ChemE 2200 - Physical Chemistry II for Engineers - Spring 2025 Solution to Homework Assignment 13

1. The fractional reaction order for $[Cl_2]$ suggests the mechanism begins with the reversible dissociation of Cl_2 by a Lindemann mechanism.

$$Cl_2 + M \underset{k_{-1}}{\overset{k_1}{\underset{k_{-1}}{\leftarrow}}} Cl \cdot + Cl \cdot + M$$
 rxn l

Given the possible intermediates, the next reaction is likely the combination of Cl· and CO.

$$Cl \cdot + CO \xrightarrow{\kappa_2} ClCO$$
 rxn 2

Reaction of this intermediate with another Cl- yields the product.

$$Cl \cdot + ClCO \xrightarrow{k_3} Cl_2CO$$

,

But the hint warns that this reaction has negligible rate and should be ignored. Instead we react Cl_2 with the intermediate ClCO.

$$Cl_2 + ClCO \xrightarrow{\kappa_3} Cl_2CO + Cl \cdot rxn 3$$

Derive a rate equation based on elementary reactions 1, 2, and 3. The rate of formation of product is given by reaction 3.

$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_3[\text{ClCO}][\text{Cl}_2] \tag{1}$$

Apply the steady-state approximation to obtain an expression for [ClCO].

$$\frac{d[\text{CICO}]}{dt} = 0 = k_2[\text{Cl·}][\text{CO}] - k_3[\text{CICO}][\text{Cl}_2]$$
$$k_2[\text{Cl·}][\text{CO}] = k_3[\text{CICO}][\text{Cl}_2]$$
(2)

Apply pre-equilibrium to obtain an expression for [Cl·].

$$k_{1}[Cl_{2}][M] = k_{-1}[Cl^{2}]^{2}[M]$$
$$[Cl^{2}] = \sqrt{\frac{k_{1}}{k_{-1}}}[Cl_{2}]^{1/2}$$
(3)

Substitute eqns (2) and (3) into the rate equation, eqn (1).

$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_3[\text{ClCO}][\text{Cl}_2] = k_2[\text{Cl}][\text{CO}] = k_2 \sqrt{\frac{k_1}{k_{-1}}}[\text{Cl}_2]^{1/2}[\text{CO}]$$
(4)

The rate equation has the correct order with respect to CO, but incorrect order with respect to Cl_2 . We need to increase the reaction order with respect to Cl_2 . Previously we assumed steady state on ClCO because the rxn 3 involved a radical, and thus should be fast. But rxn 3 may be slow as rewritten. Assume now that rxn 2 is reversible and is fast with respect to rxn 3. That is, assume rxn 2 is in equilibrium

$$Cl \cdot + CO \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} ClCO rxn 2$$

The subsequent equation is thus:

$$k_{2}[\text{Cl}\cdot][\text{CO}] = k_{-2}[\text{ClCO}]$$
$$[\text{ClCO}] = \frac{k_{2}}{k_{-2}}[\text{Cl}\cdot][\text{CO}]$$
(5)

Substitute eqn (3) into eqn (5).

$$[CICO] = \frac{k_2}{k_{-2}} [CI][CO] = \frac{k_2}{k_{-2}} \sqrt{\frac{k_1}{k_{-1}}} [Cl_2]^{1/2} [CO]$$
(6)

Substitute eqn (6) into eqn (1).

$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_3[\text{ClCO}][\text{Cl}_2] = k_3 \frac{k_2}{k_{-2}} \sqrt{\frac{k_1}{k_{-1}}} [\text{Cl}_2]^{1/2}[\text{CO}][\text{Cl}_2]$$
$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_3 \frac{k_2}{k_{-2}} \sqrt{\frac{k_1}{k_{-1}}} [\text{Cl}_2]^{3/2}[\text{CO}]$$

In summary, the mechanism of elementary steps is as follows.

$$Cl_{2} + M \stackrel{k_{1}}{\underset{k_{-1}}{\leftrightarrow}} Cl \cdot + Cl \cdot + M \quad \text{in equilibrium}$$

$$Cl \cdot + CO \stackrel{k_{2}}{\underset{k_{-2}}{\leftrightarrow}} ClCO \quad \text{in equilibrium}$$

$$Cl_{2} + ClCO \stackrel{k_{3}}{\rightarrow} Cl_{2}CO + Cl \cdot \quad \text{rate-limiting step}$$

Although the following reaction would seem plausible as an alternative first step because it creates the two intermediates,

$$\operatorname{Cl}_2 + \operatorname{CO} \xrightarrow{k_1} \operatorname{ClCO} + \operatorname{Cl},$$

this step is inconsistent with the observed rate equation. Mechanisms with this first step yield rate equations with integral reaction orders for $[Cl_2]$.

