

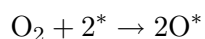
# Notes on Catalytic Kinetics

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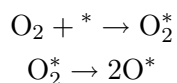
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## 1 Heterogeneous Catalytic Kinetics

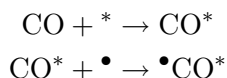
Catalyst surfaces contain active sites where species can form chemical bonds with reacting and surface species. This can be sequential or concerted:



OR



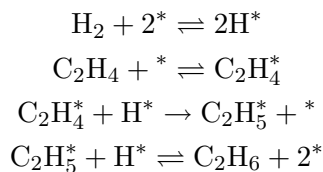
Some reactions employ a combination of sites (though this is not necessary):



Start out with the fact that there are a finite number of active sites on any catalyst!

### 1.1 Catalytic Kinetics: An Example

Consider the reaction scheme



noting that all equations add together to give the overall reaction, cancelling out all adsorbed species on both sides. All reactions are elementary (no  $\frac{1}{2}$  or  $\frac{3}{2}$  order reactions).

Paths to solution:

1. Write down sequence of elementary steps that lead from reactants to products (including empty adsorption sites and adsorbed species)
2. Determine (assume) a rate-controlling step. We'll assume the third step is rate-controlling, meaning

$$\text{rate} = k_3[\text{C}_2\text{H}_4][\text{H}^*]$$

3. Eliminate adsorbed species via equilibrium relations

$$K_1 = \frac{[\text{H}^*]^2}{[\text{H}_2][^*]} \Rightarrow [\text{H}^*] = K_1^{1/2}[\text{H}_2]^{1/2}[^*]$$

$$K_2 = \frac{[\text{C}_2\text{H}_4^*]^2}{[\text{C}_2\text{H}_4][^*]} \Rightarrow [\text{C}_2\text{H}_4^*] = K_2[\text{C}_2\text{H}_4][^*]$$

$$K_4 = \frac{[\text{C}_2\text{H}_6][^*]^2}{[\text{C}_2\text{H}_5^*][\text{H}^*]} \Rightarrow [\text{C}_2\text{H}_5^*] = \frac{[\text{C}_2\text{H}_6][^*]^2}{K_4[\text{H}^*]}$$

4. Substitute for  $C_s = \sum[X^*]$  (concentration of surface sites)
5. Simplify, if possible, and analyze the results!!!

$$\begin{aligned} \text{rate} &= k_3[\text{C}_2\text{H}_4^*][\text{H}^*] = k_3[\text{C}_2\text{H}_4][^*]K_1^{1/2}[\text{H}_2]^{1/2}[^*] \\ C_s &= [^*] + [\text{C}_2\text{H}_4^*] + [\text{H}^*] + [\text{C}_2\text{H}_5^*] \\ &= [^*] + K_2[\text{C}_2\text{H}_4][^*] + K_1^{1/2}[\text{H}_2]^{1/2}[^*] + \frac{[\text{C}_2\text{H}_6][^*]^2}{K_4K_1^{1/2}[\text{H}_2]^{1/2}[^*]} \\ &= [^*] \left( 1 + K_2[\text{C}_2\text{H}_4] + K_1^{1/2}[\text{H}_2]^{1/2} + \frac{[\text{C}_2\text{H}_6]}{K_4K_1^{1/2}[\text{H}_2]^{1/2}} \right) \\ [^*] &= \frac{C_s}{1 + K_2[\text{C}_2\text{H}_4] + K_1^{1/2}[\text{H}_2]^{1/2} + \frac{[\text{C}_2\text{H}_6]}{K_4K_1^{1/2}[\text{H}_2]^{1/2}}} \end{aligned}$$

therefore

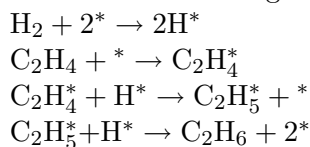
$$\text{rate} = \frac{k_3K_2K_1^{1/2}C_s^2[\text{C}_2\text{H}_4][\text{H}_2]^{1/2}}{1 + K_2[\text{C}_2\text{H}_4] + K_1^{1/2}[\text{H}_2]^{1/2} + \frac{[\text{C}_2\text{H}_6]}{K_4K_1^{1/2}[\text{H}_2]^{1/2}}}$$

