Chapt 12 summary part 2

Today I want to discuss catalytic kinetics:

Two key ideas for today:

- Measure rate as a turnover number
- Langmuir Hinshelwood kinetics

Turnover numbers

Recall our discussion from before.

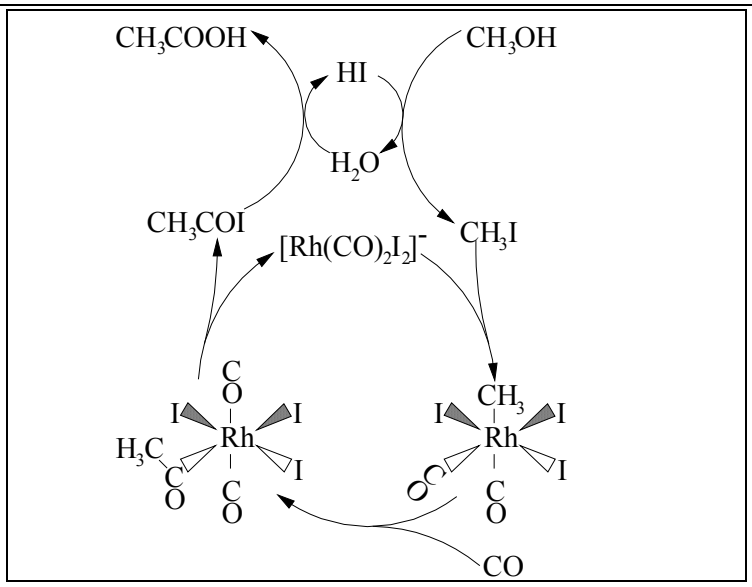


Figure 12.1 A schematic of the catalytic cycle for Acetic acid production via the Monsanto process.

Printing press analogy

- Reactants bind to sites on the catalyst surface
- Transformation occurs
- Reactants desorb

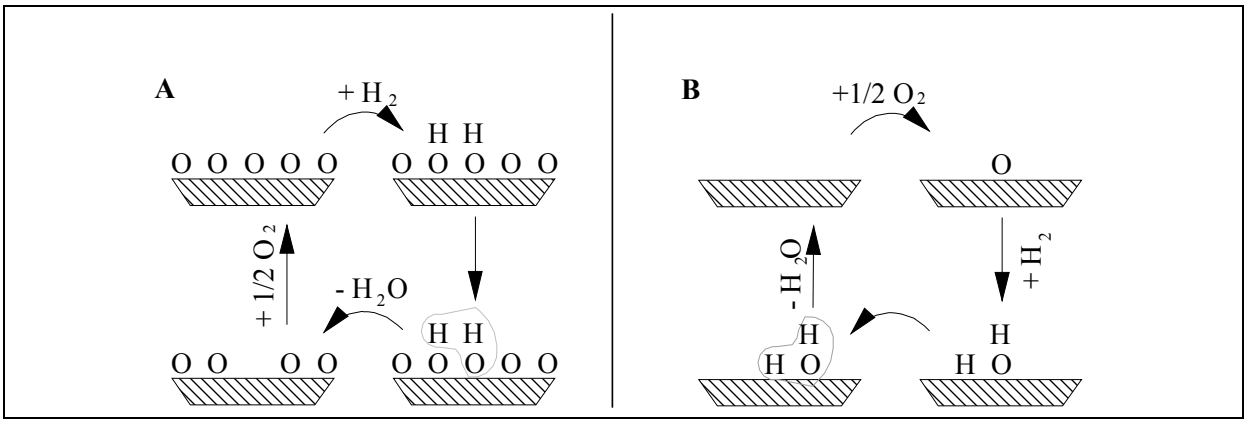


Figure 5.10 Catalytic cycles for the production of water a) via disproportion of OH groups, b) via the reaction $OH_{(ad)}+H_{)ad)}\rightarrow H_2O$.

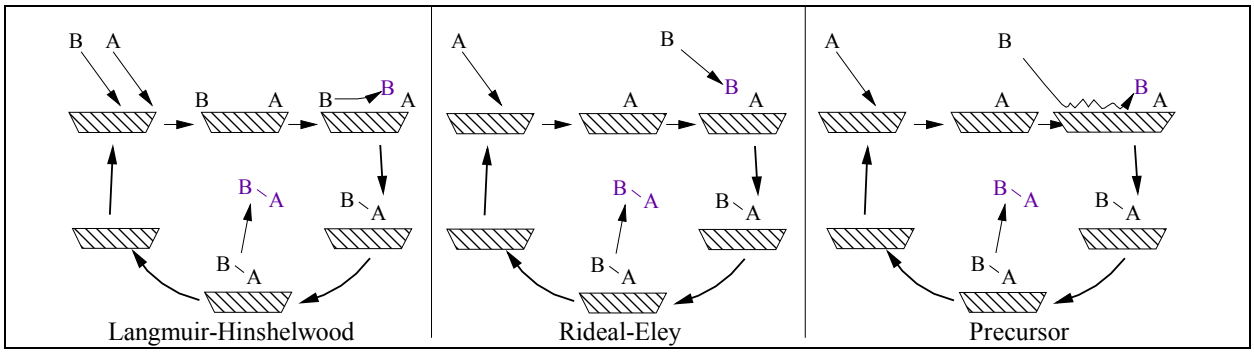


Figure 5.20 Schematic of a) Langmuir-Hinshelwood, b) Rideal-Eley, c) precursor mechanism for the reaction A+B⇒AB and AB⇒A+B.

$$T_N = \frac{R_A}{N_S}$$

(12.119)

Physically, turnover number is the rate that the catalyst prints product.

