## ChemE 2200 - Physical Chemistry II for Engineers - Spring 2025 Solution to Homework Assignment 14

1.(A) Adding the four elementary reactions and canceling substances that appear on both sides of the chemical equation yields the overall reaction:

$$CH_3OH + CO \rightarrow CH_3COOH$$

(B)



Check: The cycle agrees with the overall reaction:  $CH_3OH$  and CO enter and only  $CH_3COOH$  leaves. All other substances are inside a loop. There are four nodes (points where arrows converge and diverge), consistent with four reactions.

2. Reaction 4 is rate limiting, so the rate of any subsequent step is equal to the rate of reaction 4.

$$\frac{d[\mathrm{H}_2]}{dt} = k_6[\mathrm{H}_3\mathrm{O}^-] = k_4[\mathrm{H}_2\mathrm{O}][\mathrm{H}_2\mathrm{C}(\mathrm{O}^-)_2]$$
(1)

Or, stated another way, the intermediate  $H_3O^-$  is in steady state because reaction (6) is much faster than reaction (4).  $H_3O^-$  is produced slowly in reaction (4) and then consumed rapidly in reaction (6). This will keep  $[H_3O^-]$  small and constant. Apply the steady-state approximation to  $H_3O^-$ .

$$\frac{d[\mathrm{H}_{3}\mathrm{O}^{-}]}{dt} = 0 = k_{4}[\mathrm{H}_{2}\mathrm{O}][\mathrm{H}_{2}\mathrm{C}(\mathrm{O}^{-})_{2}] - k_{6}[\mathrm{H}_{3}\mathrm{O}^{-}]$$
$$k_{4}[\mathrm{H}_{2}\mathrm{O}][\mathrm{H}_{2}\mathrm{C}(\mathrm{O}^{-})_{2}] = k_{6}[\mathrm{H}_{3}\mathrm{O}^{-}]$$

This is the same relation assumed in eqn (1).

We need an expression for  $[H_2C(O^-)_2]$ . Reactions 1, 2, and 3 are in equilibrium. Write the equilibrium constants for each.

$$\frac{k_1}{k_{-1}} = K_1 = \frac{[\text{H}_2\text{C}(\text{OH})_2]}{[\text{H}_2\text{CO}][\text{H}_2\text{O}]}$$
$$\frac{k_2}{k_{-2}} = K_2 = \frac{[\text{H}_2\text{C}(\text{OH})\text{O}^-][\text{H}_2\text{O}]}{[\text{H}_2\text{C}(\text{OH})_2][\text{OH}^-]}$$
$$\frac{k_3}{k_{-3}} = K_3 = \frac{[\text{H}_2\text{C}(\text{O}^-)_2][\text{H}_2\text{O}]}{[\text{H}_2\text{C}(\text{OH})\text{O}^-][\text{OH}^-]}$$

Calculate the product of the equilibrium constants.

$$K_{1}K_{2}K_{3} = \frac{[H_{2}C(OH)_{2}]}{[H_{2}CO][H_{2}O]} \frac{[H_{2}C(OH)O^{-}][H_{2}O]}{[H_{2}C(OH)_{2}][OH^{-}]} \frac{[H_{2}C(O^{-})_{2}][H_{2}O]}{[H_{2}C(OH)O^{-}][OH^{-}]}$$
$$= \frac{[H_{2}C(O^{-})_{2}][H_{2}O]}{[H_{2}CO][OH^{-}]^{2}}$$
$$[H_{2}C(O^{-})_{2}][H_{2}O] = K_{1}K_{2}K_{3}[H_{2}CO][OH^{-}]^{2}$$
(2)

Substitute eqn (2) into eqn (1).

$$\frac{d[H_2]}{dt} = k_4 K_1 K_2 K_3 [H_2 CO] [OH^-]^2$$

3. From the elementary mechanism we write a rate equation for [P].

$$\frac{d[\mathbf{P}]}{dt} = k[\mathbf{A}][\mathbf{P}] \tag{1}$$

To integrate, we must express [A] as a function of [P] or as a function of t. Write a mass balance on the reactor.

 $(\text{mass of A})_0 + (\text{mass of P})_0 = (\text{mass of A})_t + (\text{mass of P})_t$ 

Divide by the reactor volume and the molecular weights to convert the equation to molar concentrations.

$$[A]_{0} + [P]_{0} = [A] + [P]$$
$$[A] = [A]_{0} + [P]_{0} - [P]$$
(2)

Substitute eqn (2) into eqn (1),

$$\frac{d[P]}{dt} = k([A]_0 + [P]_0 - [P])[P]$$

and then separate 'n' integrate.

$$\int_{[P]_0}^{[P]} \frac{d[P]}{([A]_0 + [P]_0 - [P])[P]} = k \int_0^t dt$$

Use the Method of Partial Fractions to solve the integral on the left. Some algebra yields -

$$\frac{1}{[A]_0 + [P]_0} \int_{[P]_0}^{[P]} \left[ \frac{1}{[P]} + \frac{1}{[A]_0 + [P]_0 - [P]} \right] d[P] = kt$$

$$\left( \ln[P] - \ln([A]_0 + [P]_0 - [P]) \right) \Big|_{[P]_0}^{[P]} = k([A]_0 + [P]_0)t$$

$$\ln \frac{[P]}{[P]_0} - \ln\left(\frac{[A]_0 + [P]_0 - [P]}{[A]_0}\right) = k([A]_0 + [P]_0)t$$

$$\ln\left(\frac{[P][A]_0}{[P]_0([A]_0 + [P]_0 - [P])}\right) = k([A]_0 + [P]_0)t$$

$$\frac{[P][A]_0}{[P]_0([A]_0 + [P]_0 - [P])} = e^{k([A]_0 + [P]_0)t}$$

Solve for [P].