## 1.2 Questions to Ask

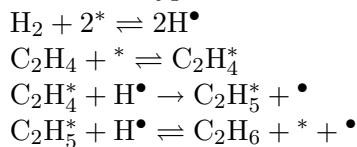
- What are the ranges of rate dependencies on the concentrations of ethylene and on hydrogen that could be measured:  $[\text{H}_2]^n[\text{C}_2\text{H}_4]^m$ ?
- What do these depend on?

### 1.3 Other Mechanisms

Different rate controlling steps; any of

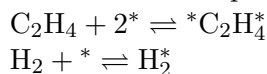


Two different types of site:

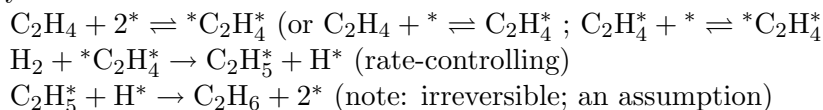


$$\text{rate} = \frac{C_{s,*} C_{s,\bullet} k_3 K_2 K_1^{1/2} [\text{C}_2\text{H}_4] [\text{H}_2]^{1/2}}{\left(1 + K_1^{1/2} [\text{H}_2]^{1/2}\right) \left(1 + K_2 [\text{C}_2\text{H}_4] + \frac{[\text{C}_2\text{H}_6]}{K_4 K_1^{1/2} [\text{H}_2]^{1/2}}\right)}$$

Other forms of adsorption steps that may be included:



Eley–Rideal mechanism<sup>1</sup>



$$\text{rate} = k_2 [^*\text{C}_2\text{H}_4^*] [\text{H}_2] \approx \frac{k_2 K_1 C_s^2 [\text{C}_2\text{H}_4] [\text{H}_2]}{1 + K_1 [\text{C}_2\text{H}_4]}$$

Several approaches; not always easily solved!

### 1.4 Considerations

General form of rate law for Langmuir–Hinshelwood kinetics:

$$\text{rate} = \frac{k_{\text{rcs}} C_s^n \prod_i K_i^{n_i} \prod_j [\text{Reactant}_j]^{m_j}}{[1 + \sum_i K_i [\text{Reactant}]^{\# \text{ sites (different sites?)}}]} \quad (1)$$

How do we distinguish between the myriad of options?

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<sup>1</sup>This mechanism has never been confirmed to exist in any real reaction. An Eley–Rideal mechanism is experimentally equivalent to a Langmuir–Hinshelwood mechanism in which the adsorption of one component is the rate-limiting step.

- From kinetics? If you only measure  $r = k[\text{H}_2]^n[\text{C}_2\text{H}_4]^m$ , what are the ranges of exponents you can see?
- Measurements of adsorption equilibria and heats of adsorption?
- What does  $C_s^m$  mean?
- How will the apparent rate coefficient depend on temperature? An “effective activation energy”!!!

## 2 Determination of Reaction Order

What types of experiments can you do?

- Constant  $T$ : vary one flow and leave others constant
- Constant  $T$  and  $Q_{\text{total}}$ : vary one flow, adjust inerts
- Constant  $T$  and  $C_i$ : vary  $Q_{\text{total}}$  and adjust all flows.

What can you measure?

- $T$  (temperature)
- $C_{i,\text{in}}$  and  $C_{i,\text{out}}$
- $Q_i$  and  $Q_{\text{total}}$ .