Most people discuss rates in terms of turnover numbers

Key plot:

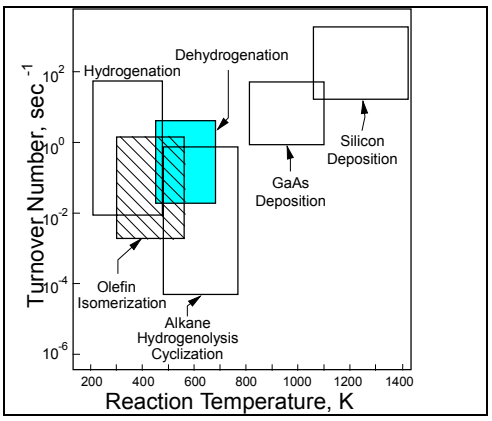


Figure 12.28 Turnover numbers for some typical processes

Next topic why catalytic kinetics weird?

Recall from earlier in the semester catalytic rates weird:

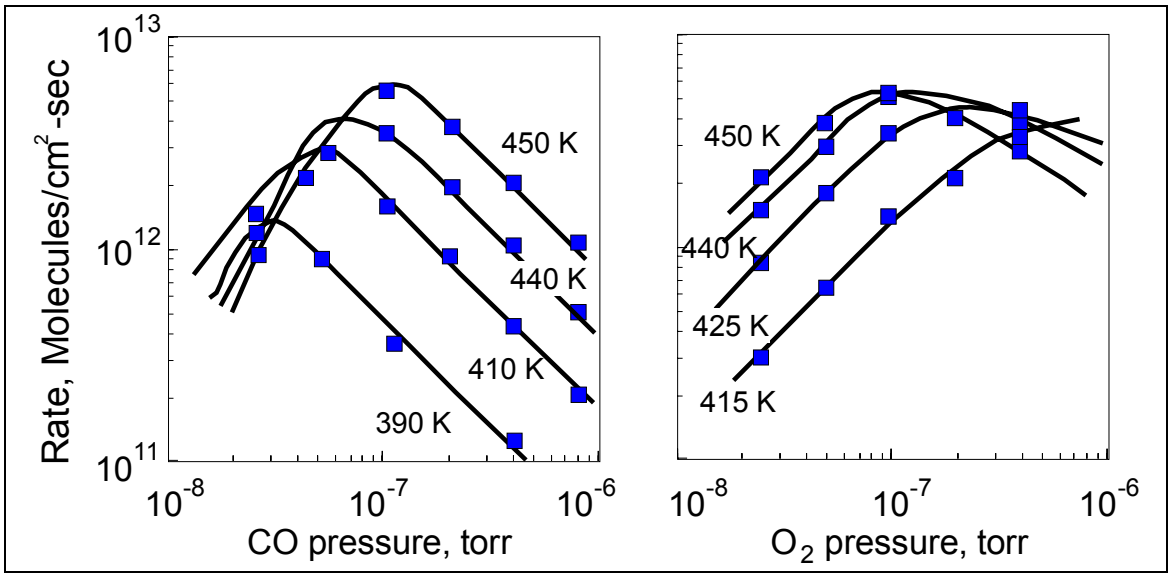


Figure 2.15 The influence of the CO pressure on the rate of CO oxidation on Rh(111). Data of Schwartz, Schmidt, and Fisher.

