

Updated: 19 November 2013

CEE 679 Kinetics Lecture #19 1

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CEE 697K

ENVIRONMENTAL REACTION KINETICS

Lecture #19

[Chloramines Cont:](#) Primary Literature
[Enzyme Kinetics:](#) basics
Brezonik, pp. 419-450

David A. Reckhow Introduction

Conclusions

2

- *“Overall the model calculations suggest that biodegradation is.....not likely to play a major role in most water distribution systems”*
 - *“the conditions needed for significant HAA removals in a distribution system (i.e., total biomass densities $> 10^5$ cells/cm² over long distances of pipe) are unlikely in the US water distribution systems where total chlorine residuals typically are high and thus inhibit the development of biofilm on pipe walls”*

But this seems to contradict their introductory conclusion - how to reconcile?

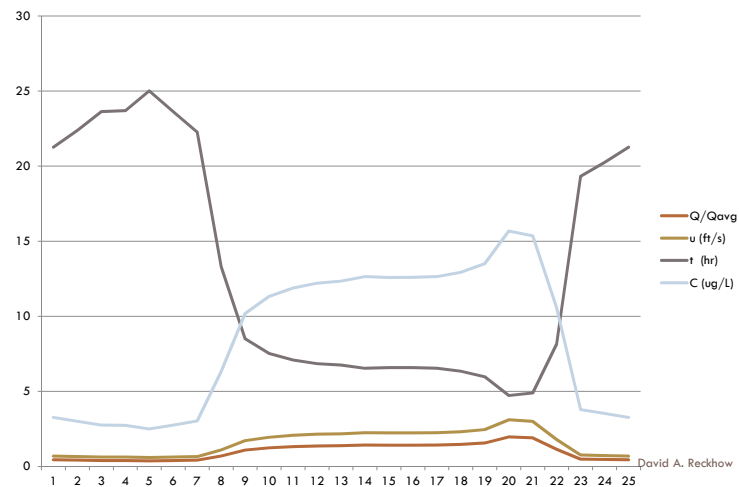
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What could they have concluded?

3

□ Variability vs diurnal demand



Objective/hypothesis

4

- Not really stated, but they did end the intro with:
 - “In this work, computer simulations were performed to predict the fate of three HAAs (MCAA, DCAA, and TCAA) along a distribution system and within a biologically active filter. Sensitivity analyses were performed to investigate the effects of physical parameters (e.g., fluid velocity) and biological parameters (e.g., biodegradation kinetics, biomass density) on HAA removal”

What could they have said?

5

- To determine if observed HAA loss could be attributed to biodegradation on pipe walls given known physical and microbial characteristics of distribution systems
- To estimate spatial and temporal variability of HAA concentrations based on a rational physical model of biodegradation in distribution systems

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What could they have done?

6

- Find some direct evidence for biodegradation of HAAs in distribution systems
 - A product of the enzymatic reaction?
 - Chlorohydroxyacetate?
- Evidence of abiotic reactions?
 - Increase in MCAA?

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What else?

7

- Consider mass transfer resistance within biofilm

Biofilm formation:

Attachment	Colonization	Growth

BULK FLUID

SURFACE

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1 2 3 4 5

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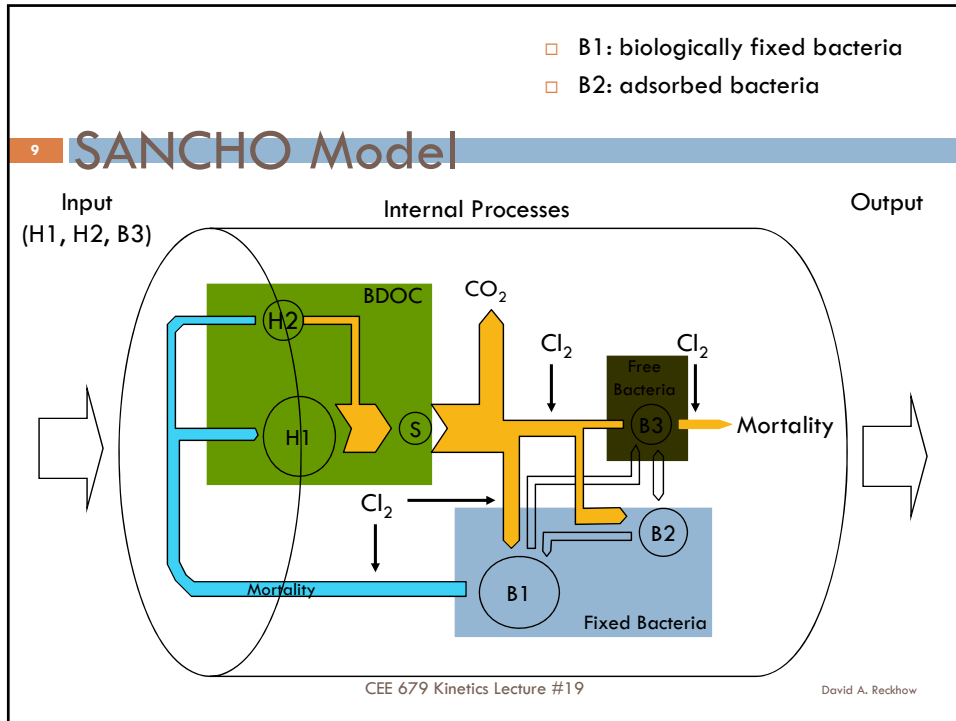
What should be done next?