A reaction that is order  $n$  in species  $A$  reacts according to the rate law

$$r_A = -k_A C_A^n \quad (2)$$

when  $A$  is a reactant. The type of reactor determines the actual time behavior of the system. In a **batch reactor**, where  $C_A$  is a function of time  $t$ , the mole balance on species  $A$  (assuming constant density and volume) yields

$$\frac{dC_A}{dt} = -k_A C_A^n. \quad (3)$$

In a **plug flow reactor** (PFR), each “plug” of fluid travels along the reactor and does not mix appreciably with the fluid from other plugs. The time variable in a PFR is therefore equivalent to the distance along the plug flow reactor ( $z$ ) times the mean fluid velocity. At the *exit* of the PFR, the residence time  $t$  is  $t = V/F$ , where  $V$  is the volume of the reactor and  $F$  is the flow rate.

Integrating these expressions, we can obtain an expression for  $C_A$  as a function of  $t$ :

$$\int_0^t dt' = t = - \int_{C_{A,0}}^{C_A} \frac{dC}{k_A C^n} = \begin{cases} \frac{1}{k_A(1-n)C_A^{n-1}} - \frac{1}{k_A(1-n)C_{A,0}^{n-1}}, & n \neq 1 \\ -\frac{1}{k_A} \log\left(\frac{C_A}{C_{A,0}}\right), & n = 1 \end{cases} \quad (4)$$

In a **continuous stirred tank reactor** (CSTR), the dynamics are completely different. A mole balance on species  $A$  in a constant volume, constant density CSTR yields

$$\frac{dC_A}{dt} = -k_A C_A^n + \frac{F}{V} C_{A,0} - \frac{F}{V} C_A \quad (5)$$

If we make the assumption that the reactor runs at steady-state, we can simplify this expression to

$$k_A C_A^n = \frac{F}{V} C_{A,0} - \frac{F}{V} C_A \Rightarrow \frac{V}{F} = \tau = \frac{C_{A,0} - C_A}{k_A C_A^n} \quad (6)$$

where  $\tau = V/F$  is the *mean residence time* of the reactor.

## 2.1 Examples

For these examples, it is useful to define the dimensionless number  $M_{A,n} = k_A \tau C_{A,0}^{n-1}$  for ease of plotting.

### 2.1.1 Negative First Order in A

**PFR**

$$t = \frac{C_{A,0}^2 - C_A^2}{2k_A} \Rightarrow \frac{C_A}{C_{A,0}} = \sqrt{2k_A t C_{A,0}^{-2} + 1} = \sqrt{1 + M_{A,0}} \quad (7)$$

**CSTR**

$$\tau = \frac{C_{A,0} C_A - C_A^2}{k_A} \Rightarrow \frac{C_A}{C_{A,0}} = \frac{1}{2} \left[ 1 + \sqrt{1 - 4k_A \tau C_{A,0}^{-2}} \right] = \frac{1}{2} \left[ 1 + \sqrt{1 - 4M_{A,-1}} \right] \quad (8)$$

### 2.1.2 Zero Order in A

**PFR**

$$t = \frac{C_{A,0} - C_A}{k_A} \Rightarrow \frac{C_A}{C_{A,0}} = 1 - \frac{k_A t}{C_{A,0}} = 1 - M_{A,0} \quad (9)$$

**CSTR**

$$\tau = \frac{C_{A,0} - C_A}{k_A} \Rightarrow \frac{C_A}{C_{A,0}} = 1 - \frac{k_A \tau}{C_{A,0}} = 1 - M_{A,0} \quad (10)$$

### 2.1.3 First Order in A

**PFR**

$$t = -\frac{1}{k_A} \log \left( \frac{C_A}{C_{A,0}} \right) \Rightarrow \frac{C_A}{C_{A,0}} = e^{-k_A t} = e^{-M_{A,1}} \quad (11)$$

