# ChE 344
# Reaction Engineering and Design

Lecture 23: Thur, Apr 7, 2022

Quasi-equilibrium, rate-determining step, heterogeneous catalysis

Reading for today's Lecture: Chapter 10

*Reading for Lecture 24: Chapter 10*

**Lecture 23: Enzyme review; quasi-equilibrium and rate-determining step + heterogeneous catalysis**
**Related Text: Chapter 10**

Quasi-equilibrium: A given step can rapidly equilibrate with respect to other steps in the same mechanism. Result is that you can say the net rate of that step is approximately zero. Can be applied to reversible or irreversible step.

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

Here we can apply QE to the second step, essentially saying $C_B$ must be zero.

$$r_2 = k_2 C_B \approx 0$$

Then the other concentrations can be solved for a batch reactor:

$$C_A = C_{A0} e^{-k_1 t}$$

$$C_C = C_{A0}\left(1 - e^{-k_1 t}\right)$$

Rate-determining step: The "slowest" step such that other steps are assumed to be at quasi-equilibrium. We could possibly apply it to a heterogeneous catalyst reaction mechanism:

$$A + * \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A* \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} B* \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} B + *$$

where * is an active catalyst site, A* is A bound to the catalyst site, and B* is bound to the catalyst site. If step 2 is the rate-determining step, and we assume once B is formed it cannot go back to A:

$$A + * \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A* \overset{k_2}{\rightarrow} B + *$$

Assuming QE on the first adsorption:

$$K_{A,ads} = \frac{k_1}{k_{-1}} = \frac{[A*]}{C_A[*]}$$

And the rate of the second step is:

$$r_B = k_2[A*]$$

Catalyst site balance:

$$[*]_0 = [*] + [A*]$$

Define coverage:

$$\theta_A \equiv \frac{[A*]}{[*]_0};\ \theta_* \equiv \frac{[*]}{[*]_0}$$

$$\theta_A = \frac{K_{A,ads}C_A[*]}{[*]_0} = \frac{K_{A,ads}C_A[*]}{[*] + [A*]} = \frac{K_{A,ads}C_A[*]}{[*] + K_{A,ads}C_A[*]} = \frac{K_{A,ads}C_A}{1 + K_{A,ads}C_A}$$

We can write the rate as:

$$\frac{r}{[*]_0} = k_2 \frac{K_{A,ads}C_A}{1 + K_{A,ads}C_A}$$

This is the rate law with an irreversible unimolecular surface reaction as the rate-determining step.

Note: M-M kinetics, this is not actually M-M mechanism

$v$ = r/$C_{E,total}$

$$E + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} EA \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} EB \xrightarrow{k_3} E + B$$

$$v = \frac{v_M C_A}{C_A + K_M}$$ Michelis-Menten eqn/kinetics have this form

Caution: In real life, just because data fits rate law does not mean mechanism is correct

Why use turnover frequency vs. total reaction rate (e.g. $r_P$)? Total reaction rate is generally used for reactor design, turnover frequency is usually used when you are trying to find how "good" a catalyst is. Turnover frequency makes it so the performance doesn't depend on amount of catalyst, so you get a better sense of each catalyst molecule's activity.

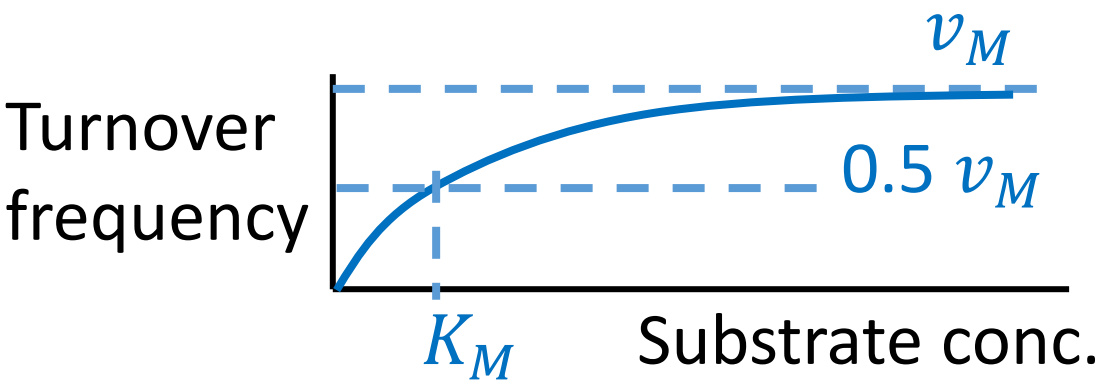
Special case is the Briggs-Haldane mechanism:

$$E + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} EA \xrightarrow{k_2} E + B$$

Also takes on a similar form (Michaelis-Menten equation):

