

## Lecture # 33 CHE331A

### Langmuir-Hinshelwood kinetics and the rate limiting/controlling step

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2020-2021 1<sup>st</sup> semester

- ❑ Catalysis
  - ❑ Porous and non-porous
  - ❑ Physisorption and chemisorption
  - ❑ Langmuir Isotherms
- ❑ Kinetics of Catalytic Reactions
- ❑ Diffusion and Reaction in porous catalysts



## Steps 3, 4 and 5 are important chemical steps in heterogeneously catalyzed reactions

- ▶ Mass transfer (diffusion) of the reactants from the bulk fluid to the external surface of the catalyst pellet – external diffusion
- ▶ Diffusion of reactant(s) from pore mouth through the catalyst pores to the active sites (not there for non-porous catalysts) – internal diffusion
- ▶ **Adsorption of species A on to the surface of the active site**
- ▶ **Reaction at active site – surface reaction (single/multiple steps)**
- ▶ **Desorption of products from the active site**
- ▶ Diffusion of products from the interior to external surface (not there for non-porous catalysts)
- ▶ Mass transfer of the products from the external surface to the bulk liquid



## Adsorbed species can react in several ways (step 4)

► Adsorbed A can react as

(i)  $A.S \rightleftharpoons B.S$  with a rate constant  $k_S$  and  $k_{-S}$

For this elementary step:  $r_S = k_S \left( C_{A.S} - \frac{C_{B.S}}{K_S} \right)$  with

where,  $r_S$  is the rate of surface reaction  $\left( \frac{\text{mol}}{\text{g-cat.time}} \right)$

$K_S = k_S / k_{-S}$  is the equilibrium constant for surface reaction

(ii)  $A.S + S \rightleftharpoons B.S + S$  and  $r_S = k_S \left( C_{A.S} C_S - \frac{C_{B.S} C_S}{K_S} \right)$  (Dual site mechanism)

► These types of mechanism are referred to as following Langmuir-Hinshelwood kinetics



## Other Langmuir-Hinshelwood surface reactions exists

► Generic case:  $A.S + B.S \rightleftharpoons C.S + D.S$ , and  $r_s = k_s \left( C_{A.S} C_{B.S} - \frac{C_{C.S} C_{D.S}}{K_S} \right)$

► Another dual site mechanism:  $A.S + B.S' \rightleftharpoons C.S' + D.S$  and

$$r_s = k_s \left( C_{A.S} C_{B.S'} - \frac{C_{C.S'} C_{D.S}}{K_S} \right)$$

where,  $S$  and  $S'$  are two different sites on the surface

For example, CO + O on Pt (S) and Fe(S') sites on the surface

► Eley-Rideal: a special type of L-H mechanism where one of the reactant is not adsorbed, e.g., propylene (gas) and benzene (adsorbed)



## The Desorption step (step 5) is the final step occurring on the active site

- ▶ The product formed, is desorbed from the active site into the fluid phase
- ▶  $C.S \rightleftharpoons C + S$  and the rate of desorption of C is

$$r_{DC} = k_D \left( C_{C.S} - \frac{P_C C_S}{K_{DC}} \right)$$

- ▶ Where,  $K_{DC}$  is the equilibrium constant for the desorption of C and
- ▶  $K_{DC} = 1/K_C$  where  $K_C$  is the equilibrium constant for the adsorption of C
- ▶ Thus,

$$r_{DC} = k_D (C_{C.S} - K_C P_C C_S)$$



## The rate limiting or rate controlling step

- ▶ During the heterogeneous reactions carried out at steady state, the three rates (adsorption, surface reaction and desorption) are equal to each other,

$$-r'_A = r_{AD} = r_S = r_D \left( \frac{\text{mol}}{\text{gcat.time}} \right)$$

- ▶ Usually, one of the three is usually found to be rate-limiting or rate-controlling
  - The reaction proceed in an accelerated rate if this step goes faster
- ▶ For example,
  - During ammonia synthesis, the adsorption and dissociation of  $N_2$  is the rate-limiting or rate-controlling steps:  $N_2 + S \rightleftharpoons N_2.S$ , and  $N_2.S + S \rightleftharpoons 2N.S$
  - Reaction of CO and NO surface species are considered rate-limiting