8

- Experimental Work
 - In-situ controlled study of flow velocity vs DCAA loss in a pipe segment?
 - Effect of biocide in above segment?
- Model Refinement
 - Account for internal mass transfer resistance
 - Combine with growth model for HAA degraders

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10

TABLE 2 Summary of equations used to compute the mass transfer rate constants for the distribution system and biologically active filter

Distribution System	Biologically Active Filter	Notation
$Sh = \frac{0.023 Re^{0.83}}{Sc^{0.33}}$ $k_m = \frac{Sh D_w}{d}$	$Sh = 1.09 \epsilon^{-2/3} Re^{1/3} Sc^{1/3}$ $k_m = \frac{Sh D_w}{d_p}$	d = pipe diameter d_p = filter media grain diameter D_w = solute diffusion coefficient in water k_m = mass transfer rate constant
$Sc = \frac{\mu_w}{\rho_w D_w}$	$Sc = \frac{\mu_w}{\rho_w D_w}$	Re = Reynolds number Sc = Schmidt number
$Re = \frac{d u \rho_w}{\mu_w}$	$Re = \frac{d_p v \rho_w}{(1 - \epsilon) \mu_w}$	Sh = Sherwood number u = water flow velocity v = filtration rate ϵ = bed porosity μ_w = water viscosity at 20°C ρ_w = water density at 20°C

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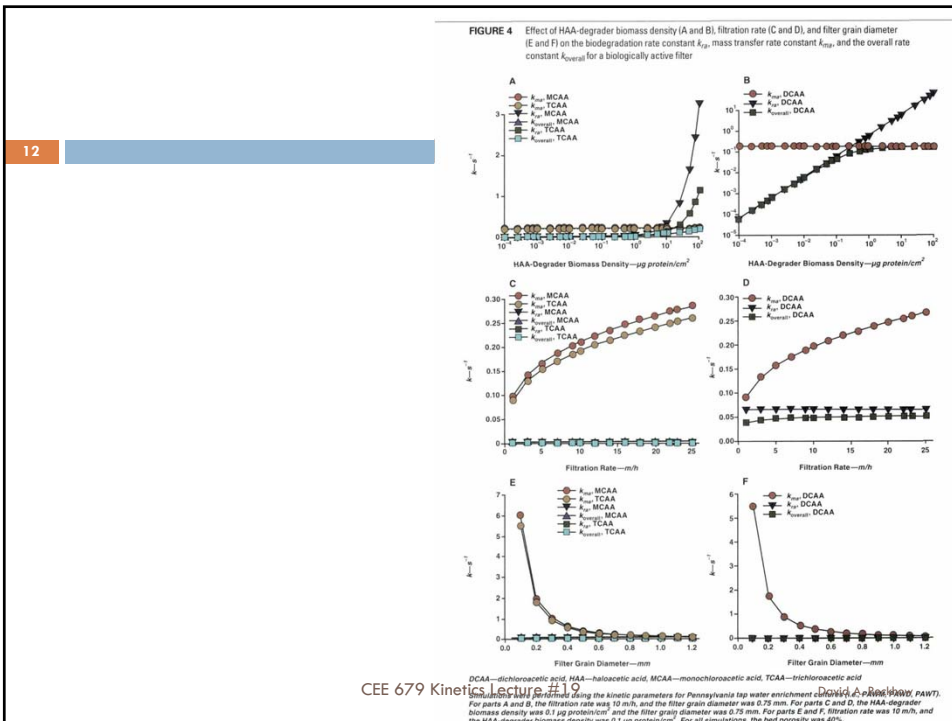
TABLE 3 General parameter values used for the model calculations