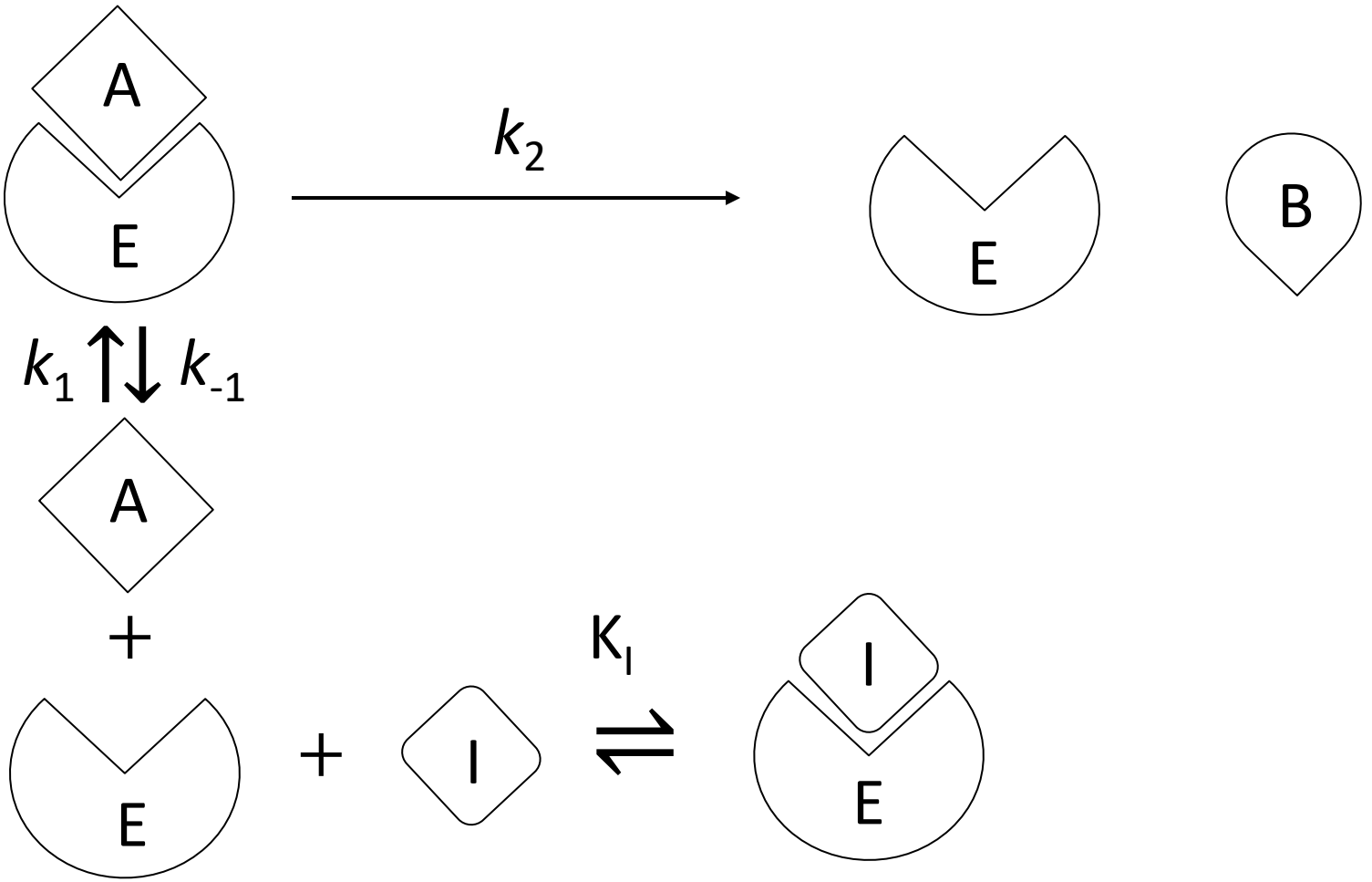
$$v = \frac{v_M C_A}{C_A + K_M}$$

$$v_{M,BH} \approx k_2, ; K_{M,BH} \approx \frac{k_{-1} + k_2}{k_1}$$



Also can have cases with "inhibitors"

Here competitive:




$$C_{E,total} = C_E + C_{EA} + C_{EB} + C_{EI}$$

Types of inhibition:

Competitive:

Prevents binding of the target molecule

Non-competitive:

Binds at a site different than the active site, but reduces activity of the enzyme (can bind to free enzyme and enzyme/substrate complex)

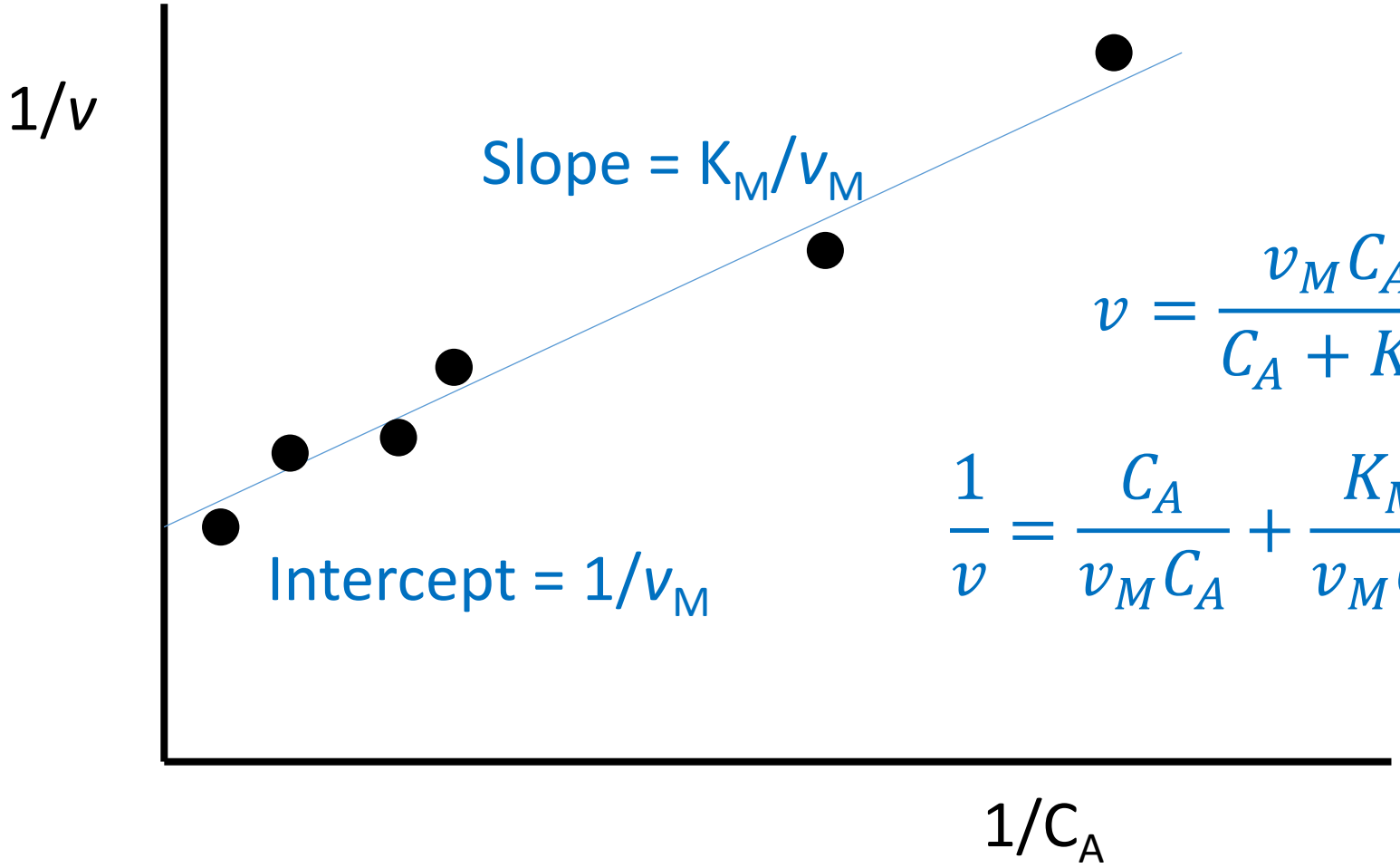
Uncompetitive:

Binds only to the complex formed between enzyme and substrate

Why would you want inhibition?

