ChE 344
Reaction Engineering and Design

Lecture 24: Tues, Apr 12, 2022

RDS review, Heterogeneous catalysis continued

Reading for today's Lecture: Chapter 10

Reading for Lecture 25/26: Chapter 14/15

Lecture 24: Heterogeneous catalysis continued
Related Text: Chapter 10

Langmuir-Hinshelwood mechanism example:

$$A + \ * \ \rightleftarrows A*$$
$$B + \ * \ \rightleftarrows B*$$
$$A* + B* \ \rightleftarrows Product + 2*$$

Catalyst site balance on all catalyst species:

$$[*]_0 = [*] + [A*] + [B*]$$
$$1 = \theta_A + \theta_B + \theta_*$$

If the surface reaction is the rate-determining step, and if we can consider it to be irreversible:

$$A* + B* \ \rightarrow Product + 2*$$

The rate law for that step is:

$$r_3 = k_3[A*][B*]$$

We are going to write this in terms of coverages:

$$r_{LH,c} = k_{LH,c}\theta_A\theta_B$$

We can get the coverages of A and B from the quasi-equilibrium approximation on reaction steps 1 and 2:

$$A + \ * \ \rightleftharpoons A*$$
$$B + \ * \ \rightleftharpoons B*$$

By approximating both of those net reaction rates as zero, and using the site balance, we can get:

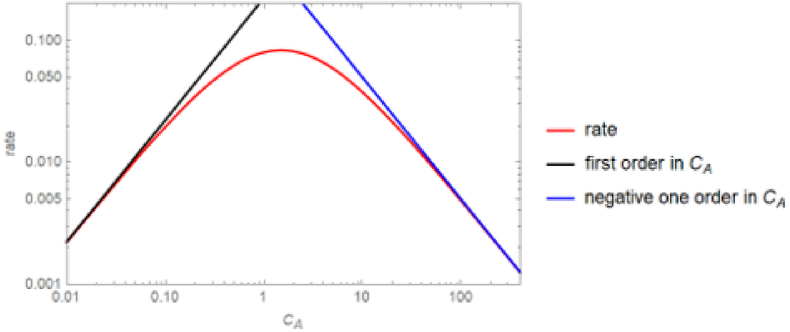
$$\theta_B = \frac{K_B C_B}{(1 + K_A C_A + K_B C_B)}$$
$$\theta_A = \frac{K_A C_A}{1 + K_A C_A + K_B C_B}$$

Thus, the overall rate (forming the product) is:

$$r_{LH,c} = k_{LH,c}\frac{K_A C_A K_B C_B}{(1 + K_A C_A + K_B C_B)^2}$$

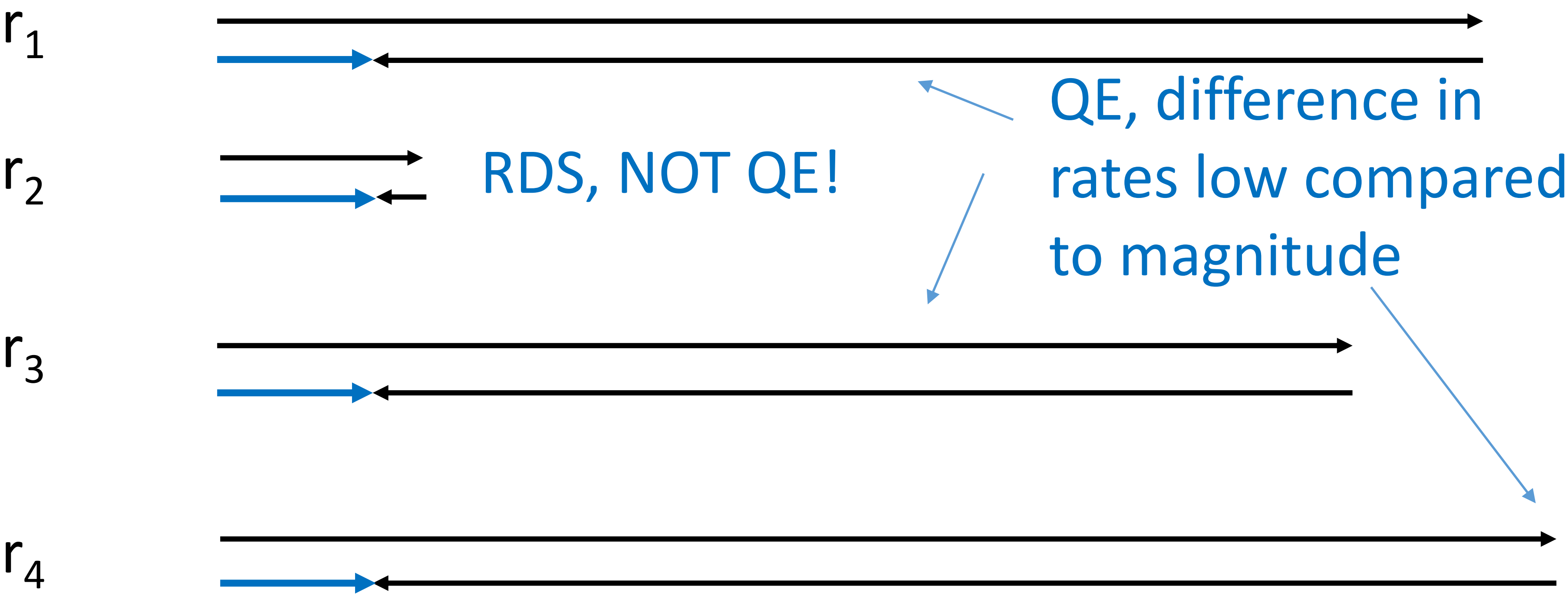
Note that our approximation of the net rate of reaction of A and B is just an approximation to solve more easily, in reality we are converting A and B to product. But if we just use those steps to estimate the rate, we have assumed that they are zero, so we have to estimate the rate law from the rate-determining step.