The hint stated that this mechanism is not a chain reaction. With the assumptions above, the mechanism is not a chain reaction. But with different assumptions, the mechanism is a chain reaction; assume the second reaction is irreversible and the second and third reactions are propagation reactions. The forward first reaction is initiation and the reverse first reaction is termination. To derive the rate equation, assume the rates of the propagation reactions are equal.

$$k_{2}[\text{Cl·}][\text{CO}] = k_{3}[\text{Cl}_{2}][\text{ClCO}]$$
$$[\text{ClCO}] = \frac{k_{2}}{k_{3}} \frac{[\text{Cl·}][\text{CO}]}{[\text{Cl}_{2}]}$$
(7)

Substitute eqn (3) into eqn (7)

$$[CICO] = \frac{k_2}{k_3} \sqrt{\frac{k_1}{k_{-1}}} \frac{[Cl_2]^{1/2}[CO]}{[Cl_2]} = \frac{k_2}{k_3} \sqrt{\frac{k_1}{k_{-1}}} \frac{[CO]}{[Cl_2]^{1/2}}$$
(8)

Substitute eqn (8) into the rate equation for Cl_2CO , eqn (1)

$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_3[\text{ClCO}][\text{Cl}_2] = k_3 \frac{k_2}{k_3} \sqrt{\frac{k_1}{k_{-1}}} \frac{[\text{CO}]}{[\text{Cl}_2]^{1/2}} [\text{Cl}_2]$$
$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{CO}][\text{Cl}_2]^{1/2}$$

The rate equation derived with a chain reaction mechanism is inconsistent with the observed rate equation.

Aside: We can use this mechanism to derive a rate equation for the reverse reaction, the decomposition of phosgene, given in exercise 2 of Calculation Session 5. The rate of decomposition of phosgene is the reverse of the third elementary step.

$$\frac{d[\text{Cl}_2\text{CO}]}{dt} = k_{-3}[\text{Cl}_2\text{CO}][\text{Cl}\cdot]$$

Use the equation for $[Cl \cdot]$ derived in eqn (3).

$$\frac{d[Cl_2CO]}{dt} = k_{-3}[Cl_2CO] \sqrt{\frac{k_1}{k_{-1}}} [Cl_2]^{1/2} = k[Cl_2CO] [Cl_2]^{1/2}$$

This is the rate equation derived from the rate equation for the formation of phosgene and the equilibrium constant.

2. The rate of emission of visible photons is

$$\frac{d[hv_{\text{visible}}]}{dt} = k_4[A_2^*] \tag{1}$$

Apply the steady-state approximation to A_2^* .

$$\frac{d[A_2^*]}{dt} = 0 = -k_4[A_2^*] + k_3[A_2^{**}][A_2]$$
$$k_4[A_2^*] = k_3[A_2^{**}][A_2]$$
(2)

Substitute eqn (2) into eqn (1).

$$\frac{d[hv_{\text{visible}}]}{dt} = k_3[A_2^{**}][A_2]$$
(3)

We need an expression for [$A_2^{\ast\ast}$]. Apply the steady-state approximation to $A_2^{\ast\ast}$.

$$\frac{d[A_2^{**}]}{dt} = 0 = \phi I_{abs} - k_2[A_2^{**}] - k_3[A_2^{**}][A_2]$$

Solve for [A_2^{**}].

$$k_{2}[A_{2}^{**}] + k_{3}[A_{2}^{**}][A_{2}] = \phi I_{abs}$$

$$[A_{2}^{**}](k_{2} + k_{3}[A_{2}]) = \phi I_{abs}$$

$$[A_{2}^{**}] = \frac{\phi I_{abs}}{k_{2} + k_{3}[A_{2}]}$$
(4)

Finally, substitute eqn (4) into eqn (3).

$$\frac{d[hv_{\text{visible}}]}{dt} = k_3 \frac{\phi I_{\text{abs}}}{k_2 + k_3 [A_2]} [A_2] = \frac{k_3 \phi I_{\text{abs}} [A_2]}{k_2 + k_3 [A_2]}$$

For low concentrations of A_2 the rate of visible photons is proportional to the concentration of A_2 . For high concentrations of A_2 the rate of visible photons is independent of the concentration of A_2 .