# The mechanism, rate-limiting step and the rate law

- ▶ Need to develop rate law for catalytic reaction → design/analysis of reactors
- ▶ Rate law is developed from a particular mechanism and rate-limiting step(s)
  - The rate law should be consistent with experimental observations
- ▶ Decomposition of Cumene to Benzene and propylene as an example
- ▶ Overall reaction:  $C_6H_5CH(CH_3)_2 \rightarrow C_6H_6 + C_3H_6$
- ▶ Steps 3, 4 and 5 (mechanism) are:
  - $C + S \rightleftharpoons C.S$  (adsorption of cumene)
  - $C.S \rightleftharpoons B.S + P$  (surface reaction of cumene showing decomposition)
  - $B.S \rightleftharpoons B + S$  (desorption of benzene)



## The rates for the different steps can be developed

- ▶ Adsorption:  $r_{AD} = k_A \left( P_C C_S - \frac{C_{C.S}}{K_C} \right) \frac{\text{mol}}{\text{g-cat.s}}$   $k_A$  units of  $(\text{kPa.s})^{-1}$

$$C_{C.S} \text{ units of } \frac{\text{mol cumene adsorbed}}{\text{g-cat}} \quad C_S \text{ units of } \frac{\text{mol vacant sites}}{\text{g-cat}} \quad K_C \text{ units of } \text{kPa}^{-1}$$

- ▶ Surface reaction:  $C.S \rightleftharpoons B.S + P$  and  $r_S = k_S \left( C_{C.S} - \frac{P_P C_{B.S}}{K_S} \right)$

$$k_S \text{ units of } (\text{s})^{-1} \quad \text{and } K_S \text{ units of } \text{kPa} \quad \text{Note: } C_{P.S} = 0$$

- ▶ Desorption:  $B.S \rightleftharpoons B + S$  and  $r_D = k_D \left( C_{B.S} - \frac{P_B C_S}{K_{DB}} \right) = k_D (C_{B.S} - K_B P_B C_S)$

- ▶ Since there is no accumulation of the reacting species, the rates of each step are equal and  $-r'_C = r_{AD} = r_S = r_D$

- ▶ Need to determine which step is rate-limiting and then proceed to find the rate law → check rate law predicted with experimental findings





## Rate law depending on the rate-limiting step chosen

- ▶ For rate of adsorption to be rate limiting:  $-r'_C = r_{AD} = k_A \left( P_C C_S - \frac{C_{C.S}}{K_C} \right)$   
since  $C_S$  and  $C_{C.S}$  are not readily measurable they need to be replaced
- ▶ For adsorption-limited,  $k_A$  (actually  $k_A P_C$ ) is small,  $k_S$  and  $k_D$  are large
- ▶ Thus,  $r_{AD}/k_A$  is large and  $r_S/k_S$  and  $r_D/k_D$  are small ( $\approx 0$ )
- ▶  $r_S = k_S \left( C_{C.S} - \frac{P_P C_{B.S}}{K_S} \right)$  and for  $r_S/k_S \approx 0$   $C_{C.S} = \frac{P_P C_{B.S}}{K_S}$  and
- ▶  $r_D = k_D (C_{B.S} - K_B P_B C_S)$ , and for  $r_D/k_D \approx 0$   $C_{B.S} = K_B P_B C_S$  and  $C_{C.S} = \frac{K_B P_P P_B C_S}{K_S}$
- ▶ Thus,  $r_{AD} = k_A \left( P_C C_S - \frac{C_{C.S}}{K_C} \right) = k_A C_S \left( P_C - \frac{K_B P_B P_P}{K_S K_C} \right) = k_A C_S \left( P_C - \frac{P_B P_P}{K_P} \right)$   
since  $\frac{K_S K_C}{K_B} = \left( \frac{P_P C_{B.S}}{C_{C.S}} \right) \left( \frac{C_{C.S}}{P_C C_S} \right) \left( \frac{P_B C_S}{C_{B.S}} \right) = \frac{P_B P_P}{P_C} = K_P$  the overall equilibrium constant