**CSTR**

$$\tau = \frac{C_{A,0} - C_A}{k_A C_A} = \frac{1}{k_A} \frac{C_{A,0}}{C_A} - \frac{1}{k_A} \Rightarrow \frac{C_A}{C_{A,0}} = \frac{1}{1 + k_A \tau} = \frac{1}{1 + M_{A,1}} \quad (12)$$

### 2.1.4 Second Order in A

**PFR**

$$t = \frac{C_{A,0} - C_A}{k_A} \Rightarrow \frac{C_A}{C_{A,0}} = \frac{1}{1 + k_A \tau C_{A,0}} = \frac{1}{1 + M_{A,2}} \quad (13)$$

**CSTR**

$$\begin{aligned} \tau = \frac{C_{A,0} - C_A}{k_A C_A^2} \Rightarrow k_A \tau C_{A,0} \left( \frac{C_A}{C_{A,0}} \right)^2 + \frac{C_A}{C_{A,0}} - 1 = 0 \Rightarrow \\ \frac{C_A}{C_{A,0}} = \frac{\sqrt{1 + 4k_A \tau C_{A,0}} - 1}{2k_A \tau C_{A,0}} = \frac{\sqrt{1 + 4M_{A,2}} - 1}{2M_{A,2}} \end{aligned} \quad (14)$$

### 2.1.5 Third Order in A

**PFR**

$$t = \frac{1}{2k_A C_{A,0}^2} - \frac{1}{2k_A C_A^2} \Rightarrow \frac{C_A}{C_{A,0}} = \frac{1}{\sqrt{1 - 2k_A t C_{A,0}^2}} = \frac{1}{\sqrt{1 - 2M_{A,3}}} \quad (15)$$

**CSTR**

$$\tau = \frac{C_{A,0} - C_A}{k_A C_A^3} \Rightarrow (k_A \tau C_{A,0}^2) \left( \frac{C_A}{C_{A,0}} \right)^3 + \frac{C_A}{C_{A,0}} - 1 = M_{A,3} \left( \frac{C_A}{C_{A,0}} \right)^3 + \frac{C_A}{C_{A,0}} - 1 = 0 \quad (16)$$

The solution to Equation (16) cannot be deduced immediately without knowing the values of  $k_A$ ,  $\tau$ , and  $C_{A,0}$  due to the cubic nature of the equation. One can either solve iteratively,

or use the general solutions:<sup>2</sup>

$$\frac{C_A}{C_{A,0}} \in \left\{ \begin{array}{l} \frac{-1}{3M_{A,3}} \left( 1 + \sqrt[3]{\frac{2-27M_{A,3}^2 + \sqrt{(2-27M_{A,3})^2 - 4}}{2}} + \sqrt[3]{\frac{2-27M_{A,3}^2 - \sqrt{(2-27M_{A,3})^2 - 4}}{2}} \right) \\ \frac{-1}{3M_{A,3}} + \frac{1+i\sqrt{3}}{6M_{A,3}} \sqrt[3]{\frac{2-27M_{A,3}^2 + \sqrt{(2-27M_{A,3})^2 - 4}}{2}} + \frac{1-i\sqrt{3}}{6M_{A,3}} \sqrt[3]{\frac{2-27M_{A,3}^2 - \sqrt{(2-27M_{A,3})^2 - 4}}{2}} \\ \frac{-1}{3M_{A,3}} + \frac{1-i\sqrt{3}}{6M_{A,3}} \sqrt[3]{\frac{2-27M_{A,3}^2 + \sqrt{(2-27M_{A,3})^2 - 4}}{2}} + \frac{1+i\sqrt{3}}{6M_{A,3}} \sqrt[3]{\frac{2-27M_{A,3}^2 - \sqrt{(2-27M_{A,3})^2 - 4}}{2}} \end{array} \right. \quad (17)$$

Two of these three solutions represent non-physical states (either negative conversion or complex conversions) and should be discarded.

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<sup>2</sup>I do not vouch for the accuracy of these expressions.