3.(A) For stepwise polymerization of an alcohol and an acid to form a polyester, the elementary reaction is

$$-\text{COOH} + \text{HOCH}_2- \rightarrow -\text{C(O)OCH}_2- + \text{H}_2\text{O}$$

and the rate equation is

$$-\frac{d[-\text{CH}_2\text{OH}]}{dt} = k[-\text{COOH}][-\text{CH}_2\text{OH}]$$

The amount of acid remaining equals the amount of acid initially, minus the amount of acid that has reacted. The amount of acid reacted equals the amount of alcohol reacted.

$$[-COOH] = [-COOH]_0 - [-COOH]_{reacted}$$

= [-COOH]_0 - ([-CH_2OH]_0 - [-CH_2OH])
Set [-COOH]_0 = n[-CH_2OH]_0 and define [-CH_2OH] = [A].
[-COOH] = n[A]_0 - ([A]_0 - [A]) = (n-1)[A]_0 + [A]

Substitute into the rate equation.

$$-\frac{d[\mathbf{A}]}{dt} = k((n-1)[\mathbf{A}]_0 + [\mathbf{A}])[\mathbf{A}]$$

Check the differential rate equation. For n = 1 (equal concentrations of acid and alcohol) the rate equation is $-d[A]/dt = k[A]^2$. Check.

Separate and integrate.

$$\int_{[A]_0}^{[A]} \frac{d[A]}{((n-1)[A]_0 + [A])[A]} = -k \int_0^t dt$$

Use partial fractions to simplify the left integrand.

$$\frac{1}{((n-1)[A]_0 + [A])[A]} = \frac{a}{(n-1)[A]_0 + [A]} + \frac{b}{[A]}$$

Such that $a[A] + b((n-1)[A]_0 + [A]) = 1$, which yields

$$b = \frac{1}{(n-1)[A]_0}$$
 and $a = -b = -\frac{1}{(n-1)[A]_0}$

Substitute the fractions into the left integral.

$$\begin{split} & \int_{[A]_{0}}^{[A]} \frac{-1}{(n-1)[A]_{0}} \left(\frac{1}{(n-1)[A]_{0} + [A]} + \frac{-1}{[A]} \right) d[A] = -k \int_{0}^{t} dt \\ & - \frac{1}{(n-1)[A]_{0}} \left(\ln((n-1)[A]_{0} + [A]) - \ln[A]) \right) \Big|_{[A]_{0}}^{[A]} = -kt \\ & \ln \left(\frac{(n-1)[A]_{0} + [A]}{[A]} \times \frac{[A]_{0}}{(n-1)[A]_{0} + [A]_{0}} \right) = (n-1)[A]_{0} kt \\ & \ln \left(\frac{(n-1)[A]_{0} + [A]}{[A]} \times \frac{1}{n} \right) = (n-1)[A]_{0} kt \\ & \frac{(n-1)[A]_{0} + [A]}{n[A]} = e^{(n-1)[A]_{0} kt} \\ & (n-1)[A]_{0} + [A] = n[A]e^{(n-1)[A]_{0} kt} \\ & [A] = \frac{(n-1)[A]_{0}}{ne^{(n-1)[A]_{0} kt} -1} \end{split}$$

(B) Check in the limit t = 0.

$$[A] = \frac{(n-1)[A]_0}{ne^{(n-1)[A]_0k0} - 1} = \frac{(n-1)[A]_0}{n-1} = [A]_0$$

This is the correct limit. Check in the limit $t \to \infty$.

$$[A] = \frac{(n-1)[A]_0}{ne^{(n-1)[A]_0k \times \infty} - 1} \to \frac{(n-1)[A]_0}{n \times \infty - 1} = 0$$

Again this is the correct limit. Check in the limit n = 1. Because both the numerator and denominator approach zero in this limit, apply L'Hôpital's rule.