# Site balance is required to find $C_S$ in measurable quantities

- ▶ For rate of adsorption to be rate limiting:  $-r'_C = r_{AD} = k_A C_S \left( P_C - \frac{P_B P_P}{K_P} \right)$ 
  - Need to determine  $C_S$  in measurable quantities
- ▶ Site balance:  $C_t = C_S + C_{B.S} + C_{C.S}$
- ▶ We have:  $C_{B.S} = K_B P_B C_S$  and  $C_{C.S} = \frac{K_B P_P P_B C_S}{K_S}$
- ▶ Thus,  $C_t = C_S + K_B P_B C_S + \frac{K_B P_P P_B C_S}{K_S} = C_S \left( 1 + K_B P_B + \frac{K_B P_P P_B}{K_S} \right)$
- ▶ And,  $C_S$  in measurable quantities is given by

$$C_S = \frac{C_t}{\left( 1 + K_B P_B + \frac{K_B P_P P_B}{K_S} \right)}$$

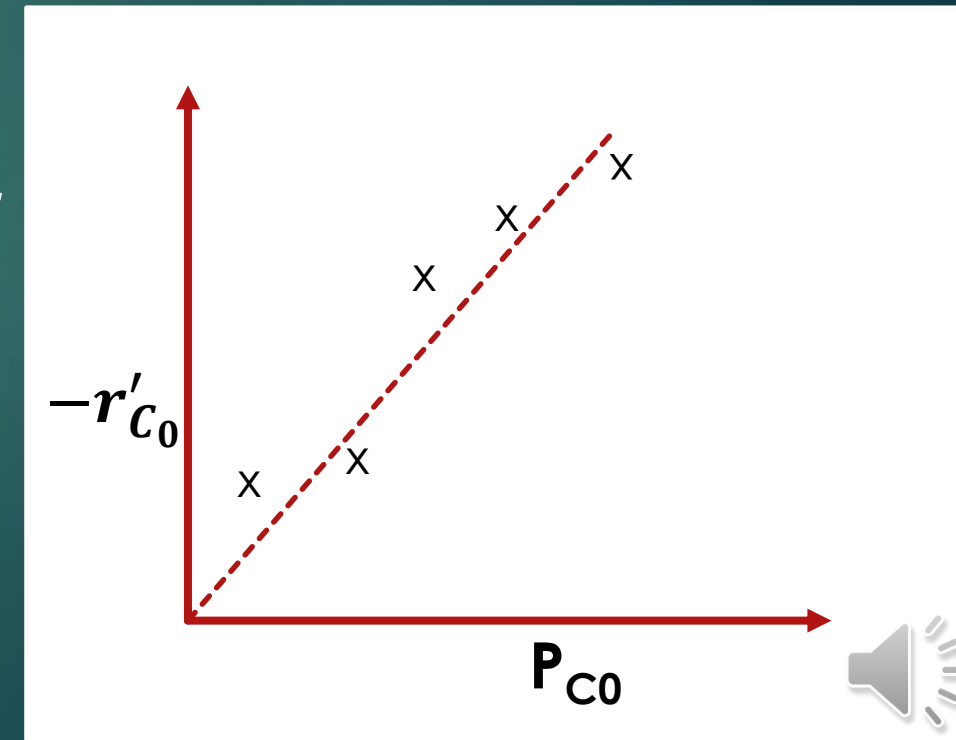


# The rate law for adsorption limited reactions

- ▶ Thus, rate law for adsorption limited reactions:

$$-r'_C = r_{AD} = \frac{k_A C_t}{\left(1 + K_B P_B + \frac{K_B P_P P_B}{K_S}\right)} \left(P_C - \frac{P_B P_P}{K_P}\right)$$