$$[P][A]_{0} = [P]_{0} ([A]_{0} + [P]_{0} - [P]) e^{k([A]_{0} + [P]_{0})t}$$

$$[P][A]_{0} = [P]_{0} ([A]_{0} + [P]_{0}) e^{k([A]_{0} + [P]_{0})t} - [P][P]_{0} e^{k([A]_{0} + [P]_{0})t}$$

$$[P] ([A]_{0} + [P]_{0} e^{k([A]_{0} + [P]_{0})t}) = [P]_{0} ([A]_{0} + [P]_{0}) e^{k([A]_{0} + [P]_{0})t}$$

$$[P] = [P]_{0} \frac{([A]_{0} + [P]_{0}) e^{k([A]_{0} + [P]_{0})t}}{[A]_{0} + [P]_{0} e^{k([A]_{0} + [P]_{0})t}}$$

This is a valid expression, but the time dependence of [P] is easier to see after additional manipulation.

$$\begin{split} [P] &= [P]_{0} \frac{\left(1 + \frac{[P]_{0}}{[A]_{0}}\right) e^{k([A]_{0} + [P]_{0})t}}{1 + \frac{[P]_{0}}{[A]_{0}} e^{k([A]_{0} + [P]_{0})t}} = [P]_{0} \frac{e^{k([A]_{0} + [P]_{0})t} + \frac{[P]_{0}}{[A]_{0}} e^{k([A]_{0} + [P]_{0})t}}{1 + \frac{[P]_{0}}{[A]_{0}} e^{k([A]_{0} + [P]_{0})t}} \\ [P] &= [P]_{0} \frac{e^{k([A]_{0} + [P]_{0})t} - 1 + 1 + \frac{[P]_{0}}{[A]_{0}} e^{k([A]_{0} + [P]_{0})t}}{1 + \frac{[P]_{0}}{[A]_{0}} e^{k([A]_{0} + [P]_{0})t}} \\ [P] &= [P]_{0} \frac{e^{k([A]_{0} + [P]_{0})t} - 1 + 1 + \frac{[P]_{0}}{[A]_{0}} e^{k([A]_{0} + [P]_{0})t}}{1 + \frac{[P]_{0}}{[A]_{0}} e^{k([A]_{0} + [P]_{0})t}} \\ [P] &= [P]_{0} \left[\frac{e^{k([A]_{0} + [P]_{0})t} - 1}{1 + \frac{[P]_{0}}{[A]_{0}} e^{k([A]_{0} + [P]_{0})t}} + \frac{1 + \frac{[P]_{0}}{[A]_{0}} e^{k([A]_{0} + [P]_{0})t}}{1 + \frac{[P]_{0}}{[A]_{0}} e^{k([A]_{0} + [P]_{0})t}} \right] \\ [P] &= [P]_{0} + [P]_{0} \frac{e^{k([A]_{0} + [P]_{0})t} - 1}{1 + \frac{[P]_{0}}{[A]_{0}} e^{k([A]_{0} + [P]_{0})t}}} = [P]_{0} + [A]_{0} \frac{e^{k([A]_{0} + [P]_{0})t} - 1}{\frac{[A]_{0}}{[P]_{0}} + e^{k([A]_{0} + [P]_{0})t} - 1}} \\ \end{array}$$

[P] is now expressed as a sum of the initial concentration and the concentration growth. [P] grows exponentially at first, but soon the exponential in the denominator dominates the sum, and the growth asymptotically approaches  $[P]_0 + [A]_0$ .

4. At equilibrium,

$$k_{ads}[A_2][M]^2 = k_{des}[M-A]^2$$
  
 $\frac{k_{ads}}{k_{des}} = K_{A_2} = \frac{[M-A]^2}{[A_2][M]^2}$  (1)

Start with the definition of the fraction of sites occupied by A,  $\theta_A$ , and derive an expression for the concentration of sites occupied by A, [M-A].

$$\theta_{A} = \frac{[M-A]}{[M]+[M-A]}$$

$$\theta_{A} ([M] + [M-A]) = [M-A]$$

$$\theta_{A} [M] = [M-A](1-\theta_{A})$$

$$\frac{\theta_{A} [M]}{1-\theta_{A}} = [M-A]$$
(2)

Use eqn (2) to substitute for [M-A] in the equilibrium expression, eqn (1),

$$K_{A_2} = \frac{[M-A]^2}{[A_2][M]^2} = \frac{\left(\frac{\theta_A[M]}{1-\theta_A}\right)^2}{[A_2][M]^2} = \frac{\theta_A^2}{[A_2](1-\theta_A)^2}$$

Solve for the fraction of occupied sites,  $\boldsymbol{\theta}_A,$ 

$$\begin{split} K_{A_2}[A_2](1-\theta_A)^2 &= \theta_A^2 \\ K_{A_2}^{1/2}[A_2]^{1/2}(1-\theta_A) &= \theta_A \\ K_{A_2}^{1/2}[A_2]^{1/2} &= \theta_A \left( 1 + K_{A_2}^{1/2}[A_2]^{1/2} \right) \\ \theta_A &= \frac{K_{A_2}^{1/2}[A_2]^{1/2}}{1 + K_{A_2}^{1/2}[A_2]^{1/2}} \end{split}$$

Convert [A<sub>2</sub>] to the partial pressure of A<sub>2</sub>. Note that [A<sub>2</sub>] =  $n_{A_2}/V = P_{A_2}/RT$ .

$$\theta_{\rm A} = \frac{K_{\rm A_2}^{1/2} [{\rm A_2}]^{1/2}}{1 + K_{\rm A_2}^{1/2} [{\rm A_2}]^{1/2}} = \frac{K_{\rm A_2}^{1/2} \frac{P_{\rm A_2}^{1/2}}{RT}}{1 + K_{\rm A_2}^{1/2} \frac{P_{\rm A_2}^{1/2}}{RT}} = \frac{K_{\rm A_2}^{1/2} P_{\rm A_2}^{1/2}}{(RT)^{1/2} + K_{\rm A_2}^{1/2} P_{\rm A_2}^{1/2}}$$