Sometimes you don't want to keep making product!

# Lineweaver-Burk plot




By plotting data from with and without inhibitor, can be used to determine competitive (same y-intercept), uncompetitive (same slope) and noncompetitive inhibitors

Discuss with your neighbors:

The following enzyme-catalyzed reaction obeys the reaction rate law for competitive inhibition (below).
Which answer is the most correct for the reaction order in species I?

$$v = \frac{v_M C_A}{C_A + K_M(1 + \frac{C_I}{K_I})}$$

Remember $v_M$, $K_M$, $K_I$ are functions of rate constants.

A) Approximately negative one

$C_A \gg K_M(1 + \frac{C_I}{K_I})$ $\quad v \approx \frac{v_M C_A}{C_A}$

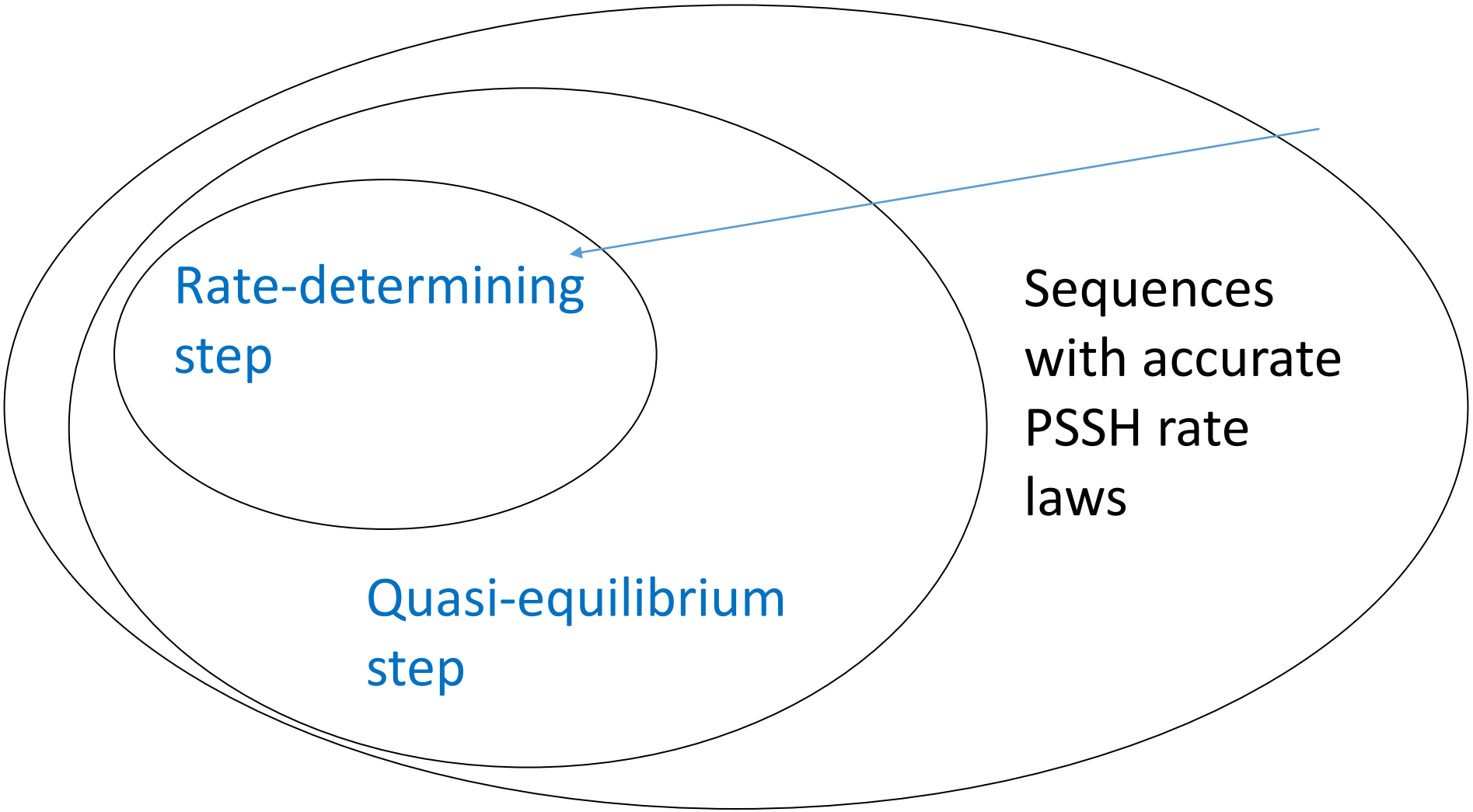
B) Approximately zero

$C_A \ll K_M(1 \ll \frac{C_I}{K_I})$ $\quad v \approx \frac{v_M C_A}{K_M \frac{C_I}{K_I}}$

