Chap 10
April 18

Pre-Equilibrium Example: Slide #5
Reaction: $Hg_2^{2+} + Tl^{3+} \rightarrow 2\,Hg^{2+} + Tl^{+}$

$$r = \frac{d[Tl^+]}{dt} = k'\frac{[Hg_2^{2+}][Tl^{3+}]}{[Hg^{2+}]}$$

$$Hg_2^{2+} \overset{K}{\rightleftharpoons} Hg + Hg^{2+} \qquad K$$

$$Hg + Tl^{3+} \xrightarrow{k} Hg^{2+} + Tl^{+} \qquad RDS$$

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

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

$$= k\left(\frac{K[Hg_2^{2+}]}{[Hg^{2+}]}\right)[Tl^{3+}]$$

$$= \frac{kK[Hg_2^{2+}][Tl^{3+}]}{[Hg^{2+}]} = kK[Hg_2^{2+}][Tl^{3+}][Hg^{2+}]^{-1}$$

Equil $K = \frac{[Hg][Hg^{2+}]}{[Hg_2^{2+}]}$

$$\therefore [Hg] = \frac{K[Hg_2^{2+}]}{[Hg^{2+}]}$$

Chap 11
April 8

Calculation of $\Delta[N_2O_2]/\Delta t$

(1) $2NO \xrightarrow{k_1} N_2O_2$

(-1) $N_2O_2 \xrightarrow{k_{-1}} 2NO$

(2) $N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$

(1) $\frac{\Delta[N_2O_2]}{\Delta t}(1) = +k_1[NO]^2$

(-1) $\frac{\Delta[N_2O_2]}{\Delta t}(-1) = -k_{-1}[N_2O_2]$

(2) $\frac{\Delta[N_2O_2]}{\Delta t}(2) = -k_2[N_2O_2][O_2]$

Chap 11
April 23

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

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightarrow}} A^*$$

$$A^* + A \xrightarrow{k_{-1}} A + A$$

$$A^* \xrightarrow{k_2} P$$

$$R = \frac{\Delta [P]}{\Delta t} = k_2 [A^*]$$

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

SS on $[A^*]$

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

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

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

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

Chap. 11
Apr. 25

Lineweaver - Burk Plot

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

Left → K_m ; ← Right $[S]$

$$\frac{1}{V_0} = \frac{K_m + [S]}{V_m [S]} = \frac{K_m}{V_m}\frac{1}{[S]} + \frac{1}{V_m}$$

↑ slope ($\frac{K_m}{V_m}$)

↑ y int. ($\frac{1}{V_m}$)

Chap 11 **Calculation of Percent Inhibition (i%)**
April 25 **Slide #45**

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

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

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

$$V_0 = \frac{V_m[S]}{K_m + [S]} = 60\,\frac{\mu M}{min}\,\frac{1.5\times10^{-4}}{6.8\times10^{-5} + 1.5\times10^{-4}} = 41.3\ \mu M/min$$

$$1 + \frac{[I]}{K_I} = 1 + \frac{3.5\times10^{-4}}{1.7\times10^{-4}} = 3.06$$

$$(V_0)_i \equiv (V_0)_i = \frac{V_m[S]}{K_m\left(1 + \frac{[I]}{K_I}\right) + [S]} = \frac{60 \times 1.5\times10^{-4}}{6.8\times10^{-5}(3.06) + 1.5\times10^{-4}}$$

$$(V_0)_i = 25.1\ \mu M/min$$

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

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

Chap 11 Calculation of Percent Inhibition (i%) [Cont'd]
April 25 Slide #45

An enzyme catalyzed reaction has the parameters,
$K_M = 6.8x10^{-5}$ M , $V_m = 60$ μM/min , [S] = $1.5x10^{-4}$ M

The inhibitor parameters are: $K_I = 1.7x10^{-4}$ M, [I] = $3.5x10^{-4}$ M

(b) Repeat the calculation for Uncompetitive inhibition.

$V_0 = 41.3$

$1 + \frac{[I]}{K_I} = 3.06$

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

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

$$a\% = \frac{(V_0)_i}{V_0} \times 100 = \frac{17.1}{41.3} \times 100 = 41\%$$

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

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

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

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

(c) Repeat the calculation for Noncompetitive inhibition.

$V_0 = 41.3$ μM/m

$1 + \frac{[I]}{K_I} = 3.06$

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

$$= 60 \times \frac{1.5 \times 10^{-4}}{6.8 \times 10^{-5}(3.06) + 1.5 \times 10^{-4}(3.06)}$$

$= 13.5$ μM/m

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

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

Chap 11 Calculation of [I] needed for specific i%
April 25 Slide #46

An enzyme catalyzed reaction has the parameters,
$K_M = 6.8\times10^{-5}$ M , $V_m = 60$ µM/min , [S] = 1.5×10^{-4} M.
The inhibitor equilibrium constant is $K_I = 1.7\times10^{-4}$ M.

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

(a) For Competitive inhibition.

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

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

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

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

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

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

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

Calc. of [I]

Cap 6. (Cont'd.)

$$2.5 = 1 + \frac{\frac{K_m [I]}{K_I}}{K_m + [S]} = 1 + \frac{\frac{6.8\times10^{-4}}{1.7\times10^{-4}}[I]}{6.8\times10^{-5} + 1.5\times10^{-4}}$$

$$2.5 = 1 + 1835[I]$$

$$1.5 = 1835[I]$$

$$[I] = \frac{1.5}{1835} = 8.2\times10^{-4}\,M$$

Chap 11 — Calculation of [I] needed for specific i% [Cont'd]

April 27 — Slide #46

An enzyme catalyzed reaction has the parameters,
$K_M = 6.8\times10^{-5}$ M , $V_m = 60$ μM/min , [S] = 1.5×10^{-4} M.
The inhibitor equilibrium constant is $K_I = 1.7\times10^{-4}$ M.

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

(b) For Uncompetitive inhibition.

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

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

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

$$2.5 = \frac{(K_m + [S]) + \frac{[S][I]}{K_I}}{K_m + [S]} = \frac{K_m + [S]}{K_m + [S]} + \frac{[S][I]/K_I}{K_m + [S]}$$

$$2.5 = 1 + \frac{\frac{[S][I]}{K_I}}{K_m + [S]} = 1 + \frac{\frac{(1.5\times10^{-4})[I]}{1.7\times10^{-4}}}{6.8\times10^{-5} + 1.5\times10^{-4}}$$

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

$$4050[I] = 2.5 - 1 \quad [I] = \frac{1.5}{4050} = 3.7\times10^{-4}\ M$$

Chap 11 **Calculation of [I] needed for specific i% [Cont'd]**
April 27 **Slide #46**

An enzyme catalyzed reaction has the parameters,
$K_M = 6.8\times10^{-5}$ M , $V_m = 60\ \mu$M/min , [S] = 1.5×10^{-4} M.
The inhibitor equilibrium constant is $K_I = 1.7\times10^{-4}$ M.

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

(c) For Noncompetitive inhibition.

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

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

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

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

$$2.5 = 1+\frac{[I]}{K_I} = 1+\frac{[I]}{1.7\times10^{-4}} = 1+5880[I]$$

$$[I] = \frac{2.5-1}{5880} = 2.6\times10^{-4}\ M$$