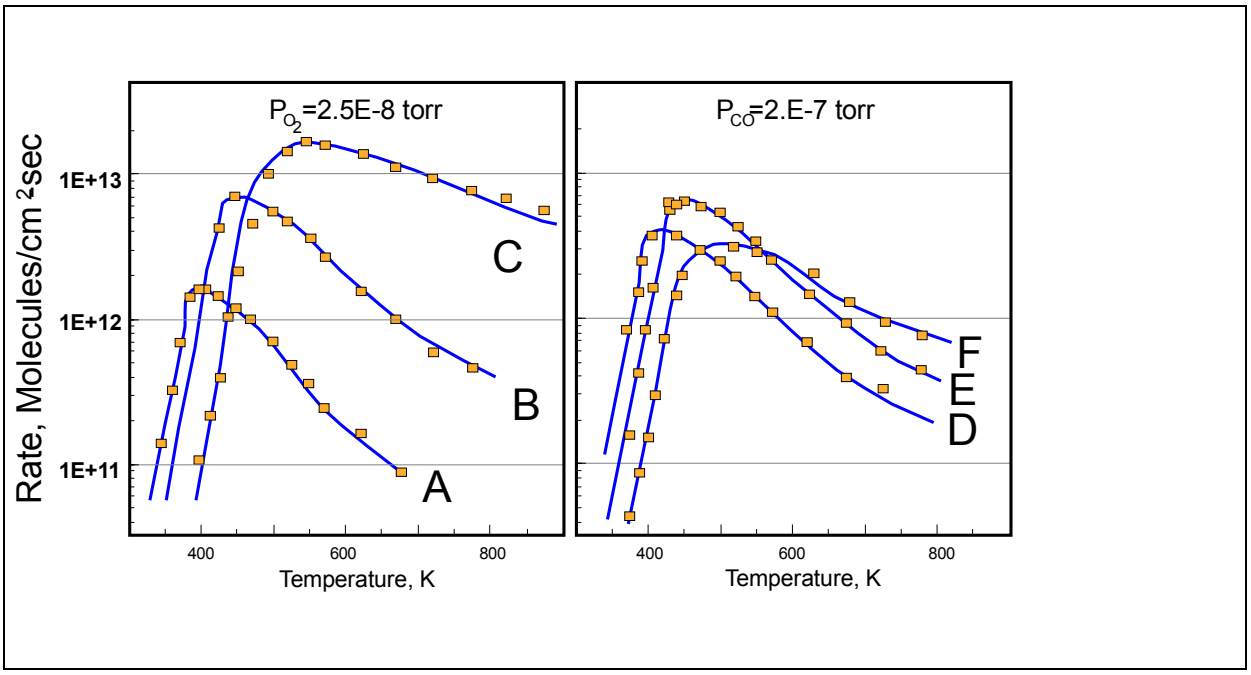


Figure 2.18 The rate of the reaction CO + ½ $O_2 \Rightarrow CO_2$ on Rh(111). Data of Schwartz, Schmidt and Fisher[1986]. A) $P_{CO} = 2.5\times10^{-8}$ torr, $P_{O_2} = 2.5\times10^{-8}$ torr, B) $P_{CO} = 1\times10^{-7}$ torr, $P_{O_2} = 2.5\times10^{-8}$ torr, C) $P_{CO} = 8\times10^{-7}$ torr, $P_{O_2} = 2.5\times10^{-8}$ torr, D) $P_{CO} = 2\times10^{-7}$ torr, $P_{O_2} = 4\times10^{-7}$ torr, E) $P_{CO} = 2\times10^{-7}$ torr, $P_{O_2} = 2.5\times10^{-8}$ torr, F) $P_{CO} = 2.5\times10^{-8}$ torr, $P_{O_2} = 2.5\times10^{-8}$ torr,

Today: Why the weird behavior?

Physical interpretation:

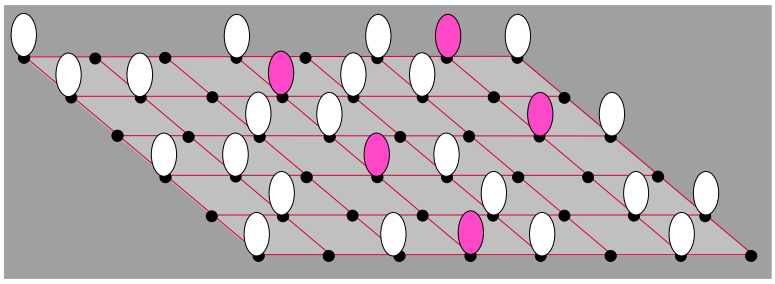


Figure 12.33 Langmuir's model for the adsorption of gas on a solid catalyst. The light gray area represents the surface of the catalyst. The black dots are the sites on the catalyst are sites that are available to adsorb gas. The white ovals are the adsorbed A molecules. The dark ovals are adsorbed B molecules.

Physical interpretation for $A + B \Rightarrow AB$

- Catalysts have finite number of sites:
- Initially rates increase because surface concentration increases.
- Eventually A takes up so many sites than no B can adsorb.
- Further increases in A decrease rate.

Can work out kinetics using steady state approximation:

$$A \Rightarrow C$$

(12.120)

Mechanism

$$S + A \underset{2}{\overset{1}{\rightleftharpoons}} A_{ad}$$

$$A_{Ad} \underset{4}{\overset{3}{\rightleftharpoons}} C_{ad}$$

$$C_{ad} \underset{6}{\overset{5}{\rightleftharpoons}} C + S$$

(12.121)

Also have a species B

$$S + B \underset{8}{\overset{7}{\leftrightharpoons}} B_{ad}$$

(12.122)

Next use the steady state approximation to derive an equation for the production rate of C_{ad} (this must be equal to the production rate of C).

$$r_C = k_3[A_{ad}] - k_4[C_{ad}]$$

(12.123)

SS on $[A_{ad}]$ and $[C_{ad}]$

$$0 = r_{A_{ad}} = k_1 P_A [S] - k_2[A_{ad}] - k_3[A_{ad}] + k_4[C_{ad}]$$

(12.124)

$$0 = r_{C_{ad}} = k_6 P_C [S] - k_5[C_{ad}] - k_4[C_{ad}] + k_3[A_{ad}]$$

(12.125)

People usually ignore reactions 3 and 4 since their rates very low rates compared to the other reactions.