5. The rate of the reaction equals the net rate of the surface reaction, the rate-limiting step.

$$\frac{d[n\mathbf{P}]}{dt} = \frac{d[\mathbf{S} \cdot n\mathbf{P}]}{dt} = -k_s[\mathbf{S} \cdot n\mathbf{P}] + k_{-s}[\mathbf{S} \cdot i\mathbf{P}]$$
(1)

The adsorption/desorption of both nP and iP are in equilibrium. Assume Langmuir isotherms for both nP and iP.

$$[S-nP] = \theta_{nP}[S]_0 = \frac{K_{nP}[nP]}{1 + K_{nP}[nP] + K_{iP}[iP]}[S]_0$$
(2)

$$[S-iP] = \theta_{iP}[S]_0 = \frac{K_{iP}[iP]}{1 + K_{nP}[nP] + K_{iP}[iP]}[S]_0$$
(3)

Use equations (2) and (3) to substitute for [S-nP] and [S-iP] in equation (1).

$$\frac{d[nP]}{dt} = -k_{s}[S-nP] + k_{-s}[S-iP]$$
(1)
$$= -k_{s}\frac{K_{nP}[nP]}{1 + K_{nP}[nP] + K_{iP}[iP]}[S]_{0} + k_{-s}\frac{K_{iP}[iP]}{1 + K_{nP}[nP] + K_{iP}[iP]}[S]_{0}$$

$$\frac{d[nP]}{dt} = -\frac{k_{s}K_{nP}[nP] - k_{-s}K_{iP}[iP]}{1 + K_{nP}[nP] + K_{iP}[iP]}[S]_{0}$$

(B) With the new rate-limiting step, the rate equation is thus

$$\frac{d[n\mathbf{P}]}{dt} = -k_s[\mathbf{S} \cdot n\mathbf{P}][\mathbf{S}] + k_{-s}[\mathbf{S} \cdot i\mathbf{P}][\mathbf{S}]$$
(4)

Because *n*P and *i*P are described by Langmuir isotherms, we can write the following equation for the concentration of empty sites.

$$[S] = \theta_{empty}[S]_0 = \frac{1}{1 + K_{nP}[nP] + K_{iP}[iP]}[S]_0$$
(5)

The expression for [S] is valid because  $[(S-nP-S)^{\ddagger}] \approx 0$ . Substitute equations (2), (3), and (5) into equation (4).

$$\frac{d[nP]}{dt} = -k_{s}[S-nP][S] + k_{-s}[S-iP][S]$$

$$= -k_{s} \frac{K_{nP}[nP]}{\left(1 + K_{nP}[nP] + K_{iP}[iP]\right)^{2}} [S]_{0}^{2} + k_{-s} \frac{K_{iP}[iP]}{\left(1 + K_{nP}[nP] + K_{iP}[iP]\right)^{2}} [S]_{0}^{2}$$

$$\frac{d[nP]}{dt} = -\frac{k_{s}K_{nP}[nP] - k_{-s}K_{iP}[iP]}{\left(1 + K_{nP}[nP] + K_{iP}[iP]\right)^{2}} [S]_{0}^{2}$$

(C) Experiment 1. First we simplify the expression for d[nP]/dt for [iP] = 0 and  $K_{nP}[nP] \ll 1$ .

Start with the expression from mechanism 1, part (A).

$$\frac{d[nP]}{dt} = -\frac{k_s K_{nP}[nP] - k_{-s} K_{iP}[iP]}{1 + K_{nP}[nP] + K_{iP}[iP]} [S]_0$$
$$\left(\frac{d[nP]}{dt}\right)_0 \approx -k_s K_{nP}[nP] [S]_0 \propto [nP]$$

- 5 -

Apply the same conditions to the expression from mechanism 2, part (B).

$$\frac{d[n\mathbf{P}]}{dt} = -\frac{k_s K_{n\mathbf{P}}[n\mathbf{P}] - k_{-s} K_{i\mathbf{P}}[i\mathbf{P}]}{\left[1 + K_{n\mathbf{P}}[n\mathbf{P}] + K_{i\mathbf{P}}[i\mathbf{P}]\right]^2} [\mathbf{S}]_0^2$$
$$\left(\frac{d[n\mathbf{P}]}{dt}\right)_0 = -k_s K_{n\mathbf{P}}[n\mathbf{P}][\mathbf{S}]_0^2 \propto [n\mathbf{P}]$$

Both mechanisms predict the same dependence on [nP]. The data show that indeed the rate is proportional to [nP] to the first power, so there is some reassurance that one mechanism may be correct.

Experiment 2. Both [nP] and [iP] are constant for each run. Again start with the rate equations and calculate the dependence on  $[S]_0$ .

Mechanism 1: 
$$\left(\frac{d[nP]}{dt}\right)_0 \propto [S]_0$$
  
Mechanism 2:  $\left(\frac{d[nP]}{dt}\right)_0 \propto [S]_0^2$ 

The data agree with mechanism 1, not mechanism 2.

6. Surface-catalyzed reactions generally involve the three steps of the Langmuir-Hinshelwood mechanism: adsorption of reactants, reaction on the surface, and desorption of the products. The form of the approximate rate equation offers some clues. The denominator could contain contributions from adsorbed A, B, and C as well as empty sites; the denominator could be the sum of four terms:  $1 + K_A[A] + K_B[B] + K_C[C]$ . In this case the denominator is approximately  $K_B[B]$  which implies B is much more strongly adsorbed than A and C. And because  $K_B[B] \gg 1$ , it implies that B saturates the surface; there are relatively few empty sites. That [B] is squared is another clue - the surface reaction likely involves two surface sites.

