p \\ B\,k3p & A\,k4p & -k3m - k4m - kr & 0 \\ 1 & 1 & 1 & 1 \end{pmatrix}$$

Definition of the intermediates

```
In[1285]:= var = {i1, i2, i, e};
```

From the right hand side of the SS aproximation equations

```
In[1286]:= var0 = {0, 0, 0, eo};

In[1289]:= ma.var // MatrixForm
```

Out[1289]//MatrixForm=

$$\begin{pmatrix} A\,e\,k1p + i\,k3m + i1\,(-k1m - B\,k3p) \\ B\,e\,k2p + i\,k4m + i2\,(-k2m - A\,k4p) \\ B\,i1\,k3p + A\,i2\,k4p + i\,(-k3m - k4m - kr) \\ e + i + i1 + i2 \end{pmatrix}$$

Calculate the inverse matrix

```
invma = Inverse[ma];
```

Solve for the intermediates

```
inter = sol[[3]] // Simplify
```

$$\frac{A\,B\,eo\,(k2p\,(k1m + B\,k3\text{}}{A^2\,k1p\,k4p\,(k3m + B\,k3p + kr) + B\,(k2m + B\,k2p)\,k3p\,(k4m + kr) + k1m\,(A\,k4p\,(k3m + kr) + k2m\,(k3m + k4m + kr) + \text{E}}$$

Consider the symmetric case

```
In[1280]:= sim1 = {k1p → kp, k2p → kp, k3p → kp, k4p → kp, k1m → km, k2m → km, k3m → km, k4m → km};

In[1294]:= rate1 = kr inter /. sim1 // Simplify
```

Out[1294]=

$$\frac{A\,B\,eo\,kp^2\,(2\,km + (A + B)\,kp)\,kr}{2\,km^3 + km^2\,(3\,A\,kp + 3\,B\,kp + kr) + kp^2\,\left(B^2\,kr + A^2\,(B\,kp + kr) + A\,B\,(B\,kp + kr)\right) + km\,kp\,\left(A^2\,kp + 2\,A\,(2\,B\,kp + kr\right.}$$

Consider two limits

```
In[1295]:= Limit[rate1, B → Infinity]
```

Out[1295]=

$$\frac{A\,eo\,kp\,kr}{km + A\,kp + kr}$$

In[1296]:= `Limit[rate1, A → Infinity]`

Out[1296]= $\frac{\text{B eo kp kr}}{\text{km} + \text{B kp} + \text{kr}}$

Consider equal concentrations for both substrates

In[1297]:= `simp = rate1 /. {A → C, B → C} // Simplify`

Out[1297]= $\frac{2\,C^2\,\text{eo}\,\text{kp}^2\,\text{kr}}{2\,\text{km}^2 + \text{km}\,(4\,C\,\text{kp} + \text{kr}) + C\,\text{kp}\,(2\,C\,\text{kp} + 3\,\text{kr})}$

In[1301]:= `Collect[Denominator[simp], C] / (2 kp^2)`

Out[1301]= $\frac{2\,\text{km}^2 + 2\,C^2\,\text{kp}^2 + \text{km}\,\text{kr} + C\,(4\,\text{km}\,\text{kp} + 3\,\text{kp}\,\text{kr})}{2\,\text{kp}^2}$

In[1302]:= `rate1f[c_, eo_, kp_, km_, kr_] :=` $\frac{(\text{eo}\,\text{kr})\,c^2}{c^2 + \left(\frac{2\,\text{km}}{\text{kp}} + \frac{3\,\text{kr}}{2\,\text{kp}}\right)c + \left(\frac{\text{km}^2}{\text{kp}^2} + \frac{\text{km}\,\text{kr}}{2\,\text{kp}^2}\right)}$

We only need relative values between km and kr with kp.

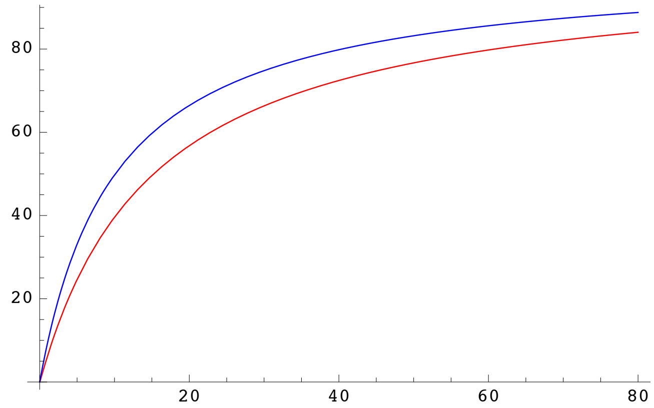
In[1310]:= `rate1f[c, 10 / kp, kp, kp / 10, 10 kp]`

Out[1310]= $\frac{100\,c^2}{\frac{51}{100} + \frac{76\,c}{5} + c^2}$

Plot of the bimolecular and unimolecular enzyme catalyzed reaction

In[1323]:=
```
Plot[{rate1f[c, 10/kp, kp, kp/10, 10 kp], 100 c/(1/10 + 10 + c)}, {c, 0, 80}, PlotStyle → {{Thickness[0.002], Red}
```

Out[1323]=



where KM=(km+kr)/kp

These two rates ahe hard to differentiate. So we use the inverse function

In[1326]:=
```
invf1 = 1/100 + 10.1 x/100;
invf2 = 1/100 + 76 x/500 + 51 x^2/10 000;
```

where x = 1/c

In[1329]:=
```
Plot[{invf1, invf2}, {x, 0.00001, 80}, PlotStyle → {{Thickness[0.002], Red}, {Thickness[0.002],
```

Out[1329]=