C) Positive one

D) A or B are both possible

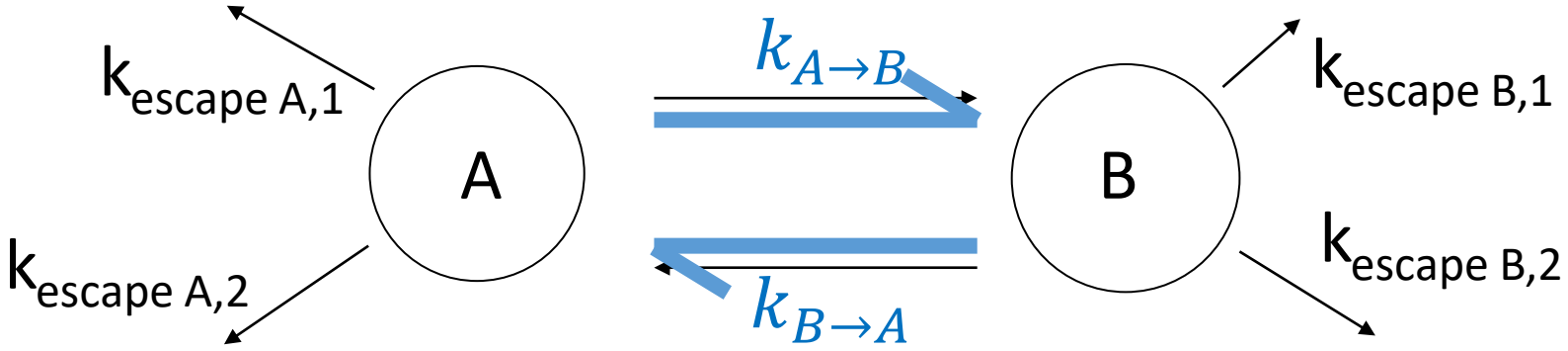
More complicated reactions will become more challenging to solve, so sometimes it is beneficial to make approximations.
More drastic approx. and eliminated parameters moving in
More accurate rate equations moving out (more difficult too)



Quasi equilibrium when one step is much faster than removal (escape) steps.

This step is useful for physisorption steps in catalysis, protonation steps in aqueous reactions with acids/bases, etc.

For two intermediates of a reaction mechanism, A and B:




To justify QE, the time scale for equilibration between A and B should be much shorter than the time of escape from the equilibrated AB state. $(k_{A\to B} + k_{B\to A})^{-1} \ll \left(x_{A|A,B} \sum k_{escape\ A,i} + x_{B|A,B} \sum k_{escape\ B,i}\right)^{-1}$

The effect of this is that we can approximate the rate of the reversible step $A \rightleftarrows B$ as zero, or that the reversible step is at equilibrium.

In class I'll indicate quasi-equilibrated steps by:

$$A \rightleftharpoons B$$

This is different than saying $r_A = 0$ (if there are multiple reactions)!

Quasi-equilibrium is different than PSSH. Don't get them confused.

PSSH net rate of a species is zero

QE where rate of a step is zero and is a limiting case of PSSH. Sometimes will be the same result, but with more complicated rate models, QE (or RDS) may give analytical solution where PSSH would not

Our PSSH from earlier (last week): Batch reactor

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

$k_1/k_2 << 1$

Assuming steady state on intermediate B based on the PSSH:

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \approx 0$$

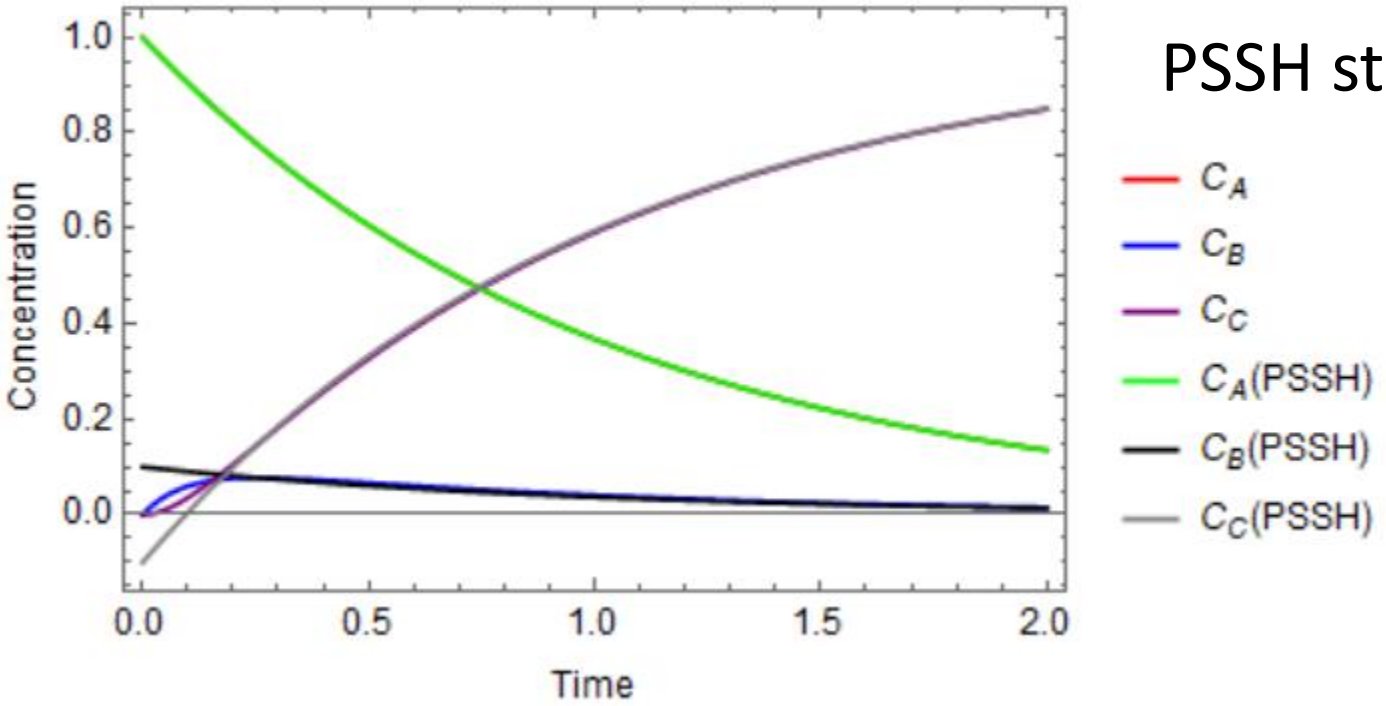
$$C_B \approx C_A \frac{k_1}{k_2} \qquad C_A = C_{A0} e^{-k_1 t}$$

