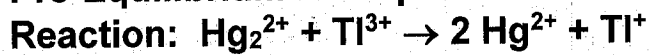
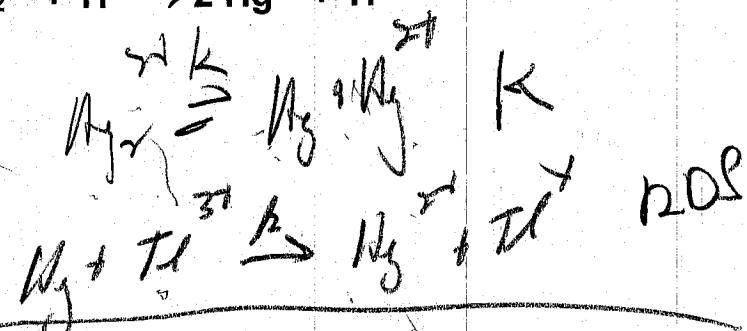


Chap 10
April 18

Pre-Equilibrium Example: Slide #5



$$r = \frac{d[\text{Tl}^+]}{dt} = k' \frac{[\text{Hg}_2^{2+}][\text{Tl}^{3+}]}{[\text{Hg}^{2+}]}$$



$$r = \frac{\Delta[\text{Tl}^+]}{\Delta t}$$

$$= k [\text{Hg}] [\text{Tl}^{3+}]$$

$$= k \left(\frac{K [\text{Hg}_2^{2+}]}{[\text{Hg}^{2+}]} \right) [\text{Tl}^{3+}]$$

$$= \frac{k K [\text{Hg}_2^{2+}] [\text{Tl}^{3+}]}{[\text{Hg}^{2+}]}$$

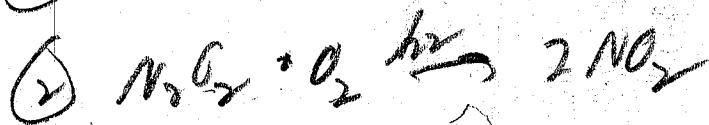
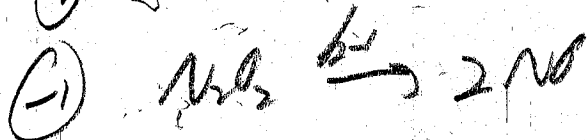
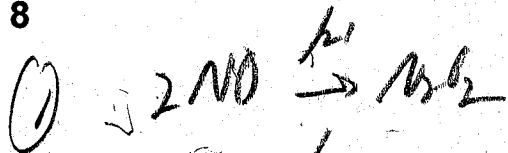
$$= k K [\text{Hg}_2^{2+}] [\text{Tl}^{3+}] [\text{Hg}^{2+}]^{-1}$$

Equl $k = \frac{[\text{Hg}] [\text{Hg}^{2+}]}{[\text{Hg}_2^{2+}]}$

$$[\text{Hg}] = \frac{K [\text{Hg}_2^{2+}]}{[\text{Hg}^{2+}]}$$

Chap 11
April 8

Calculation of $\Delta[\text{N}_2\text{O}_2]/\Delta t$



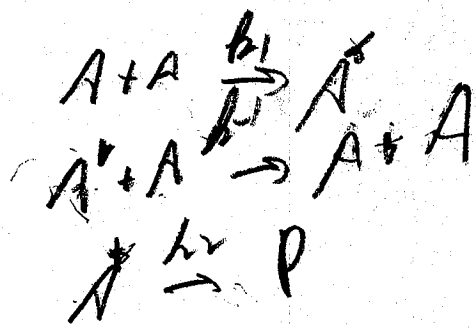
① $\frac{\Delta[\text{N}_2\text{O}_2]}{\Delta t} = +k_1[\text{NO}]^2$

② $\frac{\Delta[\text{N}_2\text{O}_2]}{\Delta t} = -k_2[\text{N}_2\text{O}_2]$

③ $\frac{\Delta[\text{N}_2\text{O}_2]}{\Delta t} = -k_3[\text{N}_2\text{O}_2][\text{O}_2]$

Chap 11
April 23

Rate Law for Unimolecular Reactions: Slides #9 = #10



$$R = \frac{\Delta [P]}{\Delta t} = k_2 [A^*]$$
$$= \frac{k_2 k_1 [A]^2}{k_{-1} [A] + k_2}$$

SS in $[A^*]$

$$0 = \frac{\Delta [A^*]}{\Delta t} = +k_1 [A]^2 + k_{-1} [A^*][A] - k_2 [A^*]$$
$$+k_{-1} [A^*][A] + k_2 [A^*] = k_1 [A]^2$$
$$[A^*] \cdot \{k_{-1} [A] + k_2\} = k_1 [A]^2$$

$$[A^*] = \frac{k_1 [A]^2}{k_{-1} [A] + k_2}$$

Chap. 1
Apr. 25

Lineweaver - Burk Plot

$$V_0 = \frac{V_m [S]}{K_m + [S]}$$

App. \rightarrow $K_m + [S]$ \nearrow Recip.