Parameter	Symbol	Value	References/Observations
Water temperature	T	20°C	Simulated summer conditions
Water viscosity	$\mu_w, 20^\circ\text{C}$	$1.0087 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$	Reynolds & Richards, 1996
Water density	$\rho_w, 20^\circ\text{C}$	998.2 kg m^{-3}	Reynolds & Richards, 1996
Diffusion coefficient of MCAA in water	$D_{w,MCAA}$	$1.12 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$	Zhang et al, 2004
Diffusion coefficient of DCAA in water	$D_{w,DCAA}$	$1.02 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$	Zhang et al, 2004
Diffusion coefficient of TCAA in water	$D_{w,TCAA}$	$9.75 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$	Zhang et al, 2004

DCAA—dichloroacetic acid, MCAA—monochloroacetic acid, TCAA—trichloroacetic acid

TABLE 4 Parameter values used to simulate the fate of haloacetic acids in water distribution systems

Parameter	Symbol	Range	References
Total bacterial density on the pipe wall	ρ	$10-10^8 \text{ cells/cm}^2$; 10^7 cells/cm^2 for simulations in which other parameters were varied	Silhan et al, 2006; Lehtola et al, 2004; Chang et al, 2003; Ollos et al, 2003; Zhang et al, 2002; Niquette et al, 2000; Donlan & Pipes, 1988; LeChevalier et al, 1987
Pipe diameter	d	2–36 in.; 6 in. for simulations in which other parameters were varied	McGhee, 1991; Rhoades, 1986
Water flow velocity	u	0.1–4 fps; 2 fps for simulations in which other parameters were varied	McGhee, 1991
Pipe distance	x	0–100 mi; 10 mi for simulations in which other parameters were varied	David A. Reckhow



Effect of Zn on HAAs

13

- Effect of Zinc on the Transformation of HAAs in Drinking Water
 - Wei Wang and Lizhong Zhu
 - Journal of Hazardous Materials 174:40-46.

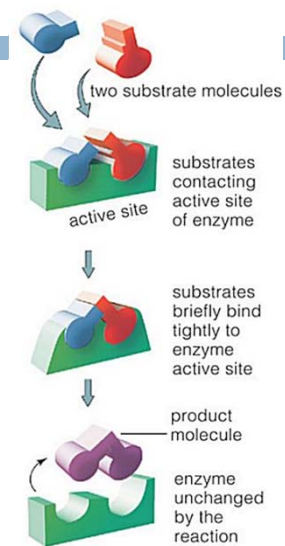
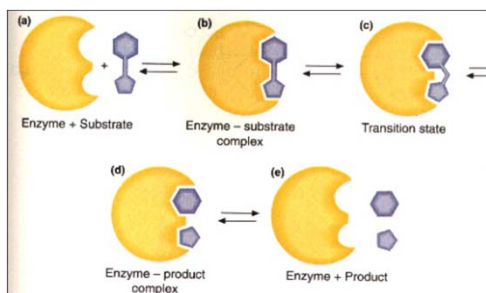
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Enzymatic Reactions

14

- Many ways of illustrating the steps
 - Substrate(s) bond to active site
 - Product(s) form via transition state
 - Product(s) are released



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Basic Enzyme Kinetics

15

□ Irreversible

□ Single intermediate

- The overall rate is determined by the RLS, k_2

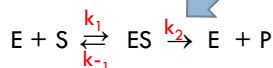
$$r \equiv -\frac{d[S]}{dt} = \frac{d[P]}{dt} = k_2[ES]$$

- But we don't know $[ES]$, so we can get it by the SS mass balance

$$\frac{d[ES]}{dt} = 0 = k_1[E][S] - k_{-1}[ES] - k_2[ES]$$

- Again, we only know $[E_0]$ or $[E_{tot}]$, not free $[E]$, so:

$$0 = k_1([E_0] - [ES])[S] - k_{-1}[ES] - k_2[ES]$$



Note that some references use k_2 for k_{-1} , and k_3 for k_2

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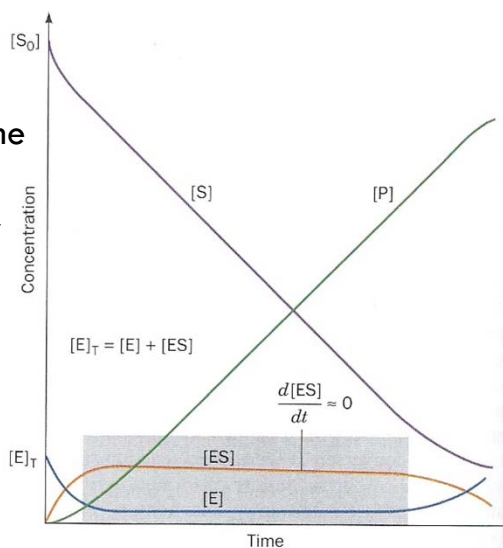
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Reactants, products and Intermediates