For this if we use QE on $B \overset{k_2}{\rightarrow} C$

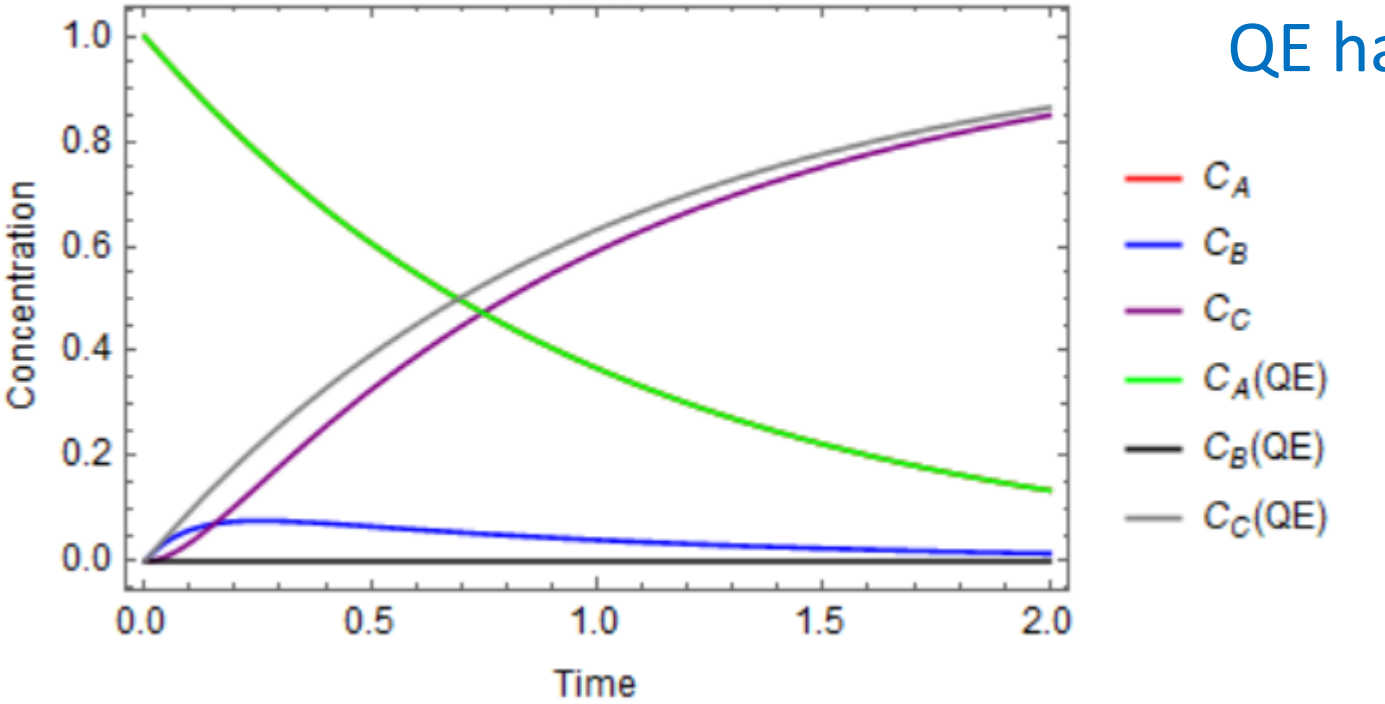
$$A \overset{k_1}{\rightarrow} C$$

$$C_A = C_{A0} e^{-k_1 t} \qquad C_B = 0 \qquad C_C = C_{A0}\left(1 - e^{-k_1 t}\right)$$

PSSH still has some B




QE has no B



Recall our special mechanism for enzymes, Briggs-Haldane:

$$E + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} EA \xrightarrow{k_2} E + B$$

More special case is the Michaelis-Menten mechanism:

$$E + A \overset{\text{QE}}{\rightleftharpoons} EA \xrightarrow{k_2} E + B$$

Reaction 2: $r = r_B = k_2 C_{EA}$

Reaction 1: $K_1 = \frac{k_1}{k_{-1}} \overset{\text{QE}}{\approx} \frac{C_{EA}}{C_E C_A} \longrightarrow C_E \approx \frac{k_{-1}}{k_1} \frac{C_{EA}}{C_A}$

Enzyme balance: $C_{E,total} = C_{EA} + C_E = C_{EA}\left(1 + \frac{k_{-1}}{k_1}\frac{1}{C_A}\right)$

$$r = r_B = k_2 C_{EA} = k_2 C_{E,total} \left(1 + \frac{k_{-1}}{k_1} \frac{1}{C_A}\right)^{-1}$$

In turnover frequency compared to the total enzyme:

$v$ =r/$C_{E,total}$

$$v = \frac{v_M C_A}{C_A + K_M}$$

For Michaelis-Menten specifically:

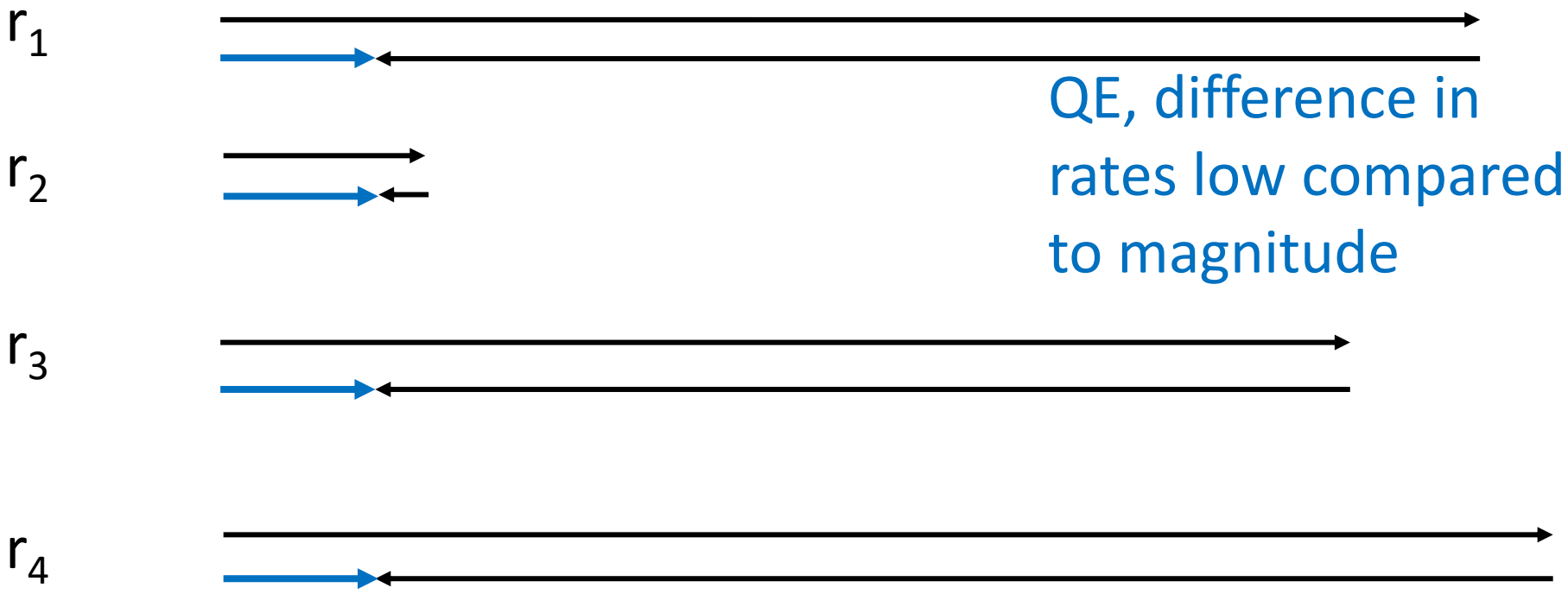
$$v_{M,MM} = k_2$$

$$K_{M,MM} = \frac{k_{-1}}{k_1}$$

Essentially same as Briggs-Haldane if $k_{-1} >> k_2$

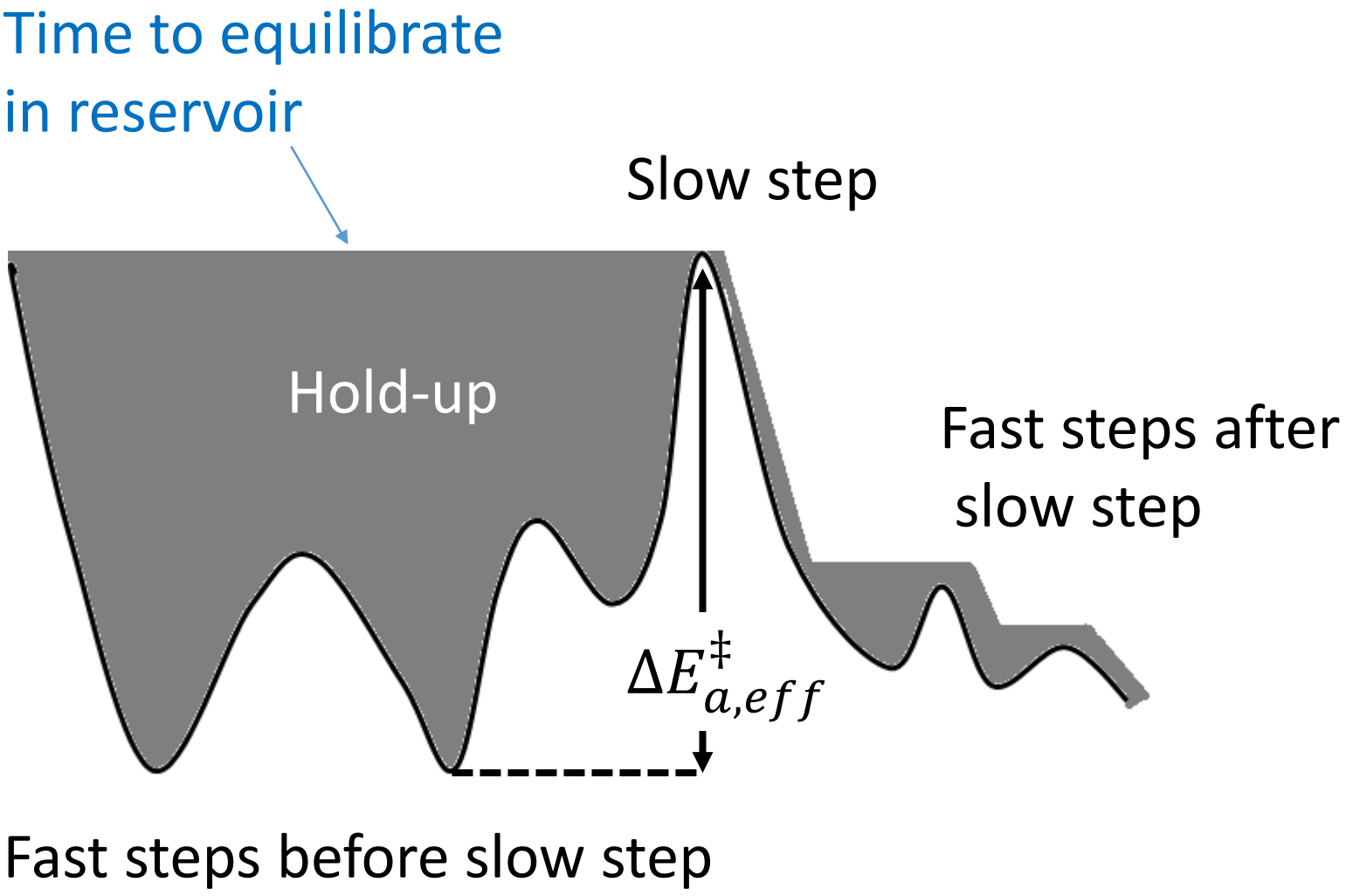
Rate determining step or rate-limiting step is when a particular forward and backward rate is much slower than other steps. Steps before RDS are QE, steps after are irrelevant (unless to consider equilibrium).

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} D \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} E$$




QE, difference in rates low compared to magnitude

# Rate determining step as a fluid mechanics model



## Heterogeneous catalysts (catalyst in diff. phase than reactant)

- Non-molecular
- Lower separations costs
- Easier to recycle
- Non-uniform active sites
- Production of bulk chemicals ($10^4$ – $10^6$ tonnes per year)

Important factor for both homogeneous and heterogeneous catalysts, number of sites.