Langmuir-Hinshelwood will have limiting behavior for very large and small values of $K_A C_A$ (likewise for $K_B C_B$):



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

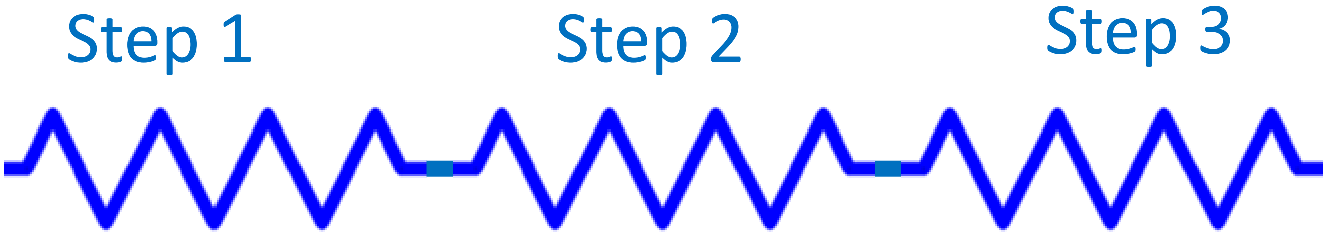
$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} D \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} E$$



RDS, NOT QE!

QE, difference in rates low compared to magnitude

Other potentially helpful ways of thinking about rate determining step: Using an electrical circuit analogy



If the resistance of Step 2 is 1 megaohm, and step 1 and step 3 are 1 ohm, the overall resistance is ~ 1 megaohm

Somewhat imperfect, because previous steps thermodynamics still influence rate (i.e., you can't completely ignore other steps)

Analogies:

- Fluidics analogy, flowing water has to go over a high point
- Exiting a classroom through a single door ('bottleneck')

Discuss with your neighbors:

You have a multiple step reaction mechanism for the overall reaction A to B. You have a detector that can measure concentrations of any species. It is so magically sensitive, if you can’t detect a species, you can approximate that species’ concentration as zero.

$$A \rightleftarrows I_1 \rightleftarrows I_2 \rightarrow B$$

After running your reactor for a while, with your detector, you can detect some A, B, and I_1, but $[I_2] \approx 0$. You know that one step is your RDS. Which could be your RDS?

A) I_1

B) I_2

[✓ C) Step 1 ($A \rightleftarrows I_1$)]

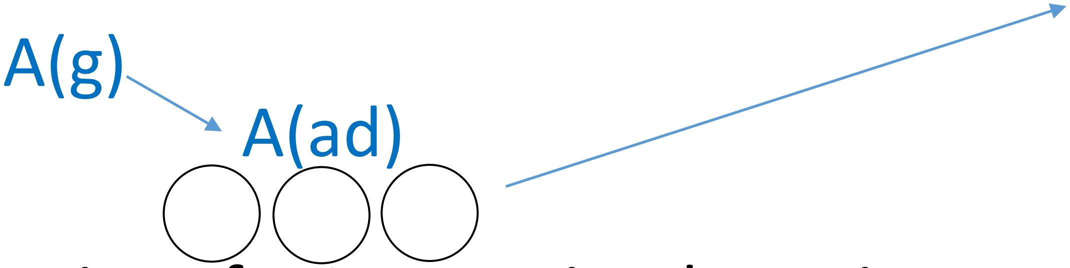
D) Step 3 ($I_2 \rightarrow B$)