Dropping the k_3 and k_4 terms in equations 12.124 and 12.125 and rearranging yields:

$$[A_{ad}] = \left(\frac{k_1}{k_2}\right) P_A [S]$$

(12.126)

$$[C_{ad}] = \left(\frac{k_6}{k_5}\right) P_C [S]$$

(12.127)

Similarly for B

$$[B_{ad}] = \frac{k_8}{k_7} P_B [S]$$

(12.128)

Rearranging Equations (12.126), (12.127) and (12.128) yields:

$$\frac{[A_{ad}]}{P_A[S]} = \left(\frac{k_1}{k_2}\right)$$

(12.129)

$$\frac{[B_{ad}]}{P_B[S]} = \left(\frac{k_8}{k_7}\right)$$

(12.130)

$$\frac{[C_{ad}]}{P_c[S]} = \left(\frac{k_6}{k_5}\right)$$

(12.131)

Equations (12.129) and (12.130) imply that there is an equilibrium in the reactions:

$$A + S \underset{2}{\overset{1}{\rightleftharpoons}} A_{ad}$$

$$B + S \underset{7}{\overset{8}{\rightleftharpoons}} B_{ad}$$

$$C + S \underset{5}{\overset{6}{\rightleftharpoons}} C_{ad}$$

(12.132)

If sites are conserved

One needs an expression for [S] to complete the analysis. One can get an expression for [S] by assuming that on any catalyst, there are a finite number of sites to hold the reactants. Each site can be bare or it can be covered by A, B or C. If we define S_0 as the total number of sites in the catalyst, one can show:

$$S_0 = [S] + [A_{ad}] + [B_{ad}] + [C_{ad}] \tag{12.133}$$

Substituting Equations (12.126), (12.127) and (12.128) into Equation (12.133) and then solving for [S] yields:

$$[S] = \frac{S_0}{1 + \frac{k_1}{k_2} P_A + \frac{k_8}{k_7} P_B + \frac{k_6}{k_5} P_C} \tag{12.134}$$

Substituting Equation (12.134) into Equations (12.126) and (12.127) yields:

$$[A_{ad}] = \frac{\left(\frac{k_1}{k_2}\right) P_A S_0}{1 + \frac{k_1}{k_2} P_A + \frac{k_8}{k_7} P_B + \frac{k_6}{k_5} P_C}$$

(12.135)

$$[C_{ad}] = \frac{\left(\frac{k_6}{k_5}\right) P_C S_0}{1 + \frac{k_1}{k_2} P_A + \frac{k_8}{k_7} P_B + \frac{k_6}{k_5} P_C}$$

(12.136)

According to the analysis in Section 4.3, the equilibrium constant for the adsorption of A is given by:

$$K_A = \frac{k_1}{k_2}$$

(12.137)

Similarly, the equilibrium constants for the adsorption of B, and C are given by:

$$K_B = \frac{k_8}{k_7}$$

(12.138)

$$K_C = \frac{k_6}{k_5}$$

(12.139)

Substituting Equations (12.137), (12.138), and (12.139) into Equations (12.135) and (12.136) yields:

$$[A_{ad}] = \frac{K_A P_A S_0}{1 + K_A P_A + K_B P_B + K_C P_C}$$

(12.140)

$$[C_{ad}] = \frac{K_C P_C S_0}{1 + K_A P_A + K_B P_B + K_C P_C}$$

(12.141)

Substituting Equations (12.140) and (12.141) into Equation (12.123) yields:

$$r = \frac{k_3 K_A P_A S_0 - k_4 K_C P_C S_0}{1 + K_A P_A + K_B P_B + K_C P_C} \quad \textbf{(12.142)}$$

In the catalysis literature, Equation (12.142) is called the **Langmuir-Hinshelwood** expression for the rate of the reaction $A \Rightarrow C$, since we assumed that the reaction obeyed a Langmuir-Hinshelwood mechanism and the equation was first derived for surface reaction by Langmuir[1914]. The same equation is called the Michaelis-Menten equation in the enzyme literature; since it was also derived by Michaelis and Menten[1914].

Qualitative behavior for A + B ⇒ products:

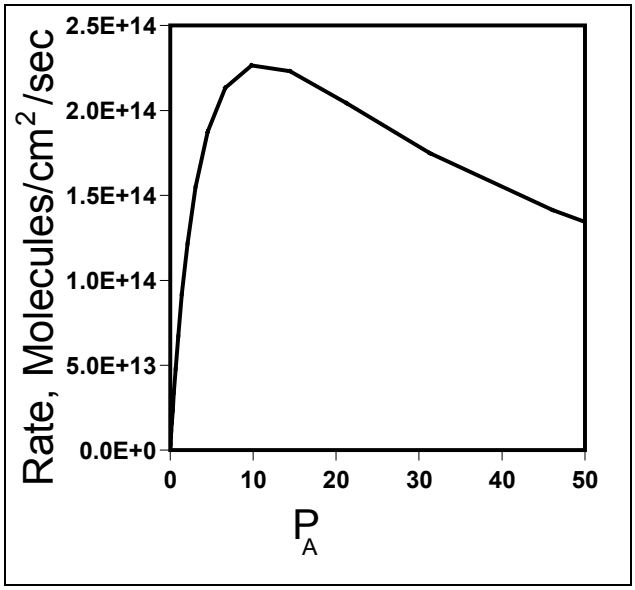


Figure 12.32 A plot of the rate calculated from equation (12.161) with $K_B P_B = 10$.

