# Lecture # 19 CHE331A

Design/Analysis of Isothermal Reactors

Collection & Analysis of Data; Isothermal Reactor Design for Multiple Reactions

**Nonelementary Homogeneous Reactions: *Active intermediates, PSSH & Chain Reactions***

**Nonelementary Homogeneous Reactions: Active intermediates, PSSH, Thermal Cracking & Michaelis-Menten kinetics**

**Michaelis-Menten kinetics: Its constants, parameter determination, and various forms**

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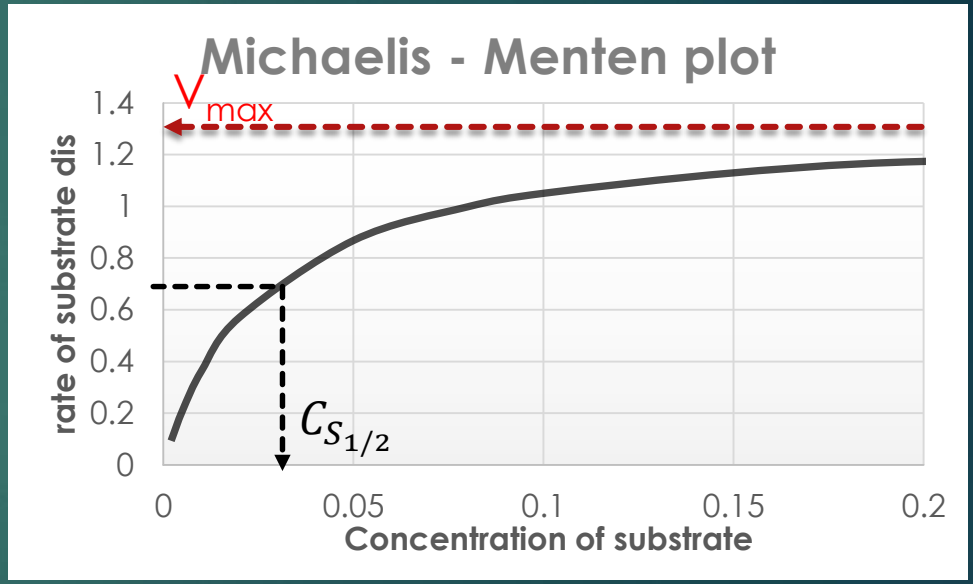
# The Michaelis – Menten equation

- $-\boldsymbol{r_S}= \frac{k_{cat} C_{E_t} C_S}{C_S + K_M}$ is a form of the Michaelis – Menten equation and contains two constants, $k_{cat}$ and $K_M$
- $k_{cat}$ is referred to as the *turnover number*
  - Is the number of substrate molecules converted in a given time on a single enzyme molecule when the enzyme is saturated with substrate, $C_S \gg K_M$
- $K_M$ (mol/dm$^3$) is the Michaelis constant and is a measure of the attraction of the enzyme for its substrate, also called affinity constant
- Further, with $V_{max}$ representing the maximum rate for a given $C_{E_t}$
- Then, $V_{max} = k_{cat} C_{E_t}$ and the Michaelis – Menten equation becomes

$$-\boldsymbol{r_S}= \frac{V_{max} C_S}{K_M + C_S}$$

# The Michaelis – Menten equation and its constants

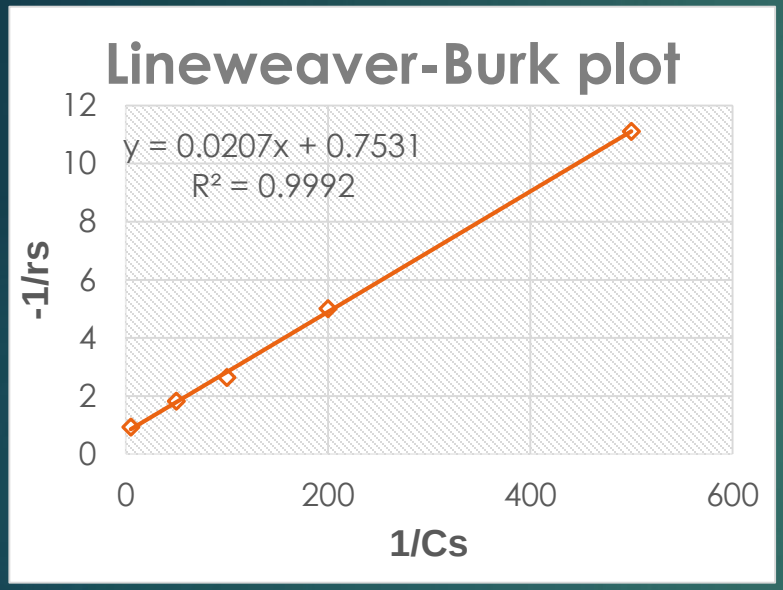
- The Michaelis – Menten equation $-\boldsymbol{r_S} = \frac{V_{max} C_S}{K_M + C_S}$
- At low $C_S$, $K_M \gg C_S$ $\quad -\boldsymbol{r_S} \cong \frac{V_{max} C_S}{K_M}$
  - Apparent 1st order in S
- At high $C_S$, $K_M \ll C_S$ $\quad -\boldsymbol{r_S} \cong V_{max}$
  - Apparent 0 order in S
- If the $C_S$ is such that the $-r_S = 0.5 V_{max}$
- Then, $0.5 V_{max} = \frac{V_{max} C_{S_{1/2}}}{K_M + C_{S_{1/2}}}$ and $K_M = C_{S_{1/2}}$
- The two constants, $V_{max}$ and $K_M$, characterize the enzymatic reaction