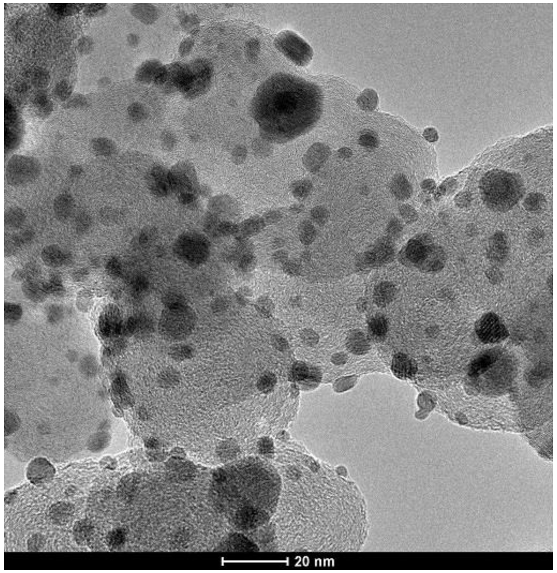
Irving Langmuir Nobel Prize in Chemistry (1932).

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

Example 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 ΔH_{rxn} for adsorption)

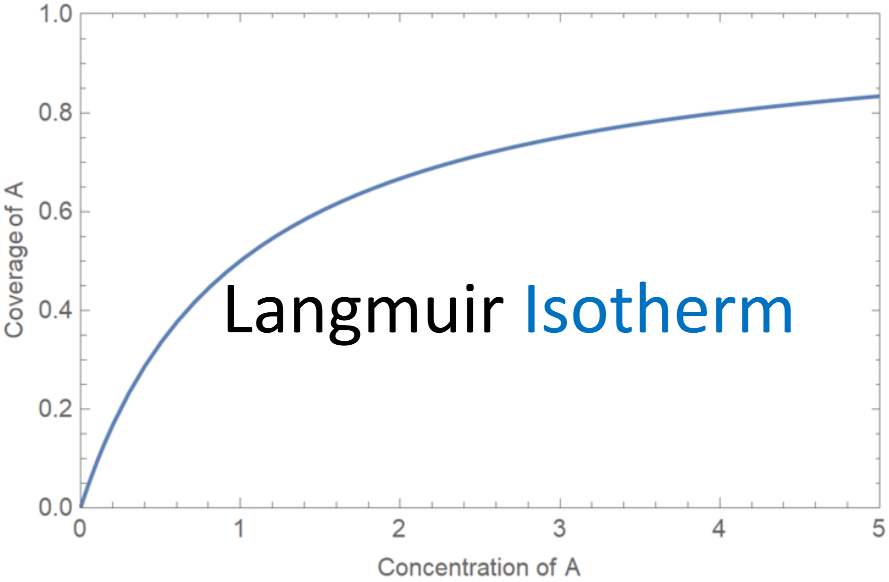
Site balance (assume either open sites or site with A adsorbed onto surface). Similar to our enzyme balance

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

Define the term “coverage”:

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

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



Langmuir Isotherm

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

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

Rate for irreversible unimolecular surface reaction as RDS

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

Discuss with your neighbors:

Langmuir discovered H_2 coverage on tungsten has a ½ order dependence on P_{H2} (for low coverages). What adsorption mechanism do you expect for H_2?

A) $H_2 + 2* \rightleftarrows 2H*$

B) $H_2 + * \rightleftarrows H_2*$

C) Either A or B

D) $H_2 + 2O* \rightleftarrows 2H* + O_2$

* represents a tungsten site

Where does the ½ come from:

Dissociative adsorption (A_2)

$$A_2 + 2* \rightleftarrows 2A*$$

$$K_1 = \frac{{\theta_A}^2}{P_{A_2}{\theta_*}^2}$$

$$\theta_A = \sqrt{K_1 P_{A_2}}\left(\underbrace{1-\theta_A}_{\theta_*}\right)$$

$$\theta_A = \frac{\sqrt{K_1 P_{A_2}}}{1+\sqrt{K_1 P_{A_2}}}$$

Order is range of 0 (at high coverages) to ½ (low coverages)