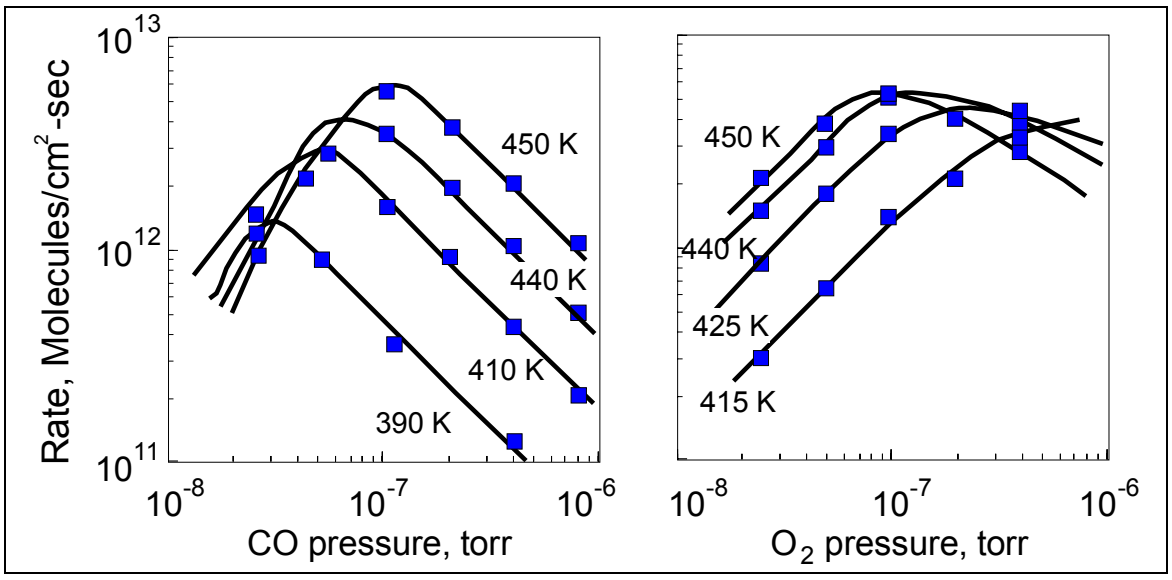
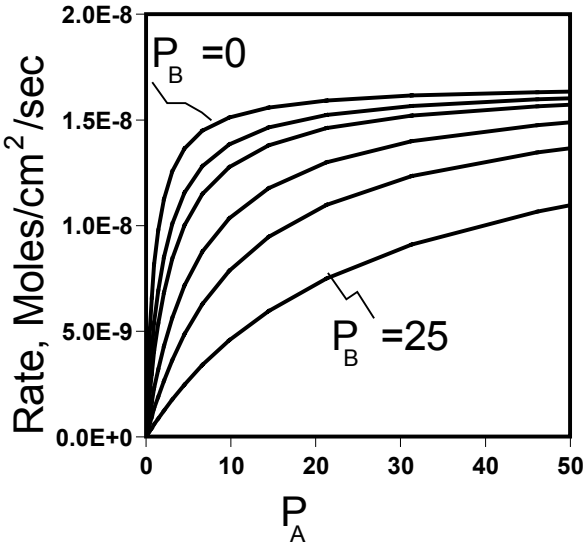


Figure 2.15 The influence of the CO pressure on the rate of CO oxidation on Rh(111). Data of Schwartz, Schmidt, and Fisher.

Qualitative behavior for A⇒C



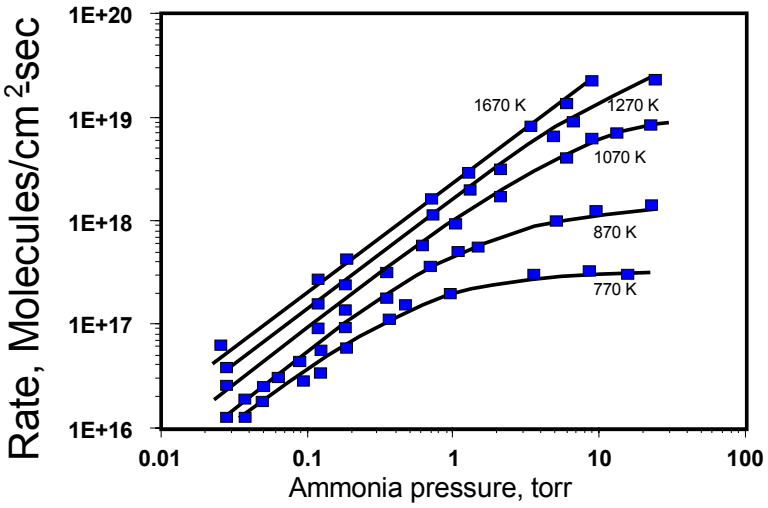


Figure 2.16 The rate of the reaction $NH_3 \Rightarrow 1/2N_2 + 3/2H_2$ over a platinum wire catalyst. Data of Loffler and Schmidt[1976].

Langmuir-Hinshelwood-Hougan-Watson rate laws

Trick to simplify the rate equation.

Hougan and watson's idea:

- Identify rate determining step (RDS)
- Assume all steps before RDS in equilibrium with recatants
- All steps after RDS in equilibrium with products
- Plug into site balance

Example:

The reaction A + B $\Rightarrow$ C obeys:

$$\begin{array}{lcccll} S & + & A & \Rightarrow & A_{ad} & (1) \\ S & + & B & \Rightarrow & B_{ad} & (2) \\ A_{ad} & + & B_{ad} & \Rightarrow & C + 2S & (3) \end{array}$$

(12.157)

Derive an equation for the rate of formation of C as a function of the partial pressures of A and B. Assume that reaction (3) is rate determining.