$$\frac{1}{V_0} = \frac{K_m + [S]}{V_m [S]} = \left(\frac{K_m}{V_m} \right) \left[\frac{1}{[S]} \right] + \frac{1}{V_m}$$

slope \uparrow $\frac{K_m}{V_m}$ $\frac{1}{[S]}$ $\frac{1}{V_m}$

An enzyme catalyzed reaction has the parameters,
 $K_M = 6.8 \times 10^{-5} \text{ M}$, $V_m = 60 \mu\text{M}/\text{min}$, $[S] = 1.5 \times 10^{-4} \text{ M}$

The inhibitor parameters are: $K_i = 1.7 \times 10^{-4} \text{ M}$, $[I] = 3.5 \times 10^{-4} \text{ M}$

(a) Calculate the percent activity and percent inhibition for Competitive inhibition.

$$v_0 = \frac{V_m [S]}{K_M + [S]} = \frac{60 \mu\text{M}}{6.8 \times 10^{-5} + 1.5 \times 10^{-4}} = 41.3 \mu\text{M}/\text{min}$$

$$1 + \frac{[I]}{K_i} = 1 + \frac{3.5 \times 10^{-4}}{1.7 \times 10^{-4}} = 3.06$$

$$(V_0)_i = \frac{V_m [S]}{K_M \left(1 + \frac{[I]}{K_i}\right) + [S]} = \frac{60 \times 1.5 \times 10^{-4}}{6.8 \times 10^{-5} (3.06) + 1.5 \times 10^{-4}}$$

$$(V_0) = 25.1 \mu\text{M}/\text{min}$$

$$\% a = \frac{(V_0)_i}{V_0} \times 100 = \frac{25.1}{41.3} \times 100 = 61\%$$

$$\% i = 100 - 61 = 39\%$$

Chap 11
April 25

Calculation of Percent Inhibition (i%) [Cont'd]
Slide #45

An enzyme catalyzed reaction has the parameters,
 $K_M = 6.8 \times 10^{-5} \text{ M}$, $V_m = 60 \mu\text{M}/\text{min}$, $[S] = 1.5 \times 10^{-4} \text{ M}$

The inhibitor parameters are: $K_i = 1.7 \times 10^{-4} \text{ M}$, $[I] = 3.5 \times 10^{-4} \text{ M}$

(b) Repeat the calculation for Uncompetitive inhibition.

$$V_o = \frac{V_m [S]}{K_M + [S] \left(1 + \frac{[I]}{K_i}\right)}$$

$$= \frac{60 \times 1.5 \times 10^{-4}}{6.8 \times (1.5 \times 10^{-4}) (3.06)} = 17.1 \mu\text{M}/\text{min}$$

$$a\% = \frac{V_o}{V_o} \times 100 = \frac{17.1}{41.3} \times 100 = 41\%$$

$$i\% = 100 - 41 = 59\%$$

$$V_o = 41.3$$

$$\frac{[S]}{K_M} = 3.06$$

Chap 11
April 25

Calculation of Percent Inhibition (i%) [Cont'd]
Slide #45

An enzyme catalyzed reaction has the parameters,
 $K_M = 6.8 \times 10^{-5} \text{ M}$, $V_m = 60 \text{ } \mu\text{M}/\text{min}$, $[S] = 1.5 \times 10^{-4} \text{ M}$

The inhibitor parameters are: $K_i = 1.7 \times 10^{-4} \text{ M}$, $[I] = 3.5 \times 10^{-4} \text{ M}$

(c) Repeat the calculation for Noncompetitive inhibition.

$$V_0 = 41.3 \text{ } \mu\text{M}/\text{min}$$

$$\frac{1.0[S]}{K_i} = 3.06$$

$$(V_0)_i = \frac{V_m [S]}{K_M \left(1 + \frac{[I]}{K_i}\right) \left(1 + \frac{[S]}{K_M}\right)}$$

$$= 60 \times \frac{1.5 \times 10^{-4}}{6.8 \times 10^{-5} (3.06) + 1.5 \times 10^{-4} (3.06)}$$
$$= 13.5 \text{ } \mu\text{M}/\text{min}$$

$$a\% = \frac{(V_0)_i}{V_0} \times 100 = \frac{13.5}{41.3} \times 100 = 33\%$$

$$i\% = 100 - 33 = 67\%$$

An enzyme catalyzed reaction has the parameters,
 $K_M = 6.8 \times 10^{-5} \text{ M}$, $V_m = 60 \text{ } \mu\text{M}/\text{min}$, $[S] = 1.5 \times 10^{-4} \text{ M}$.
 The inhibitor equilibrium constant is $K_I = 1.7 \times 10^{-4} \text{ M}$.

What inhibitor concentration, [I], is required to obtain 60% inhibition?