For the reaction A + B ⟶ Product

and competitive adsorption (both A and B can bind to the same catalyst site)

$$A + * \rightleftarrows A*$$

$$B + * \rightleftarrows B*$$

For competitive adsorption, if adsorption is equilibrated:

$$K_{A,ads} = \frac{\theta_A}{C_A \theta_*}$$

$$K_{B,ads} = \frac{\theta_B}{C_B \theta_*}$$

Catalyst site balance is:

$$1 = \theta_A + \theta_B + \theta_*$$

Plugging in for θ_*:

$$K_A = \frac{\theta_A}{C_A(1-\theta_A-\theta_B)}$$

$$\theta_A = \frac{K_A C_A(1-\theta_B)}{(1+C_A K_A)}$$

Also:

$$K_B = \frac{\theta_B}{C_B(1-\theta_A-\theta_B)}$$

$$K_B = \frac{\theta_B}{C_B\left(1-\frac{K_A C_A(1-\theta_B)}{(1+C_A K_A)}-\theta_B\right)}$$

Bring θ_B over and with algebra solve for it, then solve θ_A

$$K_B C_B \left(1 - \frac{K_A C_A (1 - \theta_B)}{(1 + C_A K_A)} - \theta_B \right) = \theta_B$$

$$K_B C_B \left(1 - \frac{K_A C_A}{(1 + C_A K_A)} \right) = \theta_B \left(1 + K_B C_B - \frac{K_A C_A K_B C_B}{1 + C_A K_A} \right)$$

$$K_B C_B \left(\frac{1 + C_A K_A}{1 + C_A K_A} - \frac{K_A C_A}{(1 + C_A K_A)} \right)$$

$$= \theta_B \left(\frac{1 + C_A K_A}{1 + C_A K_A} + \frac{K_B C_B (1 + C_A K_A)}{1 + C_A K_A} - \frac{K_A C_A K_B C_B}{1 + C_A K_A} \right)$$

Skip in class

$$K_B C_B\left(\frac{1}{1+C_A K_A}\right)=\theta_B\left(\frac{1+C_A K_A}{1+C_A K_A}+\frac{K_B C_B}{1+C_A K_A}\right)$$

$$\theta_B=\frac{K_B C_B}{(1+K_A C_A+K_B C_B)}$$

Skip in class

And thus:

$$\theta_A=\frac{K_A C_A\left(1-\frac{K_B C_B}{(1+K_A C_A+K_B C_B)}\right)}{(1+C_A K_A)}$$

$$\theta_A=\frac{K_A C_A\left(\frac{1+K_A C_A+K_B C_B}{1+K_A C_A+K_B C_B}-\frac{K_B C_B}{(1+K_A C_A+K_B C_B)}\right)}{(1+C_A K_A)}$$

$$\theta_A=\frac{K_A C_A\left(\frac{1+K_A C_A}{1+K_A C_A+K_B C_B}\right)}{(1+C_A K_A)}$$

$$\theta_B = \frac{K_B C_B}{(1 + K_A C_A + K_B C_B)}$$

$$\theta_A = \frac{K_A C_A}{1 + K_A C_A + K_B C_B}$$

Now assume that surface reaction is the RDS and mechanism is **Langmuir-Hinshelwood**:

$$A + * \rightleftharpoons A *$$

$$B + * \rightleftharpoons B *$$

$$A * + B * \rightarrow Product + 2 *$$

$$r_{LH,c} = k_{LH,c}\theta_A\theta_B$$

$k_{LH,\boldsymbol{c}}$ is the rate constant for the product forming surface reaction. **c** refers to A and B competitively adsorbing

$$r_{LH,c} = k_{LH,c} \frac{K_A C_A}{(1 + K_A C_A + K_B C_B)} \frac{K_B C_B}{(1 + K_A C_A + K_B C_B)}$$

$$r_{LH,c} = k_{LH,c} \frac{K_A C_A K_B C_B}{(1 + K_A C_A + K_B C_B)^2}$$

This is for the surface reaction as RDS, but adsorption, desorption could also be rate limiting for this mechanism. Also, if desorption of products is at quasi-equilibrium, would need to include products in denominator. Recall that RDS ignores later reactions unless equilibrium must be considered

Limiting cases:

$$r_{LH,c,K_A C_A \ll 1} \approx k_{LH,c} \frac{K_A C_A K_B C_B}{(1 + K_B C_B)^2} \propto C_A$$

Discuss with your neighbors:

For a Langmuir-Hinshelwood reaction, what is the reaction order in A if $K_A C_A \gg 1, K_B C_B$?