$$\lim_{n \to 1} [A] = \lim_{n \to 1} \frac{[A]_0}{e^{(n-1)[A]_0 kt} + n([A]_0 kt)e^{(n-1)[A]_0 kt}} = \frac{[A]_0}{1 + [A]_0 kt}$$

The limit approaches the integrated rate equation for a second-order reaction, as derived in lecture. This is correct. Check in the limit n = 1000.

$$[A] = \frac{(1000-1)[A]_0}{1000e^{(1000-1)[A]_0kt} - 1} \approx \frac{999[A]_0}{1000e^{999[A]_0kt}} \approx [A]_0 e^{-999[A]_0kt}$$

The integrated rate equation approaches a first-order decay, as expected for a large excess of the other reactant.

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4.(A) Calculate an expression for dk/dT. Assume an Arrhenius expression for the rate constant and assume the pre-exponential is independent of temperature.

$$k = Ae^{-E_a/RT}$$
$$\frac{dk}{dT} = \frac{d}{dT}Ae^{-E_a/RT} = \frac{AE_a}{RT^2}e^{-E_a/RT}$$

Find the maximum with respect to E_a . Take the derivative with respect to E_a and set equal to zero.

$$\frac{d}{dE_a} \left(\frac{dk}{dT}\right) = \frac{A}{RT^2} e^{-E_a/RT} + \frac{AE_a}{RT^2} \left(\frac{-1}{RT}\right) e^{-E_a/RT} = 0$$
$$0 = 1 - \frac{E_a}{RT}$$
$$E_a = RT$$

(B) At 1000 K,

$$RT = \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} (1000 \text{ K}) = 8.3 \text{ kJ/mol}$$

8.3 kJ/mol is a low activation barrier. This is why some explosives - such as nitroglycerin and detonators (aka blasting caps) - must be handled with care. A slight jolt or impact could provide the kinetic energy to initiate an explosion.

5. As discussed in class, the Michaelis-Menten parameters are most accurately determined from a Hanes plot of [S]/*r* versus [S]. Rearrange the Michaelis-Menten equation into the straight-line form for a Hanes plot.

$$\frac{[S]}{r} = \frac{K_M}{r_{\text{max}}} + \frac{1}{r_{\text{max}}}[S]$$

Prepare a table of [S]/r and plot the data. Use least-squares regression to fit a straight line to the data.



$$r_{\text{max}} = \frac{1777 - 62 \sec}{(350 - 0) \times 10^{-6} \text{ mol/L}} = \frac{1}{2.0 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1} \sec^{-1}} = \frac{1}{r_{\text{max}}}$$

$$r_{\text{max}} = 2.0 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1} \sec^{-1}$$
intercept = $\frac{K_{\text{M}}}{r_{\text{max}}} = 62 \sec$

$$K_{\text{M}} = (62 \sec)r_{\text{max}} = (62 \sec)(2.0 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1} \sec^{-1}) = 1.3 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

Similar results obtain from a Lineweaver-Burk plot. Rearranging the Michaelis-Menten equation into the following form provides the straight line on the Lineweaver-Burk plot.

$$\frac{1}{r} = \frac{1}{r_{\max}} + \frac{K_M}{r_{\max}} \frac{1}{[S]}$$

Prepare a table of 1/[S] and 1/r and plot the data. Use least-squares regression to fit a straight line to the data.

[ATP] (10 ⁻⁶ mol/L)	$r (10^{-6} \text{ mol/L/sec})$	1/[ATP] (10 ⁴ L/mol)	1/r (10 ⁷ L sec/mol)
7.5	0.067	13.33	1.49
12.5	0.095	8.00	1.05
20.0	0.119	5.00	0.84
32.5	0.149	3.08	0.67
62.5	0.185	1.60	0.54
155	0.191	0.65	0.52
320	0.195	0.31	0.51



The values for $K_{\rm M}$ and $r_{\rm max}$ differ slightly for the Lineweaver-Burk and Hanes methods. A least-squares fit to a Hanes plot generally yields more accurate Michaelis-Menten constants because the statistical weighting of the data is uniform. See J. Noggle, *Physical Chemistry*, 3rd ed., pp. 578-80.