16

□ Simple Progression of components for simple single intermediate enzyme reaction

- Shaded block shows steady state intermediates
- Assumes $[S] \gg [E]_t$
- From Segel, 1975; Enzyme Kinetics



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Basic Enzyme Kinetics II

17

- And solving for [ES],

$$k_1[ES][S] + k_{-1}[ES] + k_2[ES] = k_1[E_o][S]$$

$$[ES] = \frac{k_1[E_o][S]}{k_1[S] + k_{-1} + k_2}$$

$$[ES] = \frac{[E_o][S]}{[S] + \frac{k_{-1} + k_2}{k_1}}$$

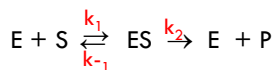
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Michaelis-Menten

18

- Irreversible



- Single intermediate

$$r \equiv \frac{d[P]}{dt} = k_2[ES]$$



$$[ES] = \frac{[E_o][S]}{[S] + \frac{k_{-1} + k_2}{k_1}}$$

$$r \equiv \frac{d[P]}{dt} = \frac{k_2[E_o][S]}{\frac{k_{-1} + k_2}{k_1} + [S]} = \frac{r_{\max}[S]}{K_s + [S]}$$

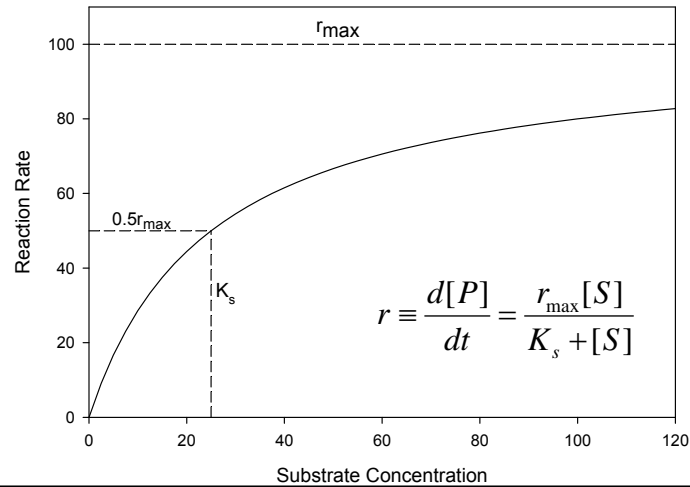
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Michaelis Menten Kinetics

19

- Classical substrate plot



Substrate and growth

20

- If we consider Y $r \equiv \frac{d[P]}{dt} = -\frac{d[S]}{dt} = \frac{1}{Y} \frac{dX}{dt}$

- We can define a microorganism-specific substrate utilization rate, U

$$U \equiv \frac{r}{X} = \frac{\frac{dX}{dt}}{YX} \equiv \frac{\mu}{Y}$$

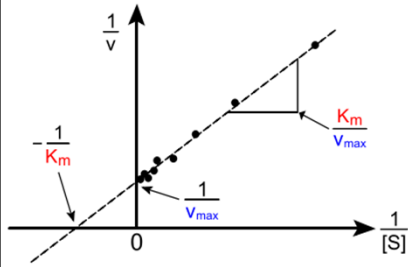
- And the maximum rates are then $U_{\max} \equiv k \equiv \frac{\mu_{\max}}{Y}$

$$U \equiv \frac{1}{X} \frac{d[S]}{dt} = \frac{k[S]}{K_s + [S]} \quad \text{and} \quad \mu \equiv \frac{1}{X} \frac{d[X]}{dt} = \frac{\mu_{\max} [S]}{K_s + [S]}$$