$$r_{LH,c} = k_{LH,c} \frac{K_A C_A K_B C_B}{(1 + K_A C_A + K_B C_B)^2}$$

$$r_{LH,c,K_A C_A \gg 1,K_B C_B} \approx k_{LH,c} \frac{K_A C_A K_B C_B}{(K_A C_A)^2} \propto (C_A)^{-1}$$

A) Negative one

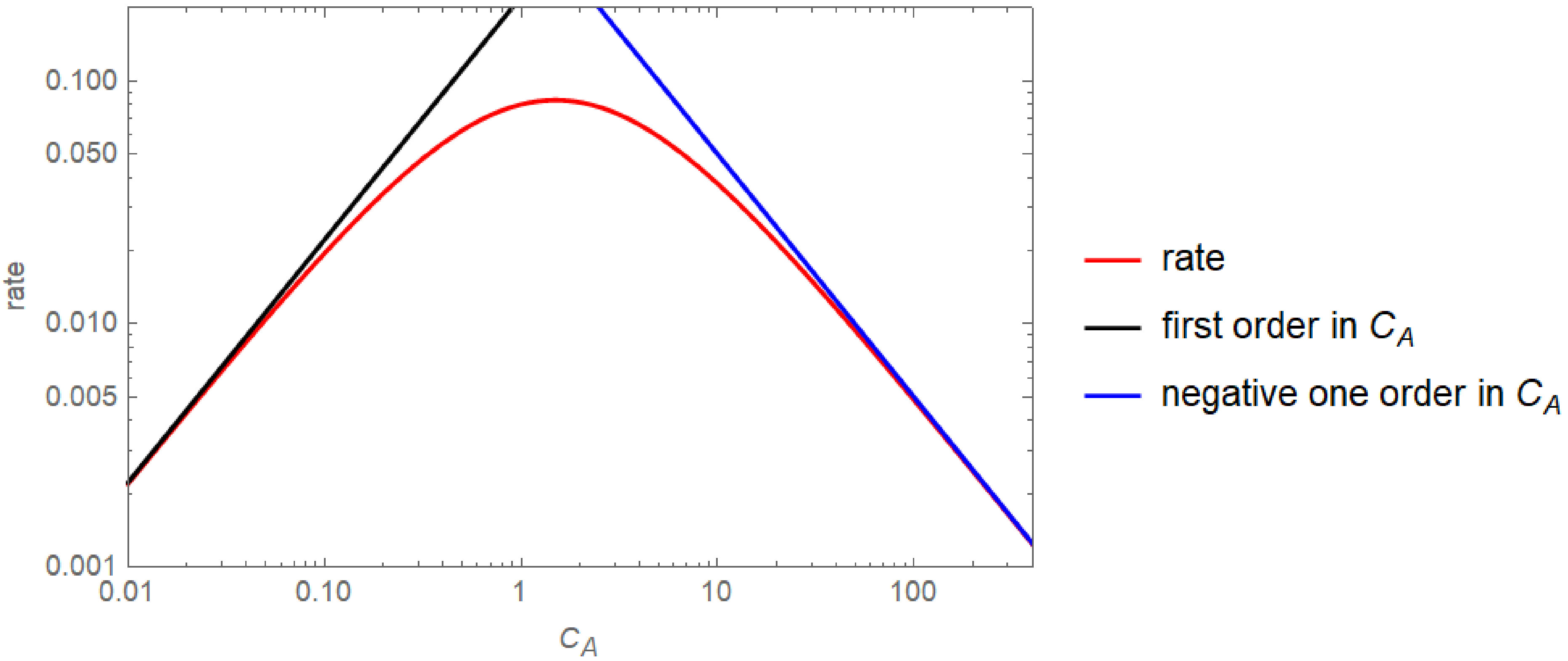
B) Positive one

C) Negative 2

D) +1/2

$$r = k\frac{K_A C_A K_B C_B}{(1 + K_A C_A + K_B C_B)^2}$$

If $C_B = 0.5$, $K_B = 1$, $K_A = 1$, $k = 1$:

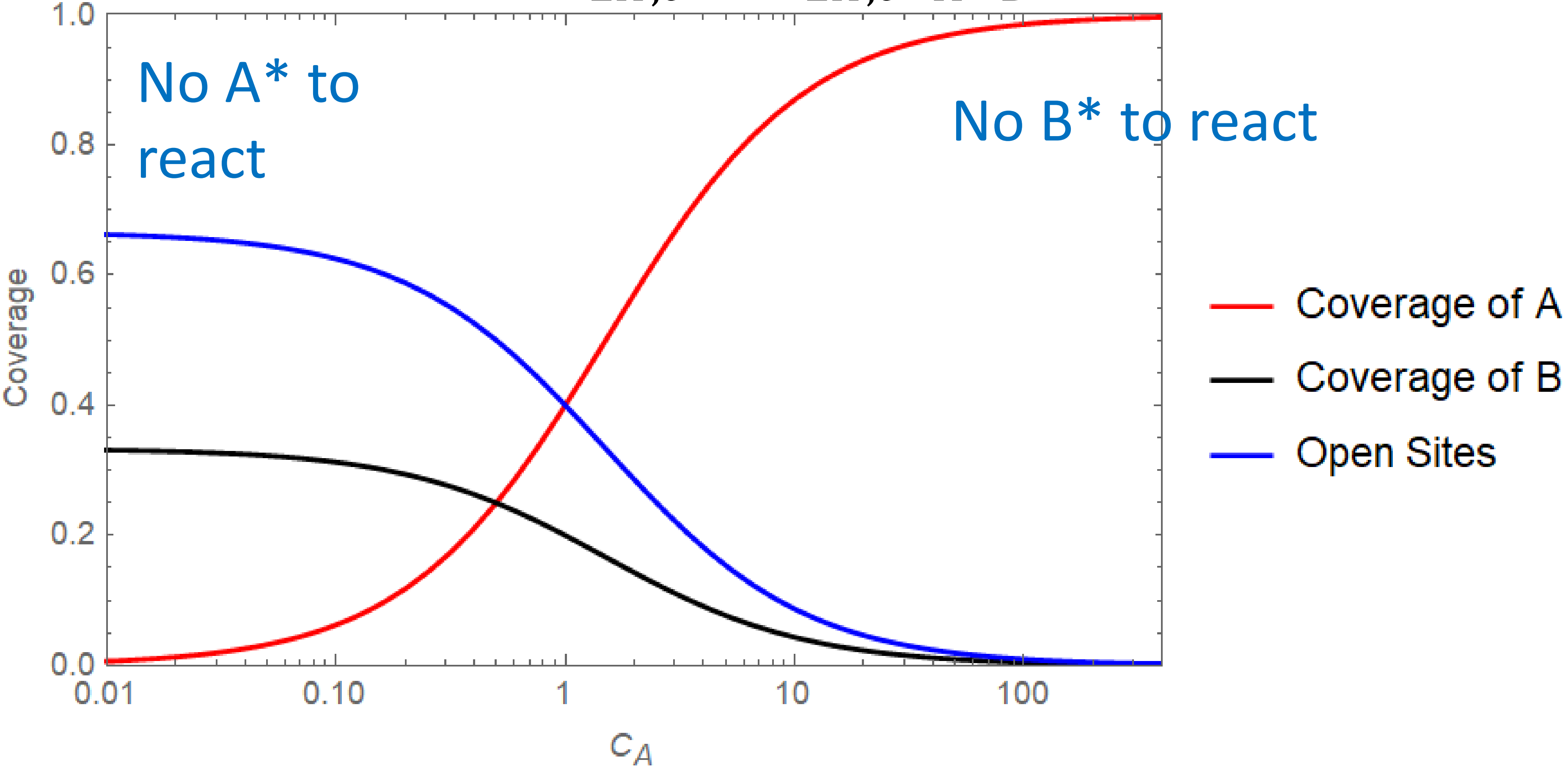


Can see that reaction order in A is a function of the concentration of A.

Because for surface reaction as RDS, the rate will depend on the coverages of A and B (related to conc. of adsorbed A, B)