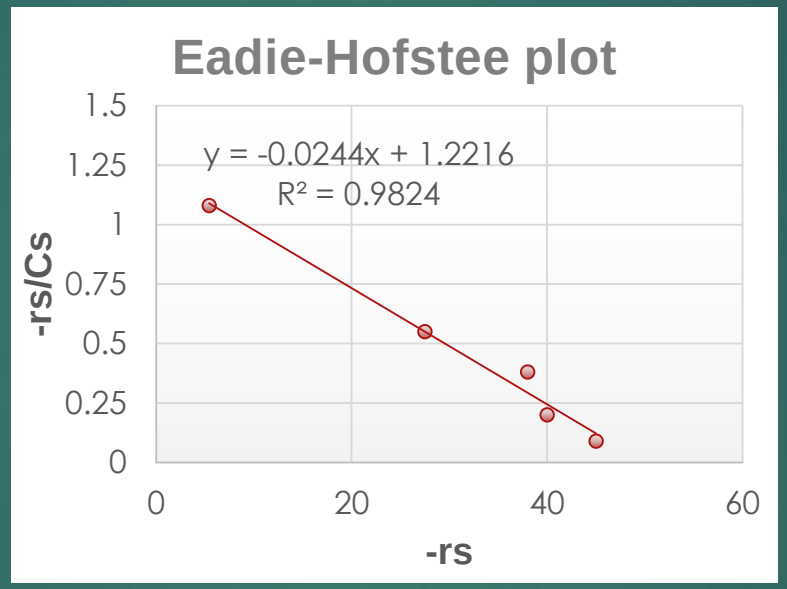


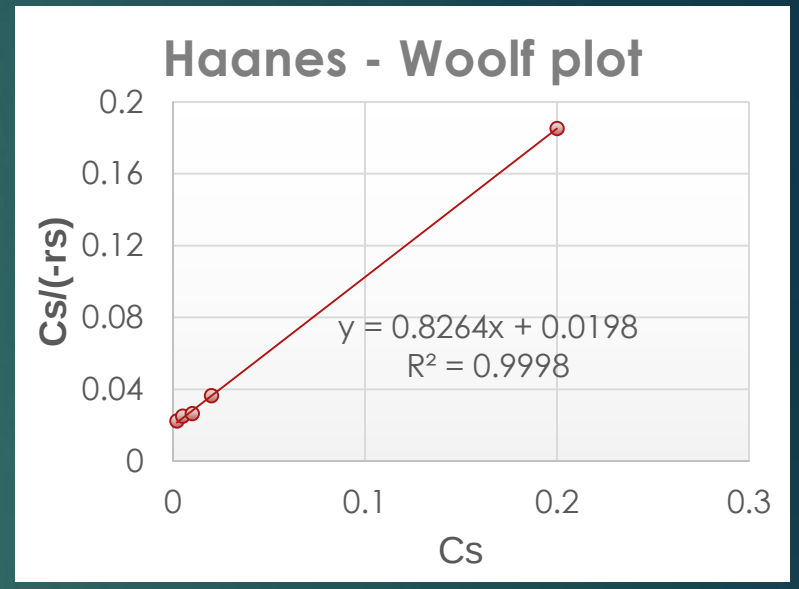
# Finding the parameters (constants) of the Michaelis – Menten equation

- Constants for the Michaelis – Menten equation $-\boldsymbol{r_S} = \frac{V_{max} C_S}{K_M + C_S}$ are found by linearizing the equation and using data for $-\boldsymbol{r_S}$ vs. $C_S$
- Three ways this can be done
  - $\frac{1}{-\boldsymbol{r_S}} = \frac{1}{V_{max}} + \frac{K_M}{V_{max}}\left(\frac{1}{C_S}\right)$ Lineweaver – Burk form: plot $\frac{1}{-\boldsymbol{r_S}}$ vs. $\frac{1}{C_S}$
  - $-\boldsymbol{r_S} = V_{max} - K_M\left(\frac{-r_S}{C_S}\right)$ Eadie – Hofstee form: plot $-\boldsymbol{r_S}$ vs. $\frac{-r_S}{C_S}$
  - $\frac{C_S}{-\boldsymbol{r_S}} = \frac{K_M}{V_{max}} + \frac{1}{V_{max}}(C_S)$ Hanes – Woolf form: plot $\frac{C_S}{-r_S}$ vs. $C_S$
- $V_{max}$ and $K_M$ are determined from the slope and intercept (example 7-3)

# Finding the parameters (constants) of the Michaelis – Menten equation




- From the slope and intercept the values of $V_{max}$ and $K_M$ can be determined
- These values can be used as initial guesses for non-linear regression

# Rate laws can be developed for different enzymatic mechanisms

- Product formation is reversible: $E + S \rightleftharpoons E.S \rightleftharpoons P + E$
  - last step is reversible instead of being irreversible, $S \rightleftharpoons P$
  - $-\boldsymbol{r_S} = \frac{V_{max}\left(C_S - {C_P}/{K_C}\right)}{K_M + C_S + K_P C_P}$
- Inhibition of Enzyme reactions: Inhibitor given as species ***I***
  - Competitive inhibition $E + S \rightleftharpoons E.S \rightarrow P + E$ & $E + I \rightleftharpoons E.I\ (inactive)$
  - Uncompetitive inhibition $E + S \rightleftharpoons E.S \rightarrow P + E$ & $E.S + I \rightleftharpoons E.S.I\ (inactive)$
  - Noncompetitive inhibition: competitive & $E.S + I \rightleftharpoons E.S.I\ (inactive)$ & $E.I + S \rightleftharpoons E.S.I\ (inactive)$
- Rate laws developed using PSSH (also quasi-equilibrium approach)