My solution

$$r_C = k_3[A_{ad}][B_{ad}] \qquad (1)$$

Assume reaction 1 in equilibrium

$$\frac{[A_{ad}]}{S\,P_A} = K_1 \qquad (2)$$

Similarly on reaction 2

$$\frac{[B_{ad}]}{S\,P_B} = K_2 \qquad (3)$$

Combining 1,2 and 3

$$r_C = K_1K_2k_3P_AP_BS^2 \qquad (4)$$

Need S to complete solution: get it from a site balance.

$$S_o = S + [A_{ad}] + [B_{ad}] \qquad (5)$$

Combining (2), (3) and (5)

$$S_o = S + SK_1P_A + K_2P_B \qquad (6)$$

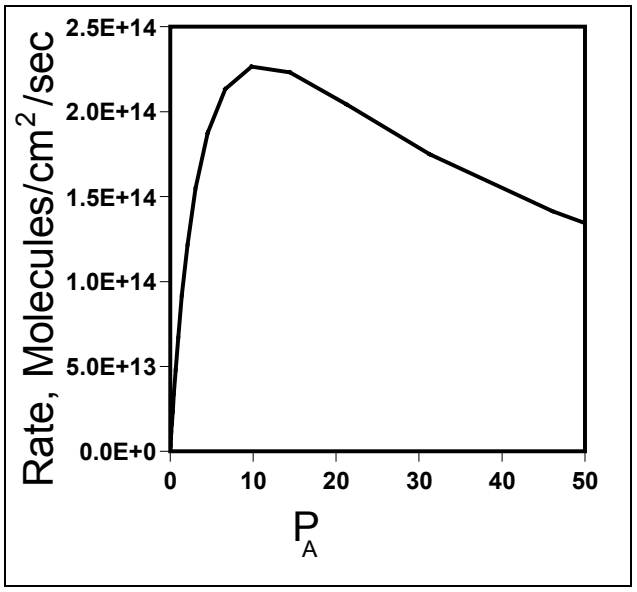
Solving (6) for S

$$S = \frac{S_o}{1 + K_1P_A + K_2P_B} \qquad (7)$$

Combining equations (4) and (7)

$$\boxed{r_C = \frac{K_1 K_2 k_3 P_A P_B (S_o)^2}{(1 + K_1 P_A + K_2 P_B)^2}} \qquad (8)$$

Next what does this look like?



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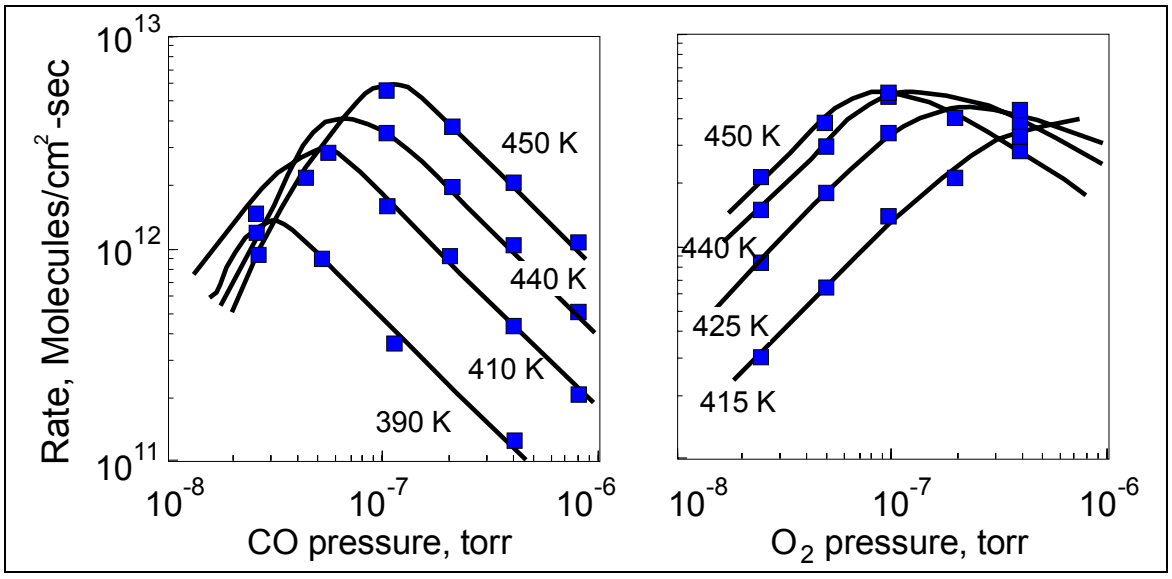

Figure 2.15 The influence of the CO pressure on the rate of CO oxidation on Rh(111). Data of Schwartz, Schmidt, and Fisher.

Discussion problem:

consider a different reaction

$$A \Rightarrow C$$

(12.120)

$$S + A \underset{2}{\overset{1}{\rightleftharpoons}} A_{ad}$$

$$A_{Ad} \underset{4}{\overset{3}{\rightleftharpoons}} C_{ad}$$

$$C_{ad} \underset{6}{\overset{5}{\rightleftharpoons}} C + S$$

(12.121)

Derivation the same:

$$r_{C_{Ad}} = k_3[A_{ad}] - k_4[C_{ad}]$$

(12.123)

Derive rate equation

$$r = \frac{k_3 K_A P_A S_0 - k_4 K_C P_C S_0}{1 + K_A P_A + K_B P_B + K_C P_C}$$

(12.142)

What does this look like?