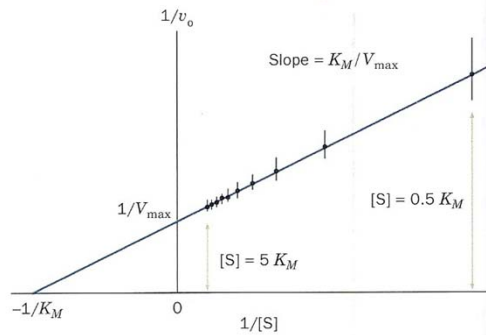
Linearizations

21

- Lineweaver-Burke
 - Double reciprocal plot



Wikipedia version



Voet & Voet version

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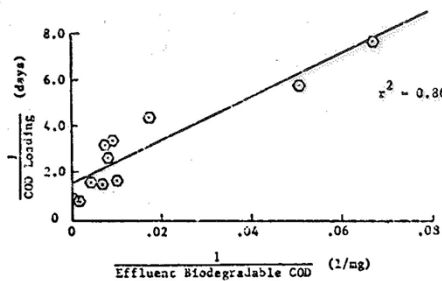
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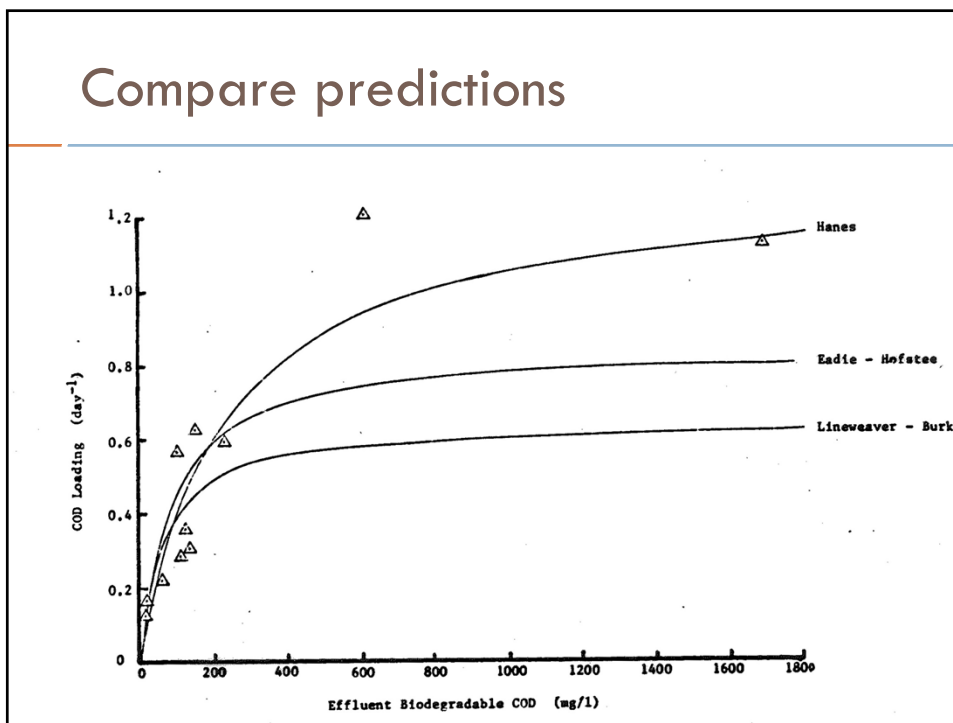
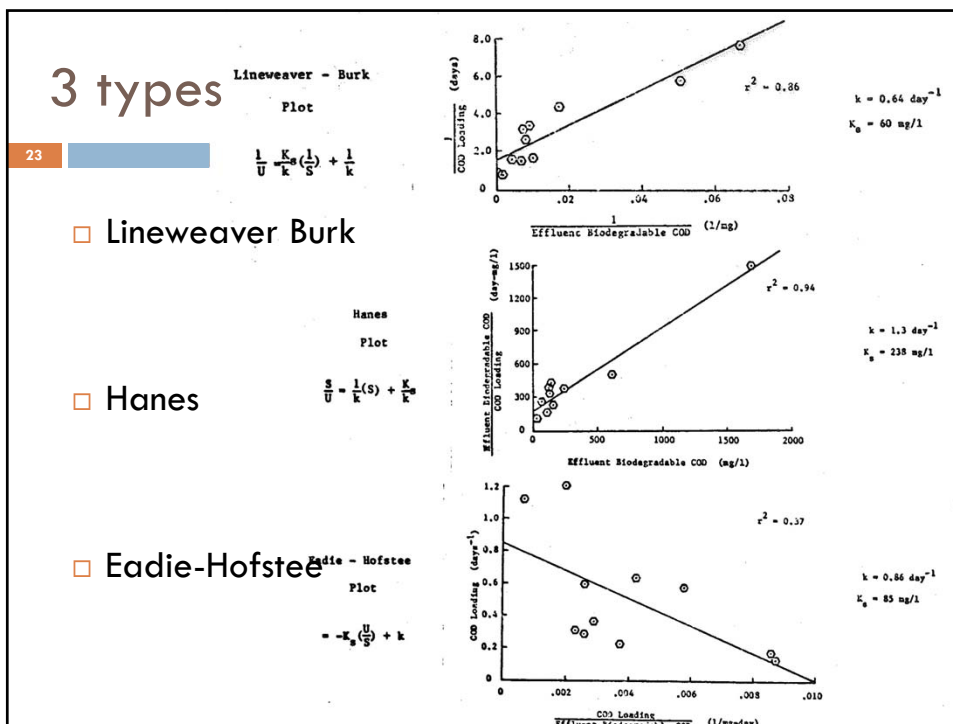
Lineweaver - Burk
Plot