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6.(A) As with the standard Michaelis-Menten mechanism we assume the third reaction is rate-limiting.

$$\frac{d[\mathbf{P}]}{dt} = k_2[\mathbf{E} \cdot \mathbf{S}] \tag{1}$$

We need to express $[E \cdot S]$ in terms of [S], [I], and $[E]_0$. If we assume the inhibition reaction is at equilibrium we obtain,

$$\frac{k_i}{k_{-i}} = \frac{[I \cdot E \cdot S]}{[I][E \cdot S]}$$
(2)
$$[I \cdot E \cdot S] = K_i [I][E \cdot S], \text{ such that } K_i = \frac{k_i}{k_{-i}}$$
(3)

Because this is a Michaelis-Menten mechanism, we apply the steady-state approximation to the intermediate E·S.

$$\frac{d[E \cdot S]}{dt} = 0 = k_1[E][S] - k_{-1}[E \cdot S] - k_i[I][E \cdot S] + k_{-i}[I \cdot E \cdot S] - k_2[E \cdot S]$$

The equilibrium of the inhibition reaction causes the 3rd and 4th terms on the right to cancel. We thus obtain,

$$0 = k_1[E][S] - k_{-1}[E \cdot S] - k_2[E \cdot S]$$

Solve for $[E \cdot S]$.

$$[E \cdot S] = \frac{k_1}{k_{-1} + k_2} [E][S]$$
(4)

Substitute eqn (4) into eqn (1).

$$\frac{d[\mathbf{P}]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [\mathbf{E}][\mathbf{S}]$$
(5)

We must express [E] in terms of $[E]_0$. Write a mass balance on E.

 $[\mathbf{E}]_0 = [\mathbf{E}] + [\mathbf{E} \cdot \mathbf{S}] + [\mathbf{I} \cdot \mathbf{E} \cdot \mathbf{S}]$

Use eqn (3) substitute for $[I \cdot E \cdot S]$.

$$\begin{bmatrix} \mathbf{E} \end{bmatrix}_0 = \begin{bmatrix} \mathbf{E} \end{bmatrix} + \begin{bmatrix} \mathbf{E} \cdot \mathbf{S} \end{bmatrix} + K_i \begin{bmatrix} \mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{E} \cdot \mathbf{S} \end{bmatrix}$$
$$= \begin{bmatrix} \mathbf{E} \end{bmatrix} + \begin{bmatrix} \mathbf{E} \cdot \mathbf{S} \end{bmatrix} (1 + K_i \begin{bmatrix} \mathbf{I} \end{bmatrix})$$

Use eqn (4) to substitute for $[E \cdot S]$ and solve for [E].

$$[E]_{0} = [E] + \frac{k_{1}[E][S]}{k_{-1} + k_{2}} (1 + K_{i}[I])$$

$$[E] = \frac{[E]_{0}}{1 + \frac{k_{1}}{k_{-1} + k_{2}} [S](1 + K_{i}[I])}$$
(6)

Substitute eqn (6) into eqn (5).

$$\frac{d[\mathbf{P}]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} \frac{[\mathbf{E}]_0}{1 + \frac{k_1}{k_{-1} + k_2}} [\mathbf{S}](1 + K_i[\mathbf{I}])$$

$$\frac{d[\mathbf{P}]}{dt} = \frac{k_1 k_2 [\mathbf{E}]_0 [\mathbf{S}]}{k_{-1} + k_2 + k_1 [\mathbf{S}](1 + K_i[\mathbf{I}])}$$

This is a valid answer. However, it can be simplified further by substituting the Michaelis-Menten constant $K_{\rm M}$,

$$K_{M} = \frac{k_{-1} + k_{2}}{k_{1}}$$

$$\frac{d[\mathbf{P}]}{dt} = \frac{k_{2}[\mathbf{E}]_{0}[\mathbf{S}]}{\frac{k_{-1} + k_{2}}{k_{1}} + [\mathbf{S}](1 + K_{i}[\mathbf{I}])} = \frac{k_{2}[\mathbf{E}]_{0}[\mathbf{S}]}{K_{M} + [\mathbf{S}](1 + K_{i}[\mathbf{I}])}$$

(B) In the limit of no inhibitor, [I] = 0, the rate equation becomes

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_M + [S](1+K_i \times 0)} = \frac{k_2[E]_0[S]}{K_M + [S]}$$

which is the standard rate equation for a Michaelis-Menten reaction. In the limit of inhibition equilibrium shifted strongly toward I $\cdot E \cdot S$, $K_i \rightarrow \infty$,

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_M + [S](1 + \infty \times [I])} = \frac{k_2[E]_0[S]}{\infty} = 0$$

The rate is zero, which would occur if the E·S complexes were completely inhibited from reacting.