- ▶ For initial rates we have:  $P_B = 0 = P_P$  and  $P_C = P_{C0}$ 
  - Insignificant amounts of products are formed
- ▶ Thus,  $-r'_{C0} = r_{AD} = k_A C_t P_{C0} \rightarrow 1^{\text{st}}$  order w.r.t.  $P_C$
- ▶ If initial rate of Cumene decomposition increases linearly with partial pressure of Cumene ( $P_{C0}$ ) then **adsorption is rate limiting**



# Surface reaction can be rate limiting/controlling

- ▶ For surface reaction rate-limiting:  $-r'_C = r_S = k_S \left( C_{C.S} - \frac{P_P C_{B.S}}{K_S} \right)$
  - ▶ Similar to before:  $\frac{r_{AD}}{k_{AD}} \cong 0$  and  $\frac{r_D}{k_D} \cong 0 \rightarrow P_C C_S = \frac{C_{C.S}}{K_C}$  and  $C_{B.S} = K_B P_B C_S$
  - ▶ Thus,  $r_S = k_S \left( K_C P_C - \frac{K_B P_P P_B}{K_S} \right) C_S$  and with  $\frac{K_S K_C}{K_B} = K_P$
  - ▶  $r_S = k_S K_C \left( P_C - \frac{P_P P_B}{K_P} \right) C_S$  need to determine  $C_S$  from site balance
  - ▶ Site balance:  $C_t = C_S + C_{B.S} + C_{C.S} = C_S + K_B P_B C_S + K_C P_C C_S$
  - ▶  $C_S = \frac{C_t}{1 + K_B P_B + K_C P_C}$  and after substituting  $r_S = k_S K_C \left( P_C - \frac{P_P P_B}{K_P} \right) \frac{C_t}{1 + K_B P_B + K_C P_C}$
- $$r_S = \frac{k_S K_C C_t}{1 + K_B P_B + K_C P_C} \left( P_C - \frac{P_P P_B}{K_P} \right)$$



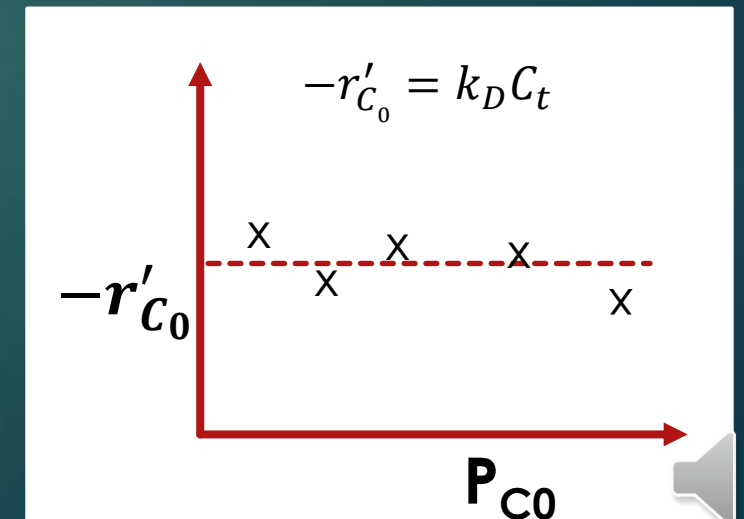
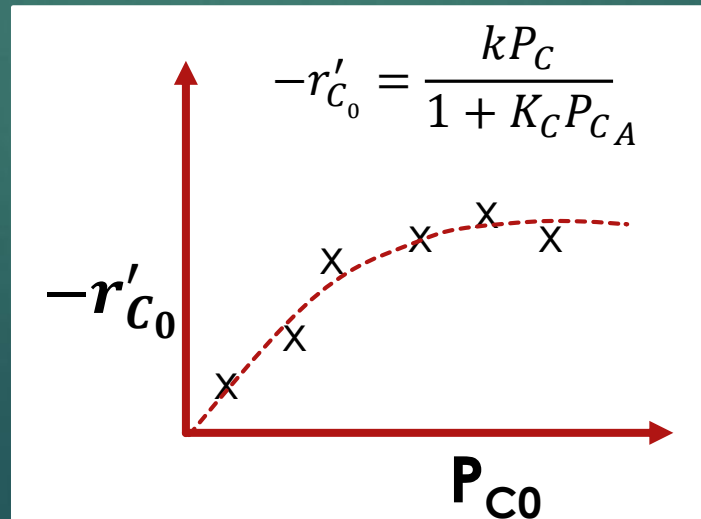
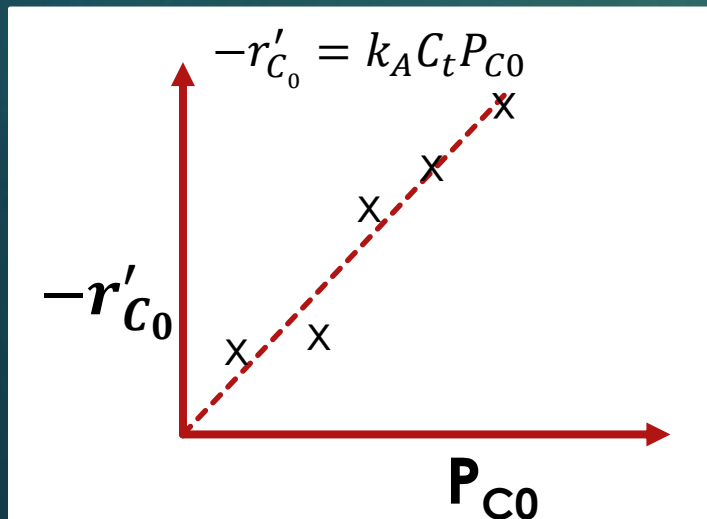
# The rate laws for surface reaction and desorption limiting can be differentiated