$$\frac{1}{U} = \frac{K_s}{k} \left(\frac{1}{S} \right) + \frac{1}{k}$$

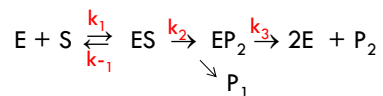


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Multi-step



25

□ Double intermediate

- Also gives:

$$r \equiv \frac{d[P]}{dt} = \frac{r_{\max}[S]}{K_s + [S]}$$



- But now:

$$r_{\max} = \frac{k_2 k_3 [E_0]}{k_2 + k_3} \quad K_s = \frac{k_3 (k_{-1} + k_2)}{(k_2 + k_3) k_1}$$

- Note what happens when: $k_3 \gg k_2$

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26

□ To next lecture

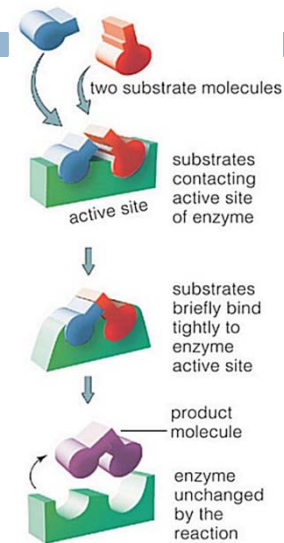
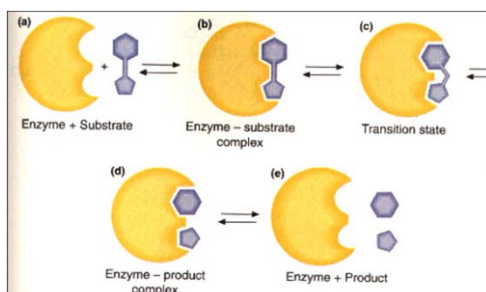
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Enzymatic Reactions

27

- Many ways of illustrating the steps
 - ▣ Substrate(s) bond to active site
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Basic Enzyme Kinetics

28

- Irreversible

- ▣ Single intermediate

- The overall rate is determined by the RLS, k_2

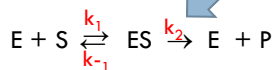
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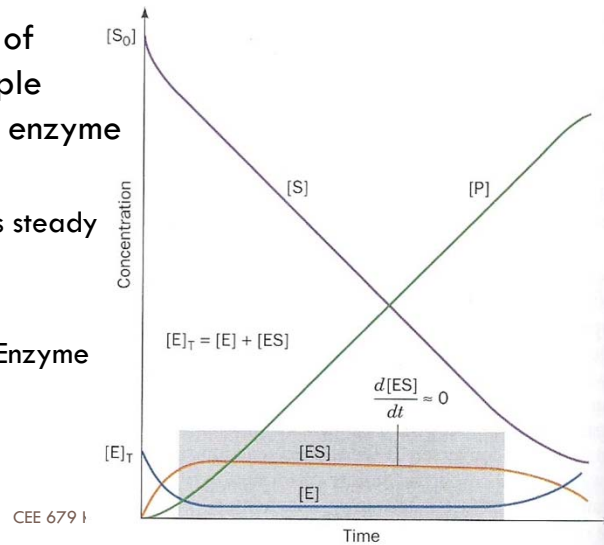
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Reactants, products and Intermediates

29

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- Assumes $[S] \gg [E]_T$
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Basic Enzyme Kinetics II

30

- And solving for $[ES]$,

$$k_1[ES][S] + k_{-1}[ES] + k_2[ES] = k_1[E_o][S]$$

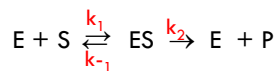
$$[ES] = \frac{k_1[E_o][S]}{k_1[S] + k_{-1} + k_2}$$

$$[ES] = \frac{[E_o][S]}{[S] + \frac{k_{-1} + k_2}{k_1}}$$

Michaelis-Menten

31

□ Irreversible



□ Single intermediate

$$r \equiv \frac{d[P]}{dt} = k_2[ES]$$

$$[ES] = \frac{[E_o][S]}{[S] + \frac{k_{-1} + k_2}{k_1}}$$

$$r \equiv \frac{d[P]}{dt} = \frac{k_2[E_o][S]}{\frac{k_{-1} + k_2}{k_1} + [S]} = \frac{r_{\max}[S]}{K_s + [S]}$$