(C) Write the rate equation in terms of rate r and maximum rate r_{max} .

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{K_M + [S](1+K_i[I])}$$
$$r = \frac{r_{\max}[S]}{K_M + [S](1+K_i[I])}$$

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Invert the equation and factor in terms of 1/r and 1/[S].

$$\frac{1}{r} = \frac{K_M + [S](1 + K_i[I])}{r_{\max}[S]} = \frac{K_M}{r_{\max}} \frac{1}{[S]} + \frac{1 + K_i[I]}{r_{\max}}$$

With uncompetitive inhibition, the slope of the Lineweaver-Burk plot is independent of [I]. The presence of an uncompetitive inhibitor is revealed by a change in the intercept. For an uncompetitive inhibitor with [I] = 0 (no inhibitor), the intercept is $1/r_{\text{max}}$. For $[I] = 1/K_i$, the intercept is $2/r_{\text{max}}$. For $[I] = 2/K_i$, the intercept is $3/r_{\text{max}}$. A qualitative Lineweaver-Burk plot is shown below.



For a Hanes plot, start with the equation from the Lineweaver-Burk plot and multiply by [S].

$$\frac{[S]}{r} = \frac{K_M}{r_{\text{max}}} + \frac{1 + K_i[I]}{r_{\text{max}}}[S]$$

With uncompetitive inhibition, the intercept of the Hanes plot is independent of [I]. The presence of a uncompetitive inhibitor is revealed by a change in the slope. For an uncompetitive inhibitor with [I] = 0 (no inhibitor), the slope is $1/r_{\text{max}}$. For $[I] = 1/K_i$, the slope is $2/r_{\text{max}}$. For $[I] = 2/K_i$, the slope is $3/r_{\text{max}}$. A qualitative Hanes plot is shown below.



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7.(A) Write a rate equation for X.

$$-\frac{d[\mathbf{X}]}{dt} = k_1[\mathbf{E}][\mathbf{X}] \tag{1}$$

We need to find the time dependence of [E] before we can separate and integrate eqn (1). Write a rate equation for [E].

$$\frac{d[E]}{dt} = -k_1[E][X] + k_2[E \cdot X] - 2k_3[E]^2 + k_4[E \cdot E]$$
(2)

Apply the steady-state approximation to $E \cdot E$ and $E \cdot X$.

$$\frac{d[E \cdot X]}{dt} = 0 = k_1[E][X] - k_2[E \cdot X]$$
(3)
$$\frac{d[E \cdot E]}{dt} = 0 = k_3[E]^2 - k_4[E \cdot E]$$
(4)

Add eqns (3) and (4) to eqn (2)

$$\frac{d[\mathrm{E}]}{dt} = -k_3[\mathrm{E}]^2$$

Separate and integrate.

$$\frac{d[\mathbf{E}]}{[\mathbf{E}]^2} = -k_3 dt$$

$$\int_{[\mathbf{E}]_0}^{[\mathbf{E}]} \frac{d[\mathbf{E}]}{[\mathbf{E}]^2} = -k_3 \int_0^t dt$$

$$-\frac{1}{[\mathbf{E}]} \Big|_{[\mathbf{E}]_0}^{[\mathbf{E}]} = -k_3 t$$

$$\frac{1}{[\mathbf{E}]} - \frac{1}{[\mathbf{E}]_0} = k_3 t$$

$$\frac{1}{[\mathbf{E}]} = \frac{1}{[\mathbf{E}]_0} + k_3 t = \frac{1 + k_3 [\mathbf{E}]_0 t}{[\mathbf{E}]_0}$$

$$[\mathbf{E}] = \frac{[\mathbf{E}]_0}{1 + k_3 [\mathbf{E}]_0 t}$$
(5)

Substitute eqn (5) into eqn (1), then separate and integrate.