- ▶ For surface reaction limiting:  $-r'_C = r_S = \frac{k_s K_C C_t}{1 + K_B P_B + K_C P_C} \left( P_C - \frac{P_P P_B}{K_P} \right)$
- ▶ And the initial rates are given by:  $r_S = \frac{k_s K_C C_t P_C}{1 + K_C P_C} = \frac{k P_C}{1 + K_C P_C}$
- ▶ Initial rates of cumene disappearance is:  $r'_C = r_S = \frac{k P_C}{1 + K_C P_C}$  with  $k = k_s K_C C_t$
- ▶ Similarly for desorption limited reaction it can be shown that:
- ▶  $-r'_C = r_D = \frac{k_D \cdot C_t \cdot K_S \cdot K_C}{P_P + K_C K_S P_C + K_C P_C P_P} \left( P_C - \frac{P_B \cdot P_P}{K_P} \right)$  and with  $P_B = 0 = P_P$  and  $P_C = P_{C0}$
- ▶ Initial rate for cumene disappearance is:  $-r'_C = r_D = k_D \cdot C_t$  which does not depend on  $P_{C0}$



# Rate-limiting step can be used to determine initial rates

- ▶ Rate law for adsorption limited: 
$$-r'_C = \frac{k_A C_t}{\left(1 + K_B P_B + \frac{K_B P_P P_B}{K_S}\right)} \left(P_C - \frac{P_B P_P}{K_P}\right)$$
- ▶ Rate law for surface-reaction limited: 
$$-r'_C = \frac{k_s K_C C_t}{1 + K_B P_B + K_C P_C} \left(P_C - \frac{P_P P_B}{K_P}\right)$$
- ▶ Rate law for desorption limited: 
$$-r'_C = \frac{k_D \cdot C_t \cdot K_S \cdot K_C}{P_P + K_C K_S P_C + K_C P_C P_P} \left(P_C - \frac{P_B \cdot P_P}{K_P}\right)$$
- ▶ Based on the corresponding initial rates:





# The rate law can be derived using other approximations

- ▶ These approximations include:
  - Pseudo steady state hypothesis
  - Quasi-equilibrium approximation
  - Irreversible step approximation
  - MARI (most abundant intermediate) approximation
  - And others
- ▶ The basic idea being to find a rate law that is able to capture the experimental data for variations of operating variables
- ▶ Use the rate-law to designing and analyze a catalytic reactor to achieve a specific conversion