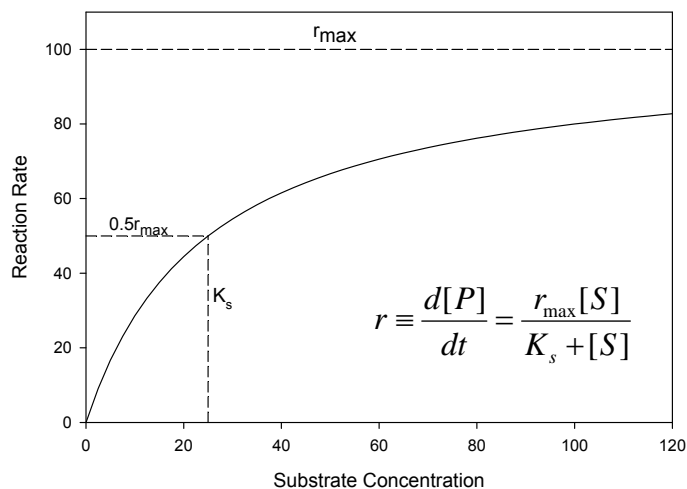
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Michaelis Menten Kinetics

32

□ Classical substrate plot



Substrate and growth

33

□ If we consider Y
$$r \equiv \frac{d[P]}{dt} = -\frac{d[S]}{dt} = \frac{1}{Y} \frac{dX}{dt}$$

□ We can define a microorganism-specific substrate utilization rate, U

$$U \equiv \frac{r}{X} = \frac{\frac{dX}{dt}}{YX} \equiv \frac{\mu}{Y}$$

□ And the maximum rates are then
$$U_{\max} \equiv k \equiv \frac{\mu_{\max}}{Y}$$

$$U \equiv \frac{1}{X} \frac{d[S]}{dt} = \frac{k[S]}{K_s + [S]} \quad \text{and} \quad \mu \equiv \frac{1}{X} \frac{d[X]}{dt} = \frac{\mu_{\max}[S]}{K_s + [S]}$$

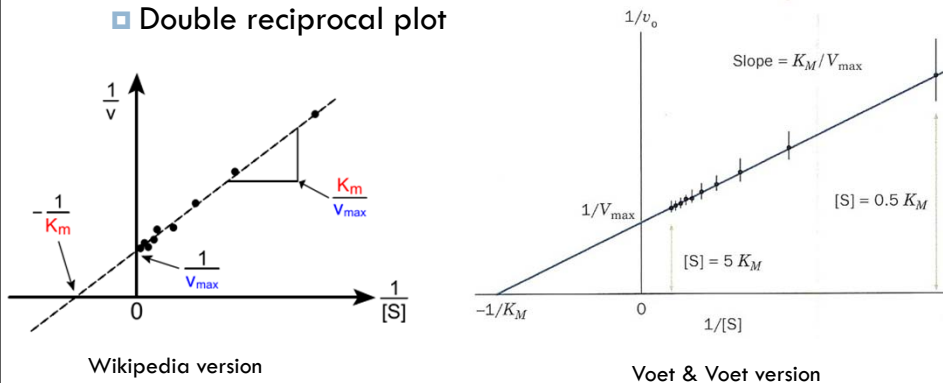
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Linearizations

34

- Lineweaver-Burke
 - Double reciprocal plot



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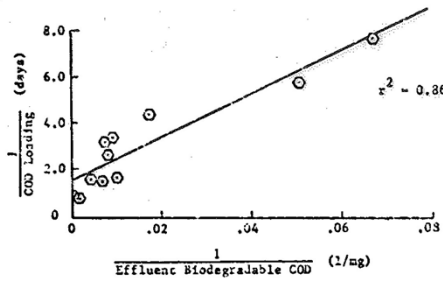
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35

□ das

Lineweaver - Burk Plot

$$\frac{1}{U} = \frac{K_s}{k} \left(\frac{1}{S} \right) + \frac{1}{k}$$



$k = 0.64 \text{ day}^{-1}$
 $K_s = 60 \text{ mg/l}$

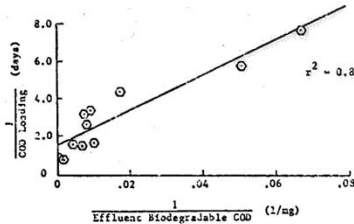
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3 types