Turnover frequency (TOF) is the rate of moles per sites reacted (units of inverse time, generally $s^{-1}$). Industrial ~ 1 $s^{-1}$

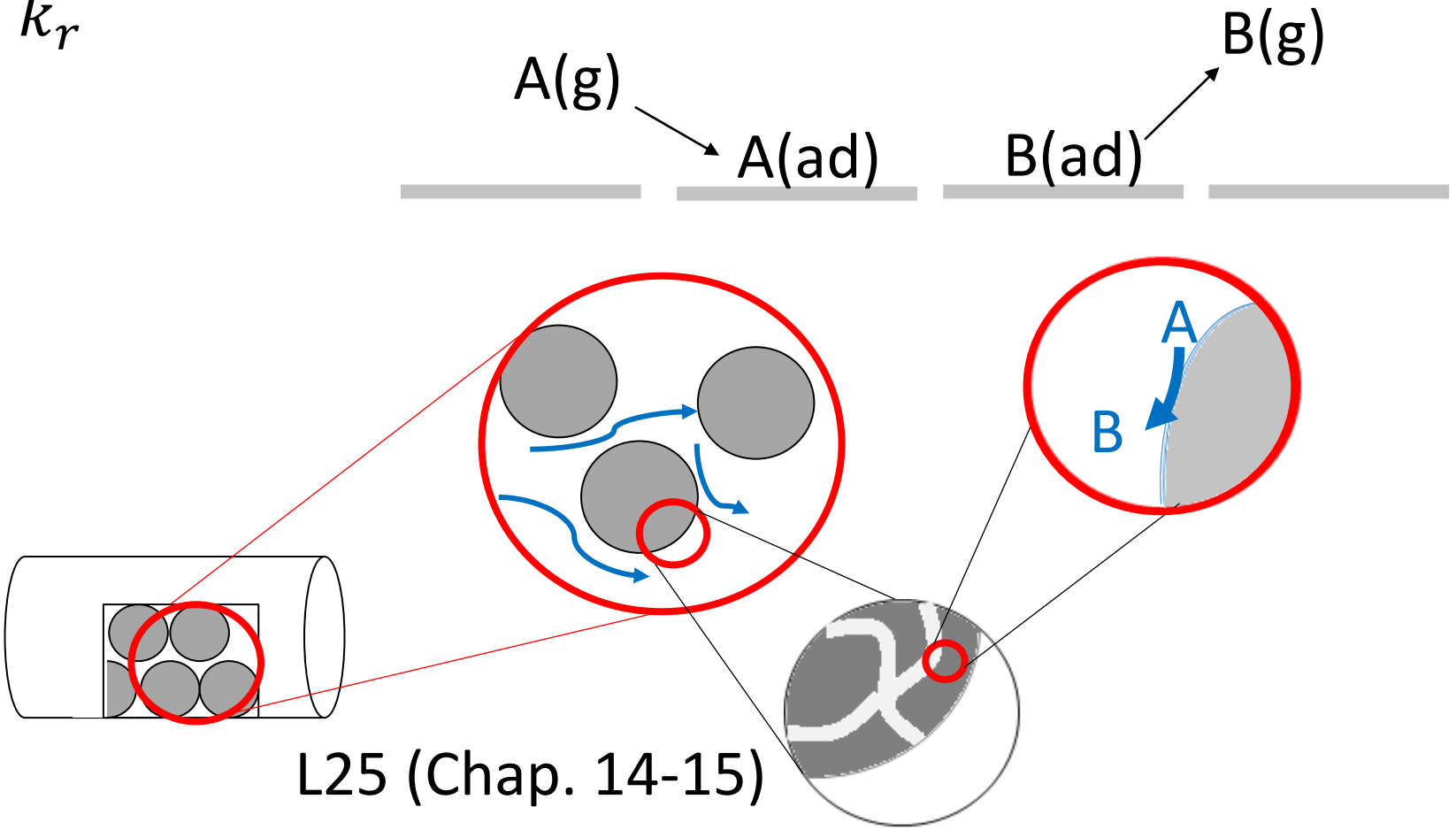
Turnover number (TON) is moles of product formed per site.

TON = Rate x lifetime

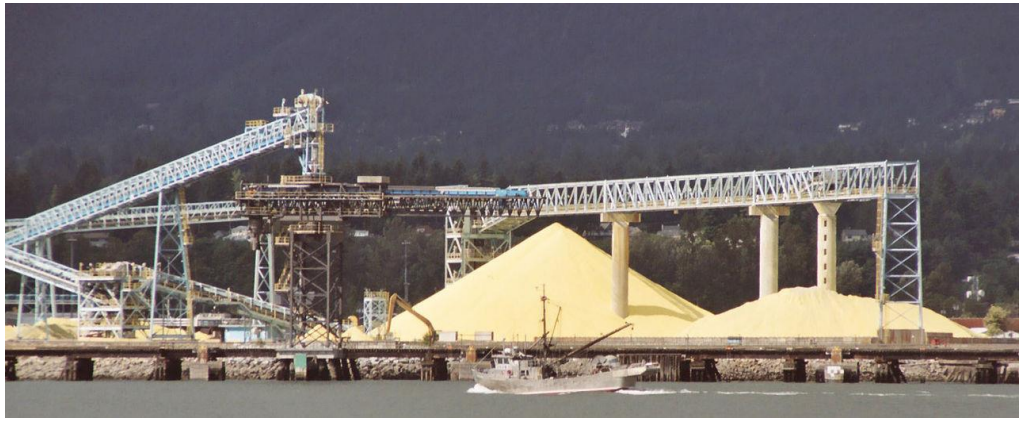
Heterogeneous catalysts, often reaction is occurring through adsorption on the surface

$$A \underset{k_r}{\overset{k_f}{\rightleftarrows}} B$$

$$A + * \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A* \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} B* \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} B + *$$



# Examples for heterogeneous catalysis



- Fuels
  - Desulfurization
  - Cracking
- Depollution
- Chemicals
  - Hydrogen (methane steam reforming)
  - Ethylene oxide and ethylene glycol (antifreeze )
  - Sulfuric acid (~280 million tons per year)
  - Ammonia (Haber-Bosch process, 1% of world's energy to feed 1/3 to ½ of world's population)
    - 3!!! Nobel prizes, Haber 1918, Bosch 1931, Ertl 2007
  - Nitric acid (Ostwald process)
  - Methanol
  - Liquid hydrocarbons (Fischer Tropsch)

Discuss with your neighbors:

Which of the following are both true and a reason you may prefer to use a heterogeneous catalyst instead of a homogeneous catalyst?