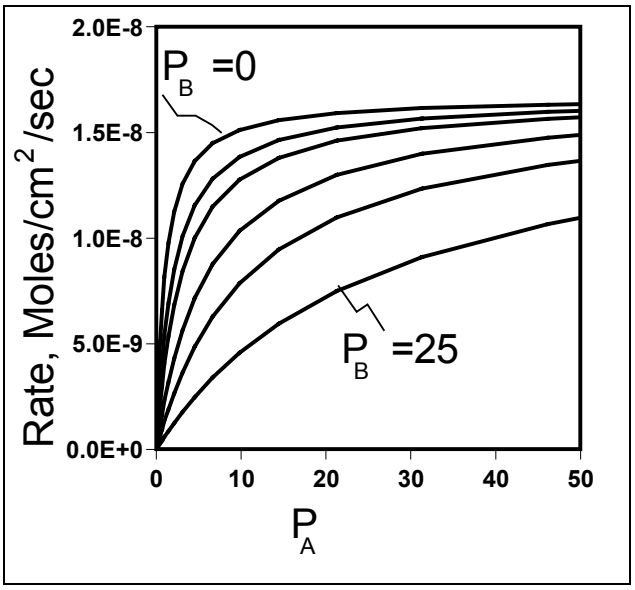

Figure 12.29 A plot of the rate of the reaction A⇒C calculated from Equation (12.142) with k_4=0, P_B = 0, 1, 2, 5, 10 and 25., K_A = K_B =1.

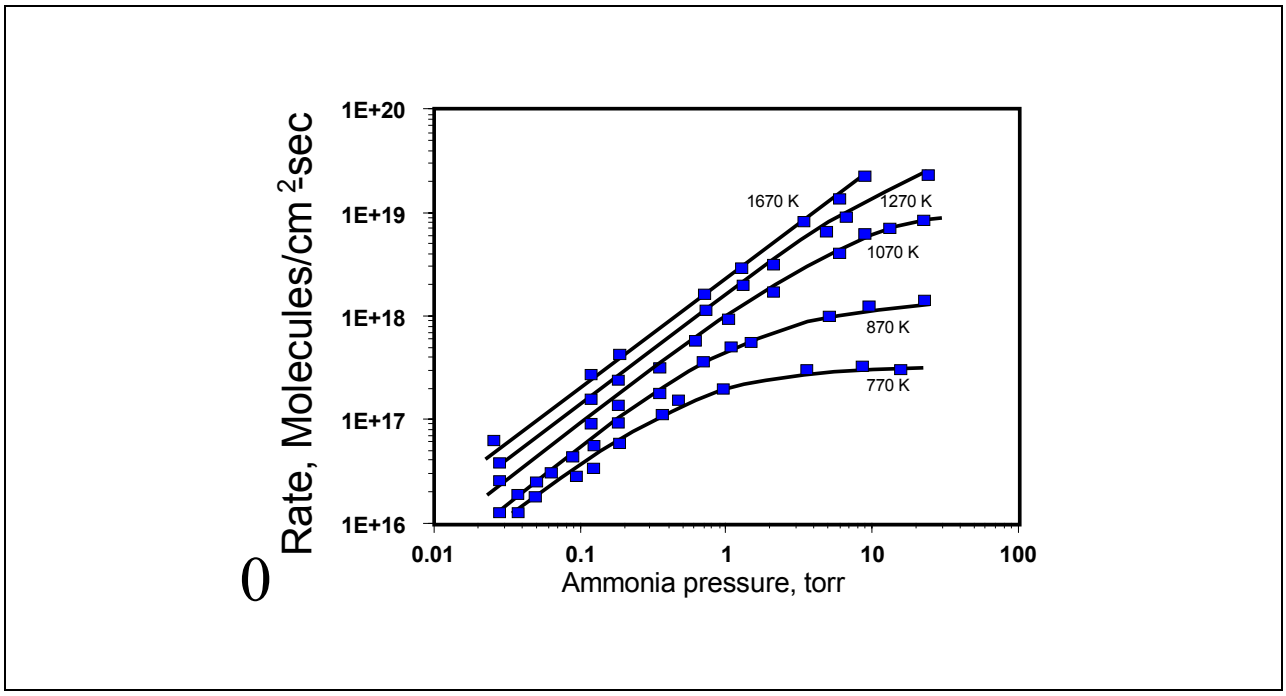

Figure 2.16 The rate of the reaction $NH_3 \Rightarrow 1/2N_2 + 3/2H_2$ over a platinum wire catalyst. Data of Loffler and Schmidt[1976].

Summary:

- Catalytic reactions follow a catalytic cycle
  reactants + S $\Rightarrow$adsorbed reactants
  Adsorbed reactants $\Rightarrow$products + S
- Different types of reactions
  Langmuir Hinshelwood
  Rideal-Eley
- Calculate kinetics via Hougan and Watson;
  - Identify rate determining step (RDS)
  - Assume all steps before RDS in equilibrium with recatants
  - All steps after RDS in equilibrium with products
  - Plug into site balance
- Predicts non-linear behavior also seen experimentally

Next topic: Mass transfer in catalysts

Mass transfer is important to catalytic reactions:

Catalyst increases Reaction rate by 10^{20}-10^{40}
Mass transfer rate does not change.

If you have a really active catalyst, mass transfer will control the rate.

Mass transfer control is good:
- design pore structure to pass desired products much faster than undesired products.