Lineweaver - Burk Plot

$$\frac{1}{U} = \frac{K_s}{k} \left(\frac{1}{S} \right) + \frac{1}{k}$$



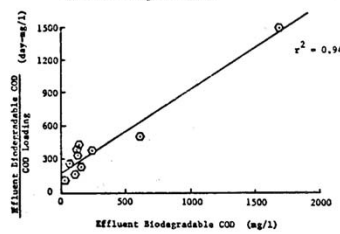
$k = 0.64 \text{ day}^{-1}$
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□ Lineweaver Burk

Hanes Plot

□ Hanes

$$\frac{U}{S} = \frac{1}{K} (S) + \frac{k}{K}$$

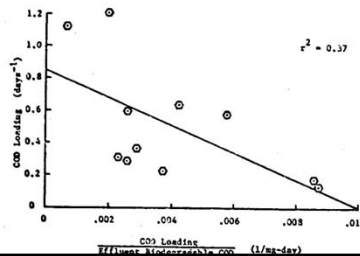


$k = 1.3 \text{ day}^{-1}$
 $K_s = 238 \text{ mg/l}$

□ Eadie-Hofstee

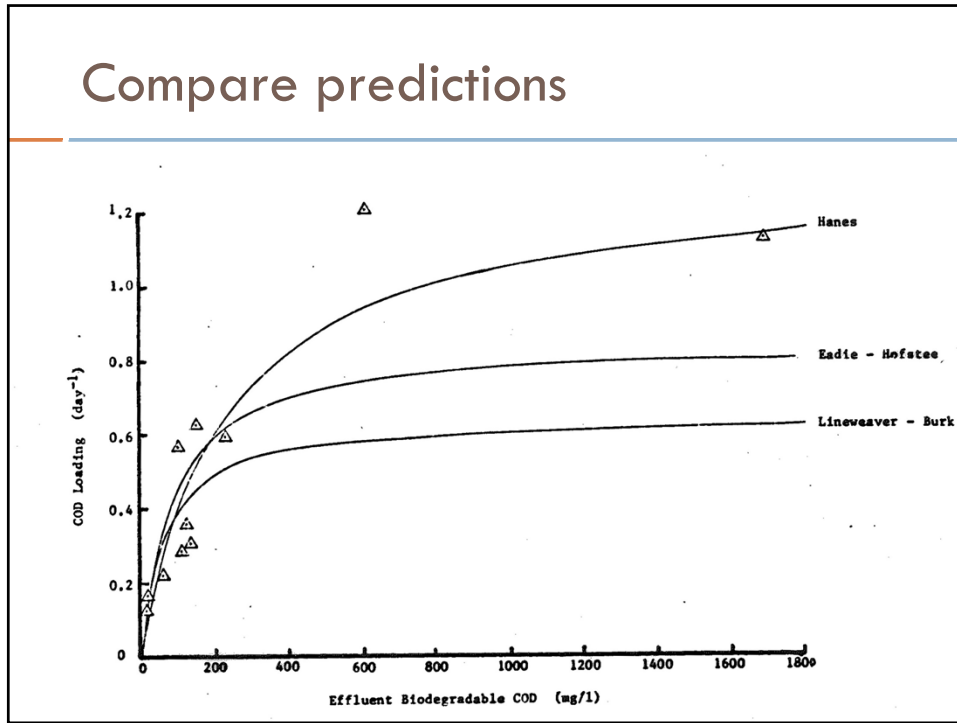
Eadie - Hofstee Plot

$$-K_s \left(\frac{U}{S} \right) + k$$

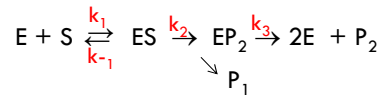


$k = 0.86 \text{ day}^{-1}$
 $K_s = 85 \text{ mg/l}$

Compare predictions



Multi-step



38

Double intermediate

- Also gives:

$$r \equiv \frac{d[P]}{dt} = \frac{r_{\max}[S]}{K_s + [S]}$$



- But now:

$$r_{\max} = \frac{k_2 k_3 [E_o]}{k_2 + k_3} \quad K_s = \frac{k_3 (k_{-1} + k_2)}{(k_2 + k_3) k_1}$$

- Note what happens when: $k_3 \gg k_2$

39

□ To next lecture