Try this mechanism.

$$\begin{array}{l} \mathbf{A}_{(\mathrm{gas})} \ + \ \mathbf{M} \ \stackrel{k_{\mathrm{ads},A}}{\underset{k_{\mathrm{des},A}}{\longrightarrow}} \ \mathbf{M} \cdot \mathbf{A} \quad \text{in equilibrium} \\ \\ \mathbf{M} \cdot \mathbf{A} \ + \ \mathbf{M} \ \stackrel{k_{\mathrm{S}}}{\longrightarrow} \ \mathbf{M} \cdot \mathbf{B} \ + \ \mathbf{M} \cdot \mathbf{C} \quad \text{rate - limiting step} \\ \\ \mathbf{M} \cdot \mathbf{B} \ \stackrel{k_{\mathrm{des},B}}{\underset{k_{\mathrm{ads},B}}{\longrightarrow}} \ \mathbf{M} \ + \ \mathbf{B}_{(\mathrm{gas})} \quad \text{in equilibrium} \\ \\ \\ \mathbf{M} \cdot \mathbf{C} \ \stackrel{k_{\mathrm{des},C}}{\underset{k_{\mathrm{ads},C}}{\longrightarrow}} \ \mathbf{M} \ + \ \mathbf{C}_{(\mathrm{gas})} \quad \text{in equilibrium} \end{array}$$

Derive the rate equation; set the overall rate equal to the rate of the rate-limiting step.

$$-\frac{d[\mathbf{A}]}{dt} = k_s[\mathbf{M}][\mathbf{M}-\mathbf{A}] \tag{1}$$

Use the equilibrium of the first step to provide an expression for [M-A]; assume a Langmuir Isotherm.

$$[M-A] = \theta_{A}[M]_{0} = \frac{K_{A}[A]}{1 + K_{A}[A] + K_{B}[B] + K_{C}[C]}[M]_{0}$$
(2)

and use the assumption that B is strongly adsorbed;  $K_{B}[B] \gg K_{A}[A], K_{C}[C]$ , and 1.

$$[M-A] \approx \frac{K_A[A]}{K_B[B]} [M]_0$$
(3)

Express the concentration of empty sites in terms of the fractional coverage of empty sites. Again assume a Langmuir Isotherm.

$$[M] = \theta_{empty}[M]_0 = \frac{1}{1 + K_A[A] + K_B[B] + K_C[C]}[M]_0$$
(4)

and use the assumption that B is strongly adsorbed;  $K_{B}[B] \gg K_{A}[A], K_{C}[C]$ , and 1.

$$[\mathbf{M}] \approx \frac{1}{K_{\mathrm{B}}[\mathbf{B}]} [\mathbf{M}]_{0} \tag{5}$$

Substitute eqns (3) and (5) into the rate equation, eqn (1).

$$-\frac{d[A]}{dt} = k_s[M][M-A] \approx k_s \frac{1}{K_B[B]}[M]_0 \frac{K_A[A]}{K_B[B]}[M]_0 = \frac{k_s K_A[M]_0^2}{K_B^2} \frac{[A]}{[B]^2}$$
$$-\frac{d[A]}{dt} = k \frac{[A]}{[B]^2} \quad \text{such that} \quad k = \frac{k_s K_A[M]_0^2}{K_B^2}$$

The mechanism is consistent with the observed rate equation.

7. The observed rate equation provides clues. The denominator could have the form  $1 + K_{O_2}[O_2] + K_{SO_2}[SO_2] + K_{SO_3}[SO_3]$  (and perhaps a term from M-O), but instead the denominator is just [SO<sub>2</sub>]. This indicates that the surface is mostly covered with adsorbed SO<sub>2</sub>. Stated mathematically,

- 6 -

Another clue: the exponent on  $[M]_0$  is 1, which suggests only one surface site in the rate-limiting step. Because  $[O_2]$  is in the numerator,  $O_2$  is likely in the rate-limiting step. Assume the adsorption of  $O_2$  is the rate-limiting step.

$$M + O_2 \xrightarrow{k_{ads,O_2}} M-O_2$$
 rate – limiting step

Write a Langmuir-Hinshelwood mechanism; all reactions involve adsorbates bonded to the surface. Write a reaction for the reversible adsorption of reactant  $SO_2$ .

$$\mathbf{M} + \mathbf{SO}_2 \stackrel{k_{\mathrm{ads},\mathrm{SO}_2}}{\underset{k_{\mathrm{des},\mathrm{SO}_2}}{\rightleftharpoons}} \mathbf{M} \cdot \mathbf{SO}_2, \qquad K_{\mathrm{SO}_2} = \frac{k_{\mathrm{ads},\mathrm{SO}_2}}{k_{\mathrm{des},\mathrm{SO}_2}}$$

Write surface reactions. Begin with the dissociation of adsorbed  $O_2$ .

$$M-O_2 + M \xrightarrow{k_{s1}} M-O + M-O$$

React an adsorbed O with adsorbed SO<sub>2</sub>. Because [M-SO<sub>3</sub>] is small, assume the SO<sub>3</sub> desorbs immediately.

$$M-O + M-SO_2 \xrightarrow{k_{s2}} 2M + SO_3$$

Use the rate-limiting step to write a rate equation.

$$\frac{d[SO_3]}{dt} = -2\frac{d[O_2]}{dt} = 2k_{ads,O_2}[M][O_2]$$
(1)

Write an expression for [M] in terms of [M]<sub>0</sub>.

$$[M] = \theta_{empty}[M]_{0} = \frac{[M]}{[M] + [M - O_{2}] + [M - O] + [M - SO_{2}] + [M - SO_{3}]}[M]_{0}$$
$$[M] \approx \frac{[M]}{[M - SO_{2}]}[M]_{0} = \frac{1}{K_{SO_{2}}[SO_{2}]}[M]_{0}$$
(2)