(a) For Competitive inhibition.

$$a\% = 100 - i\% = 100 - 60 = 40\% = \frac{(V_0)_i}{(V_0)_a} \times 100$$

$$\frac{(V_0)_i}{(V_0)_a} = 0.40$$

$$\frac{(V_0)_a}{(V_0)_i} = \frac{1}{0.40} = 2.5$$

$$\frac{V_0}{(V_0)_i} = 2.5 = \frac{V_m [S]}{K_M (1 + \frac{[I]}{K_I}) + [S]} \cdot \frac{K_M [S]}{V_m [S]}$$

$$\Rightarrow \frac{K_M (1 + \frac{[I]}{K_I}) + [S]}{K_M [S]} = \frac{K_M [S]}{K_M [S]} + \frac{K_M [I]}{K_I [S]}$$

$$= \frac{K_M [S] + \frac{K_M [I]}{K_I}}{K_M [S]} = 1 + \frac{K_M [I]}{K_I [S]}$$

$$= \frac{K_M [S]}{K_M [S]} + \frac{K_M [I]/K_I}{K_M [S]}$$

Calc. $[\Sigma]$
Cape 6. (cont'd.)

$$2.5 = 1 + \frac{K_{in} [\Sigma]}{K_{out} [\Sigma]} = 1 + \frac{6.8 \times 10^{-4} [\Sigma]}{1.7 \times 10^{-4} [\Sigma]} = \frac{6.8 \times 10^{-4} + 6.8 \times 10^{-4}}{1.7 \times 10^{-4}}$$

$$2.5 = 1 + 1835 [\Sigma]$$

$$1.5 = 1835 [\Sigma]$$

$$[\Sigma] = \frac{1.5}{1835} = 8.2 \times 10^{-4} M$$

An enzyme catalyzed reaction has the parameters,
 $K_M = 6.8 \times 10^{-5} \text{ M}$, $V_m = 60 \mu\text{M}/\text{min}$, $[S] = 1.5 \times 10^{-4} \text{ M}$.
 The inhibitor equilibrium constant is $K_i = 1.7 \times 10^{-4} \text{ M}$.

What inhibitor concentration, [I], is required to obtain 60% inhibition?

(b) For Uncompetitive inhibition.

$$i\% = 60\% \quad r\% = 100 - 60 = 40\% = \frac{(V_0)_i}{V_0} \times 100$$

$$\frac{(V_0)_i}{V_0} = 0.40 \rightarrow \frac{V_0}{(V_0)_i} = \frac{1}{0.40} = 2.5$$

$$\frac{V_0}{(V_0)_i} = 2.5 = \frac{\frac{V_m[S]}{K_M + [S]}}{\frac{V_m[S]}{K_M + [S] \left(1 + \frac{[I]}{K_i}\right)}} = \frac{K_M + [S] \left(1 + \frac{[I]}{K_i}\right)}{K_M + [S]}$$

$$2.5 = \frac{K_M + [S] + \frac{[S][I]}{K_i}}{K_M + [S]} = \frac{K_M + [S]}{K_M + [S]} + \frac{[S][I]/K_i}{K_M + [S]}$$

$$2.5 = 1 + \frac{[S][I]/K_i}{K_M + [S]} = 1 + \frac{(1.5 \times 10^{-4}) [I]}{6.8 \times 10^{-5} + 1.5 \times 10^{-4}}$$

$$2.5 = 1 + 4050 [I]$$

$$4050 [I] = 2.5 - 1$$

$$[I] = \frac{1.5}{4050} = 3.7 \times 10^{-4} \text{ M}$$

An enzyme catalyzed reaction has the parameters,
 $K_M = 6.8 \times 10^{-5} \text{ M}$, $V_m = 60 \mu\text{M}/\text{min}$, $[S] = 1.5 \times 10^{-4} \text{ M}$.
 The inhibitor equilibrium constant is $K_I = 1.7 \times 10^{-4} \text{ M}$.

What inhibitor concentration, [I], is required to obtain 60% inhibition?

(c) For Noncompetitive inhibition.

$$\frac{v_0}{(v_0)_i} = 2.5 \quad (\text{from earlier part c.})$$

$$(v_0)_i = \frac{V_m [S]}{K_M \left(1 + \frac{[I]}{K_I}\right) + [S] \left(1 + \frac{[I]}{K_I}\right)}$$

$$2.5 = \frac{V_m [S]}{\left(1 + \frac{[I]}{K_I}\right) (K_M + [S])}$$

$$2.5 = \frac{\cancel{V_m [S]}}{\cancel{K_M + [S]} \left(1 + \frac{[I]}{K_I}\right) (K_M + [S])}$$

$$2.5 = \frac{1 + \frac{[S]}{K_I}}{1 + \frac{[I]}{1.7 \times 10^{-4}}} = 1 + 5880 [I]$$

$$[I] = \frac{2.5 - 1}{5880} = 2.6 \times 10^{-4} \text{ M}$$