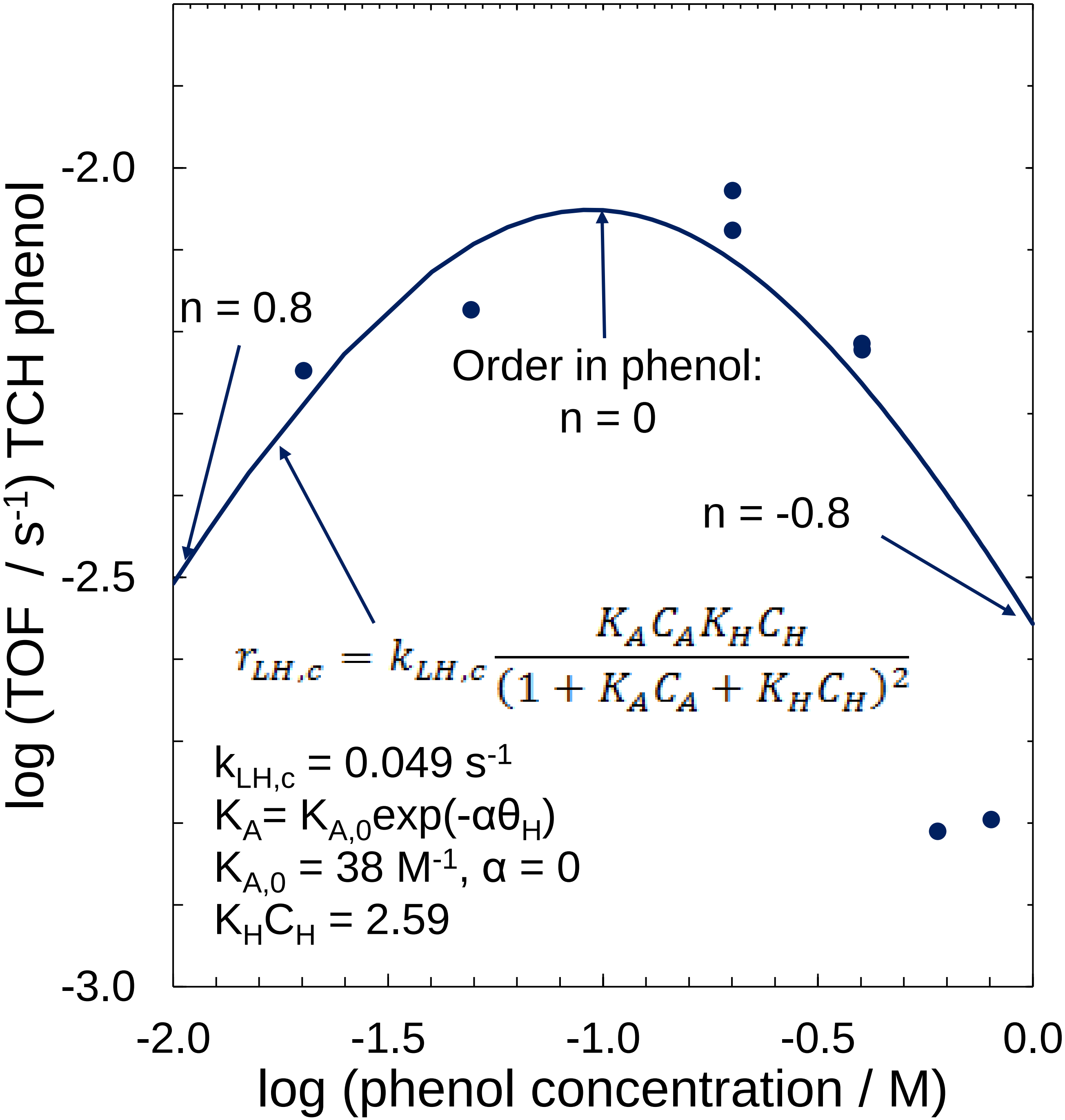
$$\theta_B = \frac{K_B C_B}{(1 + K_A C_A + K_B C_B)}; \; \theta_A = \frac{K_A C_A}{1 + K_A C_A + K_B C_B}$$

$$r_{LH,c} = k_{LH,c} \theta_A \theta_B$$



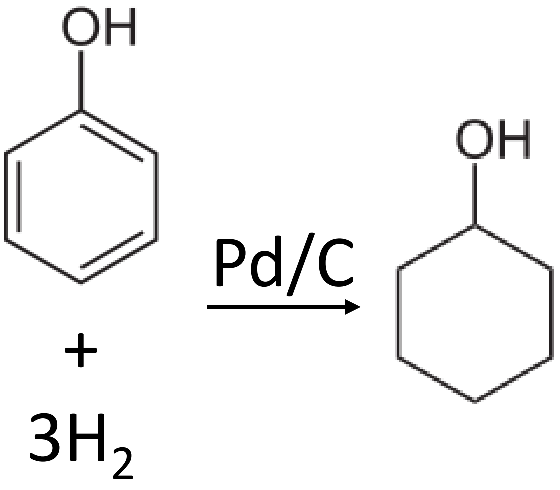
No A* to react

No B* to react



$$r_{LH,c} = k_{LH,c}\frac{K_A C_A K_H C_H}{(1 + K_A C_A + K_H C_H)^2}$$

$k_{LH,c} = 0.049\ s^{-1}$
$K_A = K_{A,0}\exp(-\alpha\theta_H)$
$K_{A,0} = 38\ M^{-1}$, $\alpha = 0$
$K_H C_H = 2.59$



Journal of Catalysis, **2020**, 382, 372-384.