Substitute eqn (2) into eqn (1) to obtain the observed rate equation.

$$\frac{d[SO_3]}{dt} = 2k_{ads,O_2}[M][O_2] = \frac{2k_{ads,O_2}[O_2]}{K_{SO_2}[SO_2]}[M]_0$$

In summary, a mechanism of elementary steps and assumptions is

$$M + SO_{2} \stackrel{k_{ads,SO_{2}}}{\underset{k_{des,SO_{2}}}{\xrightarrow{}}} M-SO_{2}$$
 in equilibrium  

$$M + O_{2} \stackrel{k_{ads,O_{2}}}{\xrightarrow{}} M-O_{2}$$
 rate – limiting step  

$$M-O_{2} + M \stackrel{k_{s1}}{\xrightarrow{}} M-O + M-O$$
 fast  

$$M-O + M-SO_{2} \stackrel{k_{s2}}{\xrightarrow{}} 2M + SO_{3}$$
 fast

Also acceptable are the following two surface reactions.

Or, the SO<sub>3</sub> could desorb immediately.

The most common errors were to propose a gas-phase reactant striking an adsorbed reactant. Examples of invalid reactions are

 $M-O_2 + SO_2 \rightarrow M-O + SO_3$ 

and

$$M-SO_2 + O_2 \rightarrow M-O + SO_3$$

This is an Eley-Rideal mechanism. It is highly improbable.

8. The observed rate equation provides clues. The exponent on  $[M]_0$  is 2, which suggests two surface sites in the rate-limiting step. Subsequently, there should be a squared term in the denominator, the result of multiplying the  $\theta$ 's (fractional coverages) of the two adsorbed species involved in the rate-limiting surface reaction. And the squared term could be a polynomial of the form  $1 + K_{CO}[CO] + K_{H_2O}[H_2O] + K_{CO_2}[CO_2] + K_{H_2}[H_2]$  and perhaps terms from M-OH and M-H.

Instead the denominator has just two terms: a *product* of [CO] and  $[H_2]^{1/2}$ ; not a sum. What reactions contribute terms to the denominator? In heterogeneous catalysis, the reaction rate is slowed by any species that monopolizes the surface sites; that species will have a term in the denominator. But we encountered terms in the denominator prior to heterogeneous catalysis: an intermediate in a pre-equilibrium reaction has a term in the denominator.

Chemical insight can guide our first guess. Which denominator term - CO or  $H_2$  - do we expect to adsorb strongly and which denominator term do we expect is in pre-equilibrium? Typically, CO adsorbs more strongly than  $H_2$ . The  $\frac{1}{2}$  power on the [H<sub>2</sub>] term suggests a dissociative equilibrium: H<sub>2</sub> desorbs immediately after formed from M-H + M-H.

So if the surface reaction involves two surface sites, why is the [CO] term not squared? It is likely that there was a [CO] term in the numerator (from [M-CO]) that reduced the [CO]<sup>2</sup> in the denominator to [CO].

Start with these guesses. Assume the surface is mostly covered with adsorbed CO. Stated mathematically,

[M-CO] » [M], [M-H<sub>2</sub>O], [M-CO<sub>2</sub>], [M-H<sub>2</sub>], [M-OH], and [M-H].

Write a Langmuir-Hinshelwood mechanism. Start with reversible adsorption of the reactants.

©Copyright Cornell University 2025. All rights reserved. Reproduction or retransmission of this document, in whole or in part, in any manner, without the written consent of T.M. Duncan, is a violation of copyright law.

$$M + CO \stackrel{k_{ads,CO}}{\underset{k_{des,CO}}{\underset{k_{ads,H_{2}O}}{\xrightarrow{}}}} M-CO \qquad in equilibrium$$
$$M + H_2O \stackrel{k_{ads,H_{2}O}}{\underset{k_{des,H_{2}O}}{\xrightarrow{}}} M-OH_2 \qquad in equilibrium$$

Write surface reactions. To move the oxygen atom from H<sub>2</sub>O to CO, we must break the two O-H bonds in two steps.

$$M-OH_2 + M \xrightarrow{k_{s1}} M-OH + M-H$$
$$M-OH + M-CO \xrightarrow{k_{s2}} M-CO_2 + M-H$$

Assume reversible adsorption of the products. Assume that H<sub>2</sub> desorbs immediately after formed on the surface.

$$M-H + M-H \stackrel{k_{des,H_2}}{\underset{k_{ads,H_2}}{\leftarrow}} 2M + H_2$$
 in equilibrium  
$$M-CO_2 \stackrel{k_{des,CO_2}}{\underset{k_{ads,CO_2}}{\leftarrow}} M + CO_2$$
 in equilibrium

Because CO dominates the surface, it is probable that the second surface reaction is the rate-limiting step. If the first surface reaction were rate-limiting, then subsequent reactions should be fast; adsorbed CO would react quickly and therefore there would be little CO on the surface, which is contrary to our assumption. Use the second surface reaction to write a rate equation.

$$\frac{d[\text{CO}_2]}{dt} = k_{s2}[\text{M-OH}][\text{M-CO}]$$
(1)

Assume the preceding surface reaction is reversible and in equilibrium.

$$k_{s1}[M-OH_{2}][M] = k_{s-1}[M-OH][M-H]$$
  
[M-OH] =  $\frac{k_{s1}}{k_{s-1}} \frac{[M-OH_{2}][M]}{[M-H]}$  (2)

Substitute eqn (2) into the rate equation.

$$\frac{d[\text{CO}_2]}{dt} = k_{s2}[\text{M-OH}][\text{M-CO}] = k_{s2} \frac{k_{s1}}{k_{s-1}} \frac{[\text{M-OH}_2][\text{M}][\text{M-CO}]}{[\text{M-H}]}$$
(3)