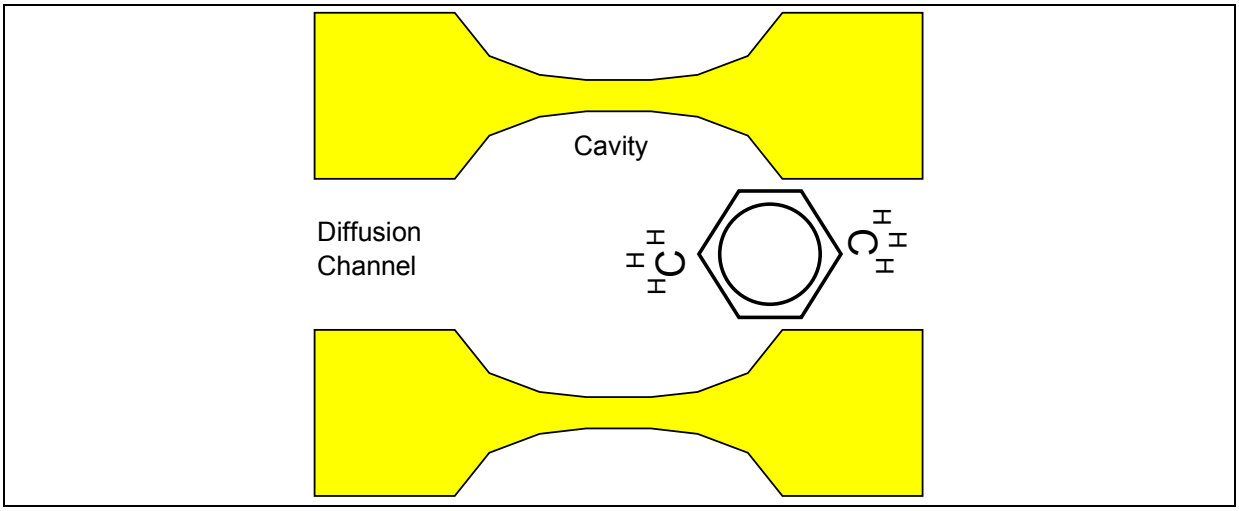

Figure Error! No text of specified style in document..**1** An interconnecting pore structure which is selective for the formation of paraxylene.

Equations for mass transfer limitations

Define Thiele Parameter

$$\Phi_p = \frac{\text{Reaction Rate}}{\text{Diffusion Rate}}$$

Define mass transfer factor (literature calls this effectiveness factor).

$$\eta_e = \frac{\text{Actual Reaction Rate}}{\text{Reaction Rate If Mass Transfer Was Instantaneous}}$$

Derive equation:

Consider a spherical catalyst particle

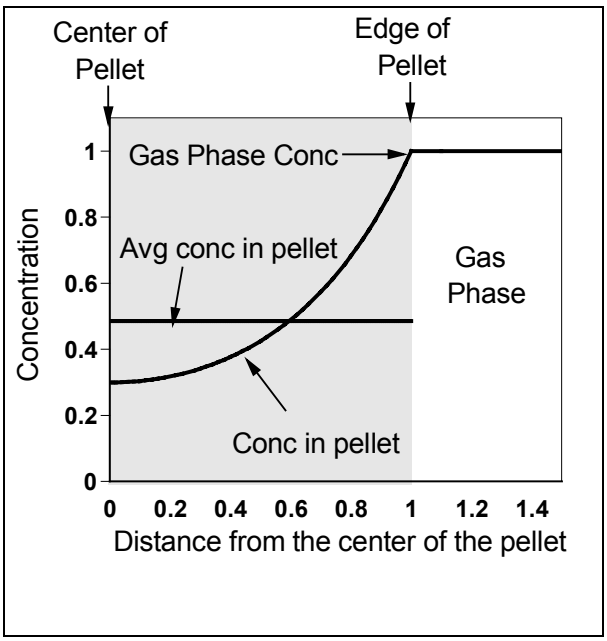

Figure 12.29 **The concentration of species in a spherical catalyst pellet.**

The diffusion equation is

$$\frac{d^2C_A}{dy}+\frac{2}{y}\frac{dC_A}{dy}+\frac{r_A}{D_e}=0$$

Solution:

$$C_A=C_A^0\frac{y_P}{y}\frac{\mathrm{Sinh}(3\Phi_P y/y_P)}{\mathrm{Sinh}(3\Phi_P)}$$

with

$$\Phi_P = \frac{y_P}{3}\sqrt{\frac{k_A}{D_e}}$$

Calculating the reaction rate:

$$\eta_e = \frac{1}{\Phi_P}\left[\frac{1}{\tanh(3\Phi_P)} - \frac{1}{3\Phi_P}\right]$$

A plot of the mass transfer factor versus the Thiele parameter for diffusion in a porous catalyst pellet.

The mass transfer factor does not measure the effectiveness of a catalyst. *Good catalysts can have low mass transfer factors while bad catalysts can have high mass transfer factors.* Generally if a catalyst is not speeding up the reaction very much the Thiele parameter will be small, which means that according to the Figure the mass transfer factor will be close to unity. Thus, a bad catalyst can have a large mass transfer factor.

In contrast, if the catalyst speeds up a reaction a lot, Φ_p will be large. The figure shows that the mass transfer factor is reduced under such circumstances.

Actual equations not useful - never know D_e, but ideas useful.