A) Separation of product and catalyst is easier

B) Heterogeneous catalysts are more uniform and thus more selective

C) The math is easier with heterogeneous catalysts

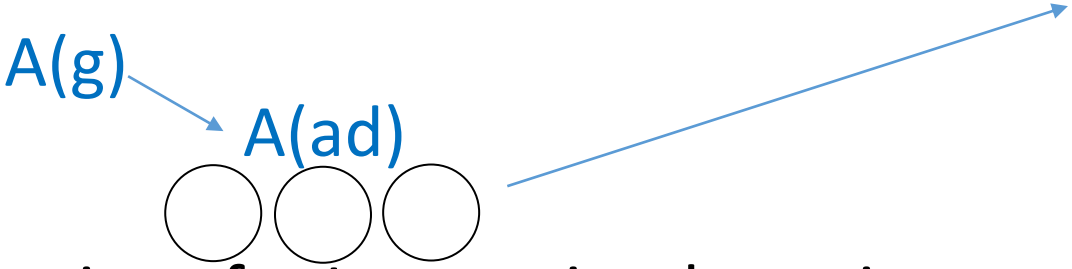
D) Homogeneous catalysts are inherently consumed as part of the reaction

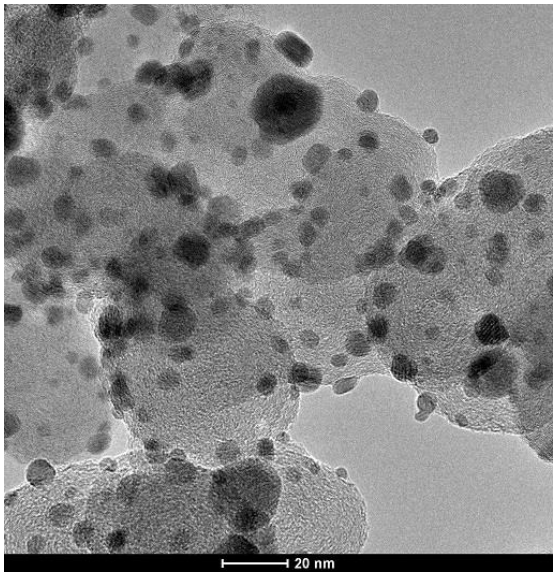
Irving Langmuir Nobel Prize in Chemistry (1932).

Observed that the amount of $H_2$ adsorbed onto a W filament was proportional to $P_{H_2}^{0.5}$.

Most common way of understanding adsorption is Langmuir Adsorption

$$A + * \rightleftharpoons A*$$




Assumptions for Langmuir adsorption:

1. All sites are equivalent and unaffected by occupancy of neighboring sites (no lateral interactions)
2. Fixed number of sites that are either empty or filled
3. Fixed adsorption stoichiometry (generally 1 molecule/site). 1 molecule/site = monolayer

# Adsorption

Chemisorption is for covalent bonds (80 to 400 kJ $mol^{-1}$)

Physisorption is van der Waals mostly (<40 kJ $mol^{-1}$)

Chemisorption generally for catalysis, new bonds between reactant and catalyst, and ‘activates’ reactant

It is this bonding to the catalyst that allows the catalyst to modify the reaction mechanism and lower activation barriers

Full reaction would be (for one-site):

Adsorption

Surface reaction

Desorption

$$A + * \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A* \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} B* \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} B + *$$

Simplified:

$$A + * \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A* \xrightarrow{k_2} B + *$$

Quasi-equilibration applied to adsorption:

$$K_{A,ads} = \frac{k_1}{k_{-1}} = \frac{[A*]}{C_A[*]}$$

$K_{A,ads}$ is large if A binds strongly (negative $\Delta H_{rxn}$ for adsorption)

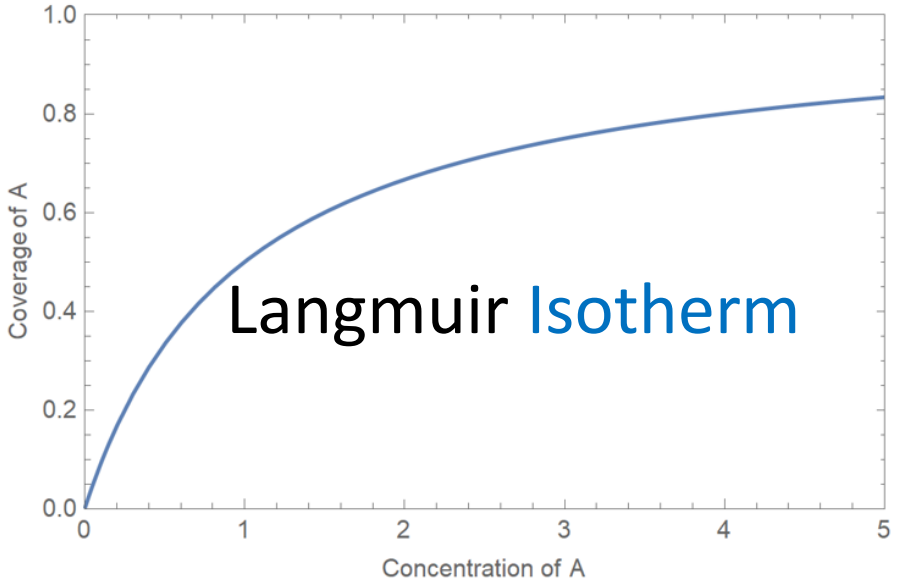
Site balance (assume either open sites or site with A adsorbed onto surface). Similar to our enzyme balance

Total sites = $[*]_0 = [*] + [A*]$

Define the term “coverage”:

$$\theta_A = \frac{[A*]}{[*]_0}$$

$$\theta_* = \frac{[*]}{[*]_0}$$




$$\theta_A = \frac{K_{A,ads}C_A[*]}{[*]_0} = \frac{K_{A,ads}C_A[*]}{[*]+[A*]} = \frac{K_{A,ads}C_A[*]}{[*]+K_{A,ads}C_A[*]}$$

$$= \frac{K_{A,ads}C_A}{1+K_{A,ads}C_A}$$

Rate for irreversible unimolecular surface reaction as RDS

$$\frac{r}{[*]_0} = k_2 \frac{K_{A,ads}C_A}{1+K_{A,ads}C_A}$$