We need expressions for [M-OH<sub>2</sub>], [M], [M-CO], and [M-H]. Assume Langmuir Isotherms for the equilibrium adsorption/desorption of H<sub>2</sub>O and CO.

$$[M-CO] = \theta_{CO}[M]_0 = \frac{[M-CO]}{[M] + [M-OH_2] + [M-OH] + [M-CO] + [M-CO_2] + [M-H]} [M]_0$$

Because we assumed CO atoms monopolize the surface sites,

$$[M] + [M-OH_2] + [M-OH] + [M-CO] + [M-CO_2] + [M-H] \approx [M-CO]$$

the expression for [M-CO] simplifies to

$$[M-CO] \approx \frac{[M-CO]}{[M-CO]} [M]_0 \approx [M]_0$$
(4)

Use the same approximation for [M-OH<sub>2</sub>] and [M]

©Copyright Cornell University 2025. All rights reserved. Reproduction or retransmission of this document, in whole or in part, in any manner, without the written consent of T.M. Duncan, is a violation of copyright law.

$$[M-OH_{2}] = \theta_{H_{2}O}[M]_{0} \approx \frac{[M-OH_{2}]}{[M-CO]}[M]_{0} = \frac{K_{H_{2}O}[H_{2}O]}{K_{CO}[CO]}[M]_{0}$$
(5)

- 9 -

$$[M] = \theta_{empty}[M]_0 \approx \frac{[M]}{[M-CO]}[M]_0 = \frac{1}{K_{CO}[CO]}[M]_0$$
(6)

For [M-H], assume the dissociative adsorption of H<sub>2</sub> is in equilibrium.

$$k_{\text{des, H}_2}[\text{M-H}]^2 = k_{\text{ads, H}_2}[\text{M}]^2[\text{H}_2]$$
  
 $[\text{M-H}] = K_{\text{H}_2}^{1/2}[\text{H}_2]^{1/2}[\text{M}]$  (7)

Substitute eqns (4), (5), (6), and (7), into eqn (3).

$$\frac{d[\text{CO}_2]}{dt} = k_{s2} \frac{k_{s1}}{k_{s-1}} \frac{[\text{M-OH}_2][\text{M}][\text{M-CO}]}{[\text{M-H}]}$$
(3)  
$$= k_{s2} \frac{k_{s1}}{k_{s-1}} \frac{\frac{K_{\text{H}_2\text{O}}[\text{H}_2\text{O}]}{K_{\text{CO}}[\text{CO}]} [\text{M}]_0 [\text{M}][\text{M}]_0}{K_{\text{H}_2}^{1/2} [\text{H}_2]^{1/2} [\text{M}]}$$
$$= k_{s2} \frac{k_{s1}}{k_{s-1}} \frac{K_{\text{H}_2\text{O}}[\text{H}_2\text{O}][\text{M}]_0^2}{K_{\text{CO}} K_{\text{H}_2}^{1/2} [\text{CO}][\text{H}_2]^{1/2}}$$

This agrees with the observed rate equation.

9. The observed rate equation provides clues. Consider the denominator. The  $b[N_2O]$  term suggests the surface has substantial M-ONN species. The  $c[O_2]^{1/2}$  term is the signature of  $O_2$  adsorbing dissociatively. Or in this case, M-O and M-O react to form  $O_2$  gas and two M sites. Dissociative adsorption / associative desorption of  $O_2$  is corroborated by the lack of a  $[O_2]$  term in the denominator. The denominator also lacks a  $[N_2]$  term, which suggests  $N_2$  is not a substantial absorbed species. The denominator suggests the surface is mostly vacant metal sites, M-ONN species, and M-O species. Stated mathematically,

[M], [M-O], [M-ONN] » [M-N<sub>2</sub>], and [M-O<sub>2</sub>]

Because the exponent on the  $[M]_0$  term is 1 and the exponent on the denominator polynomial is also 1, the rate-limiting step likely involves a single M site. In general, it is likely that the rate-limiting step is a surface reaction.

Assume a Langmuir-Hinshelwood mechanism; all reactions involve adsorbates bonded to the metal surface. The first step is the reversible adsorption of reactant  $N_2O$ .

$$\mathbf{M} + \mathbf{N}_{2}\mathbf{O} \underset{k_{\text{des, N}_{2}\mathbf{O}}}{\overset{k_{\text{ads, N}_{2}\mathbf{O}}}{\underset{k_{\text{des, N}_{2}\mathbf{O}}}{\overset{k_{\text{ads, N}_{2}\mathbf{O}}}{\overset{k_{\text{ads, N}_{2}\mathbf{O}}}} \mathbf{M}\text{-}\mathbf{ONN}, \qquad K_{\mathbf{N}_{2}\mathbf{O}} = \frac{k_{\text{ads, N}_{2}\mathbf{O}}}{k_{\text{des, N}_{2}\mathbf{O}}}$$

We have at least two options for the next step. A reaction involving two M sites,

$$M-ONN + M \xrightarrow{k_1} M-O + M-N_2$$

or a reaction involving one M site,

M-ONN 
$$\xrightarrow{k_1}$$
 M-O + N<sub>2</sub>

Again the rate equation indicates the correct choice. A reaction involving two M sites (which is also the rate-limiting step) will produce a rate equation with a squared polynomial in the denominator and a  $[M]_0^2$  term in the numerator. Our best bet is the reaction involving one M site.

The subsequent steps react two M-O sites to produce O2. Again we have two choices: O2 adsorbs to the surface

$$M-O + M-O \xrightarrow{k_2} M-O_2 + M$$
$$M-O_2 \xrightarrow{k_{des,O_2}} M + O_2, \qquad K_{O_2} = \frac{k_{ads,O_2}}{k_{des,O_2}}$$

or O<sub>2</sub> desorbs immediately.