$$-\frac{d[X]}{dt} = \frac{k_{1}[E]_{0}[X]}{1+k_{3}[E]_{0}t}$$

$$\frac{d[X]}{[X]} = \frac{-k_{1}[E]_{0}}{1+k_{3}[E]_{0}t}dt$$

$$\int_{[X]_{0}}^{[X]} \frac{d[X]}{[X]} = \int_{0}^{t} \frac{-k_{1}[E]_{0}}{1+k_{3}[E]_{0}t}dt$$

$$\ln[X]|_{[X]_{0}}^{[X]} = \frac{-k_{1}[E]_{0}}{k_{3}[E]_{0}}\ln(1+k_{3}[E]_{0}t)\Big|_{0}^{t}$$

$$\ln\frac{[X]}{[X]_{0}} = \frac{-k_{1}}{k_{3}}[\ln(1+k_{3}[E]_{0}t) - \ln(1)]$$

$$\ln\frac{[X]}{[X]_{0}} = \frac{-k_{1}}{k_{3}}\ln(1+k_{3}[E]_{0}t) \qquad (6)$$

Solve for [X].

$$\frac{[X]}{[X]_0} = \exp\left[\frac{-k_1}{k_3}\ln(1+k_3[E]_0t)\right] = \exp\left[\ln(1+k_3[E]_0t)^{-k_1/k_3}\right] = (1+k_3[E]_0t)^{-k_1/k_3}$$
$$[X] = [X]_0(1+k_3[E]_0t)^{-k_1/k_3}$$
(7)

The most common error on this exercise is an improper mol balance on E. Note that $[E]_0 \neq [E] + [EX] + [EE]$. The amount of enzyme is *not* constant. Rather, a proper mol balance on the enzyme is $[E]_0 = [E] + [EX] + [EE] + \frac{1}{2}([Y] + [Z]) \approx [E] + [Y]$.

(B) At
$$t = 0$$
,

$$[X] = [X]_0 (1)^{-k_1/k_3} = [X]_0$$
 okay

As $t \to \infty$,

$$[X] = [X]_0(\infty)^{-k_1/k_3} = 0$$
 okay

(C) To evaluate the limit $k_3 = 0$, use eqn (6) above.

$$\ln\frac{[X]}{[X]_0} = \frac{-k_1}{k_3}\ln(1+k_3[E]_0t) = \frac{-k_1}{0}\ln(1) = -k_1\frac{0}{0}$$

which is indeterminate. Apply L'Hôpital's rule.

$$\lim_{k_3 \to 0} \frac{-k_1}{k_3} \ln(1 + k_3[\mathbf{E}]_0 t) = -k_1 \lim_{k_3 \to 0} \frac{\frac{d}{dk_3} \ln(1 + k_3[\mathbf{E}]_0 t)}{\frac{d}{dk_3} k_3} = -k_1 \lim_{k_3 \to 0} \frac{\frac{[\mathbf{E}]_0 t}{1 + k_3[\mathbf{E}]_0 t}}{1} = -k_1 [\mathbf{E}]_0 t$$

Thus

$$\ln \frac{[X]}{[X]_0} = -k_1[E]_0 t$$
$$[X] = [X]_0 e^{-k_1[E]_0 t}$$

The system behaves as if the enzyme does not degrade, as expected.

To evaluate the limit $k_3 \rightarrow \infty$, again start with equation (6).

$$\ln \frac{[X]}{[X]_0} = \lim_{k_3 \to \infty} \frac{-k_1}{k_3} \ln(1 + k_3 [E]_0 t) = \frac{-k_1}{\infty} \ln(\infty) = -k_1 \frac{\infty}{\infty}$$

which is indeterminate. Again apply L'Hôpital's rule.

$$\lim_{k_3 \to \infty} \frac{-k_1}{k_3} \ln(1 + k_3[\mathbf{E}]_0 t) = -k_1 \lim_{k_3 \to \infty} \frac{[\mathbf{E}]_0 t}{1 + k_3[\mathbf{E}]_0 t} = -k_1 \frac{[\mathbf{E}]_0 t}{1 + \infty} = 0$$

Thus

$$\ln \frac{[X]}{[X]_0} = 0$$
$$[X] = [X]_0$$

Because the enzyme disappears instantaneously, [X] remains at its initial value, as expected.

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