Other sample reaction mechanisms might involve dissociative adsorption (A_2) like we saw for hydrogen

$$A_2 + 2* \rightleftarrows 2A*$$

$$2A* \rightarrow R* + S*$$

$$R* \rightarrow R + *$$

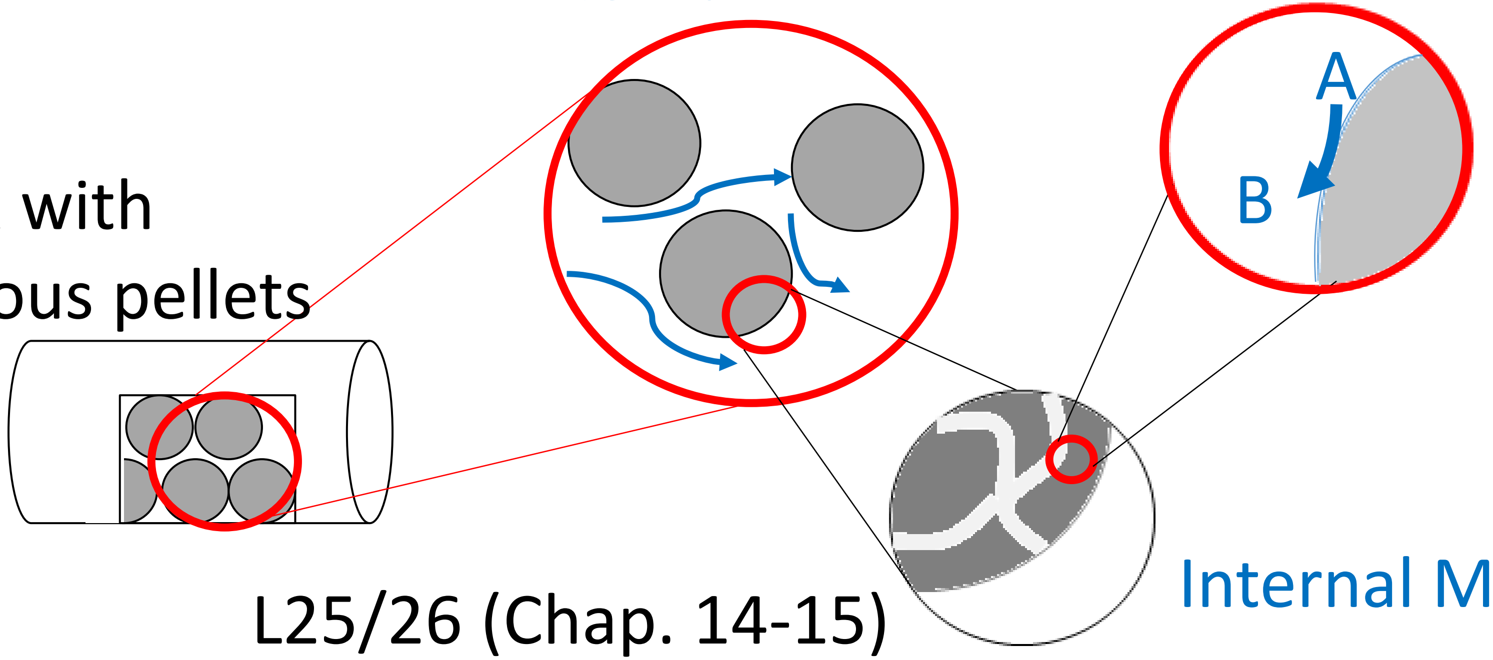
$$S* \rightarrow S + *$$

Depending on the RDS you will get different rate laws even with the same set of elementary steps.

The above mechanisms are what describes reaction ‘kinetics’, when you know the concentrations of your reactants near your catalyst (near enzyme site, near het. catalyst surface)

But what about mass transport?

What if the slowest step is not the reaction itself, but just the reactant molecule transporting to be near the catalyst surface (inside a porous pellet)?



External MT

Surface reaction kinetics

PBR with porous pellets

L25/26 (Chap. 14-15)

Internal MT

Lets think back again to our resistor model, but now apply it to include mass transport as well.

External mass transfer

Internal mass transfer

Surface kinetics

A

B

Reactant

Product

Any or all of these could be controlling the rate. We will learn more on Thursday, but a handy reference for PBRs:

Limitation	Fluid velocity	Pellet Size	Temp.
External	$(\text{Velocity})^{1/2}$	$(d_p)^{-3/2}$	~Linear
Internal	Independent	$(d_p)^{-1}$	Exp.
Surface rxn	Independent	Independent	Exp.