M-O + M-O 
$$\underset{k_{\text{ads},O_2}}{\overset{k_{\text{des},O_2}}{\longrightarrow}} 2M + O_2 \qquad K_{O_2} = \frac{k_{\text{ads},O_2}}{k_{\text{des},O_2}}$$

The  $c[O_2]^{1/2}$  in the denominator of the rate equation suggests  $O_2$  desorbs immediately. We thus begin with the following mechanism.

$$M + N_2 O \xrightarrow{k_{ads, N_2O}} M - ONN, \qquad K_{N_2O} = \frac{k_{ads, N_2O}}{k_{des, N_2O}}$$
$$M - ONN \xrightarrow{k_1} M - O + N_2$$
$$M - O + M - O \xrightarrow{k_{des, O_2}} 2M + O_2 \qquad K_{O_2} = \frac{k_{ads, O_2}}{k_{des, O_2}}$$

Assume the surface reaction of M-ONN is the rate-limiting step.

$$\frac{d[N_2O]}{dt} = -k_1[M-ONN]$$
(1)

We need an expression for [M-ONN]. Start with the definition of fraction coverage, with the approximation that the surface is mostly empty sites, M-O-N-N species, and M-O species.

$$[M-ONN] = \theta_{ONN}[M]_0 = \frac{[M-ONN]}{[M] + [M-ONN] + [M-O]}[M]_0$$
(2)

Assume a Langmuir isotherm for the equilibrium adsorption/desorption of  $N_2O$ .

$$[M-ONN] = K_{N_2O}[N_2O][M]$$
(3)

Assume the associative desorption of  $\mathbf{O}_2$  is in equilibrium.

$$k_{\text{des, O}_2}[\text{M-O}]^2 = k_{\text{ads, O}_2}[\text{M}]^2[\text{O}_2]$$
  
 $[\text{M-O}] = K_{\text{O}_2}^{1/2}[\text{O}_2]^{1/2}[\text{M}]$  (4)

Substitute eqns (3) and (4) into eqn (2).

$$[M-ONN] = \frac{K_{N_2O}[N_2O][M]}{[M] + K_{N_2O}[N_2O][M] + K_{O_2}^{1/2}[O_2]^{1/2}[M]} [M]_0$$
$$[M-ONN] = \frac{K_{N_2O}[N_2O]}{1 + K_{N_2O}[N_2O] + K_{O_2}^{1/2}[O_2]^{1/2}} [M]_0$$
(5)

Substitute eqn (5) into eqn (1).

$$\frac{d[N_2O]}{dt} = -\frac{k_1 K_{N_2O}[N_2O]}{1 + K_{N_2O}[N_2O] + K_{O_2}^{1/2}[O_2]^{1/2}} [M]_0$$

The constants are  $a = k_1 K_{N_2O}$ ,  $b = K_{N_2O}$ , and  $c = K_{O_2}^{1/2}$ .

©Copyright Cornell University 2025. All rights reserved. Reproduction or retransmission of this document, in whole or in part, in any manner, without the written consent of T.M. Duncan, is a violation of copyright law.

- 11 -

In summary, the mechanism is

$$M + N_{2}O \stackrel{k_{ads, N_{2}O}}{\underset{k_{des, N_{2}O}}{\xrightarrow{}}} M-ONN \text{ in equilibrium}$$
$$M-ONN \stackrel{k_{1}}{\rightarrow} M-O + N_{2} RLS$$
$$M-O + M-O \stackrel{k_{des, O_{2}}}{\underset{k_{ads, O_{2}}}{\xrightarrow{}}} 2M + O_{2} \text{ in equilibrium}$$

A common error is to use two reactions to convert M-O into  $O_2$ , and assume M-O is short-lived, such that [M-O] « [M-O<sub>2</sub>], as shown below. This does not yield a  $[O_2]^{1/2}$  term in the rate equation denominator.

$$M-O + M-O \xrightarrow{k} M-O_2 + M \quad \text{fast}$$
$$M-O_2 \xrightarrow{k_{\text{des},O_2}} M + O_2 \quad \text{in equilibrium}$$

Also invalid is a two-step process with the second step irreversible, as shown below. This, too, does not yield a  $[O_2]^{1/2}$  term in the rate equation denominator.

M-O + M-O 
$$\stackrel{k_s}{\underset{k_{-s}}{\leftrightarrow}}$$
 M-O<sub>2</sub> + M in equilibrium  
M-O<sub>2</sub>  $\stackrel{k_{des}}{\xrightarrow{}}$  M + O<sub>2</sub> fast

However, it is valid to convert M-O into  $O_2$  in two steps and assume both steps are reversible and in equilibrium.

M-O + M-O 
$$\stackrel{k_s}{\underset{k_{-s}}{\leftrightarrow}}$$
 M-O<sub>2</sub> + M in equilibrium  
M-O<sub>2</sub>  $\stackrel{k_{des,O_2}}{\underset{k_{ads,O_2}}{\leftrightarrow}}$  M + O<sub>2</sub> in equilibrium

And as usual, a few proposed Eley-Rideal mechanisms, in which one reactant is not absorbed, such as

$$M-O + N_2O \xrightarrow{k} M-O_2 + N_2$$

and

$$N_2O + M \xrightarrow{k} M-O + N_2$$

Although Eley-Rideal reactions are possible, they are improbable, similar to ternary gas-phase reactions.

10. The observed rate equation provides clues. The denominator should be a polynomial of the form  $1 + K_{H_2}[H_2] + K_{C_2H_4}[C_2H_4] + K_{C_2H_6}[C_2H_6]$ , and perhaps terms owing to Cu-H and other surface species. But instead the denominator is only  $1 + K[C_2H_4]$ . This indicates that  $H_2$  and  $C_2H_6$  are weakly absorbed on the Cu surface. The surface is chiefly free Cu sites and Cu-C\_2H\_4. There are relatively few sites occupied by  $H_2$  or  $C_2H_6$ .

The second clue from the rate equation is that the denominator is squared, which suggests the rate-limiting step involves two surface sites.

Assume the mechanism involves the standard elementary steps for surface-catalyzed reactions:

- · reversible adsorption of all reactants and products.
- a reaction between two adsorbed species (Langmuir-Hinshelwood mechanism).
- the surface reaction is the rate-limiting step.

Adsorption/desorption steps:

$$Cu + H_{2} \stackrel{k_{ads, H_{2}}}{\underset{k_{des, H_{2}}}{\rightleftharpoons}} Cu-H_{2}$$
$$Cu + C_{2}H_{4} \stackrel{k_{ads, C_{2}H_{4}}}{\underset{k_{des, C_{2}H_{4}}}{\rightleftharpoons}} Cu-C_{2}H_{4}$$

Surface reactions:

Set the overall rate equal to the rate of the rate-limiting step.

$$\frac{d[C_2H_6]}{dt} = k_2[Cu-H][Cu-C_2H_4]$$
(1)

We need expressions for [Cu-H] and [Cu- $C_2H_4$ ]. Apply pre-equilibrium to the dissociation of  $H_2$  on the Cu surface (rxn 1).

$$k_{-1}[\text{Cu-H}]^{2} = k_{1}[\text{Cu-H}_{2}][\text{Cu}]$$
$$[\text{Cu-H}] = \left(\frac{k_{1}}{k_{-1}}\right)^{1/2} [\text{Cu-H}_{2}]^{1/2} [\text{Cu}]^{1/2} = K_{1}^{1/2} [\text{Cu-H}_{2}]^{1/2} [\text{Cu}]^{1/2}$$
(2)

Assume the adsorption/desorption of  $H_2$  is in equilibrium.

$$[Cu-H_2] = \theta_{H_2}[Cu]_0 = \frac{[Cu-H_2]}{[Cu]_0}[Cu]_0$$
(3)

We decided that the surface is chiefly unoccupied Cu sites and Cu sites occupied by  $C_2H_4$ . Stated mathematically,

$$[Cu], [Cu-C_2H_4] \gg [Cu-H_2], [Cu-H], [Cu-CH_2CH_3], and [Cu-CH_3CH_3].$$

Apply this approximation to the mass balance on surface sites.

$$[Cu]_{0} = [Cu] + [Cu-H_{2}] + [Cu-H] + [Cu-C_{2}H_{4}] + [Cu-C_{2}H_{5}]$$
$$[Cu]_{0} \approx [Cu] + [Cu-C_{2}H_{4}]$$
(4)

Substitute eqn (4) into eqn (3) and convert to equilibrium constants.

$$[Cu-H_2] = \frac{[Cu-H_2]}{[Cu]_0} [Cu]_0 = \frac{[Cu-H_2]}{[Cu] + [Cu-C_2H_4]} [Cu]_0 = \frac{K_{H_2}[H_2]}{1 + K_{C_2H_4}[C_2H_4]} [Cu]_0$$
(5)

Use adsorption/desorption equilibrium to write expressions for [Cu] and [Cu-C $_2H_4$ ] as well.

$$[Cu] = \theta_{empty}[Cu]_0 = \frac{1}{1 + K_{C_2H_4}[C_2H_4]}[Cu]_0$$
(6)  
$$K_{C_2H_4}[C_2H_4]$$

$$[\operatorname{Cu-C}_{2}\operatorname{H}_{4}] = \theta_{\operatorname{C}_{2}\operatorname{H}_{4}}[\operatorname{Cu}]_{0} = \frac{K_{\operatorname{C}_{2}\operatorname{H}_{4}}[\operatorname{C}_{2}\operatorname{H}_{4}]}{1 + K_{\operatorname{C}_{2}\operatorname{H}_{4}}[\operatorname{C}_{2}\operatorname{H}_{4}]}[\operatorname{Cu}]_{0}$$
(7)

Substitute eqns (5) and (6) into eqn (2).

$$[Cu-H] = K_1^{1/2} [Cu-H_2]^{1/2} [Cu]^{1/2} = K_1^{1/2} \left( \frac{K_{H_2}[H_2]}{1 + K_{C_2H_4}[C_2H_4]} [Cu]_0 \right)^{1/2} \left( \frac{1}{1 + K_{C_2H_4}[C_2H_4]} [Cu]_0 \right)^{1/2} \left( \frac{1}{1 + K_{C_2H_4}[C_2H_4]} [Cu]_0 \right)^{1/2} [Cu-H] = \frac{K_1^{1/2} K_{H_2}^{1/2} [H_2]^{1/2} [Cu]_0}{1 + K_{C_2H_4}[C_2H_4]}$$
(8)

Substitute eqns (7) and (8) into the rate equation, eqn (1).

$$\frac{d[C_2H_6]}{dt} = k_2[Cu-H][Cu-C_2H_4] = k_2 \left(\frac{K_1^{1/2}K_{H_2}^{1/2}[H_2]^{1/2}[Cu]_0}{1+K_{C_2H_4}[C_2H_4]}\right) \left(\frac{K_{C_2H_4}[C_2H_4]}{1+K_{C_2H_4}[C_2H_4]}[Cu]_0\right)$$
$$\frac{d[C_2H_6]}{dt} = k_2 K_1^{1/2} K_{H_2}^{1/2} K_{C_2H_4} \frac{[H_2]^{1/2}[C_2H_4][Cu]_0^2}{(1+K_{C_2H_4}[C_2H_4])^2}$$

The constants k and K in the observed rate equation are as follows.

$$k = k_2 K_1^{1/2} K_{H_2}^{1/2} K_{C_2 H_4}$$
$$K = K_{C_2 H_4}$$

Finally, the same rate equation can be obtained by assuming the  $H_2$  adsorbs dissociatively. That is, rather than the two following steps,

$$\begin{array}{rcl} \mathrm{Cu} &+ &\mathrm{H}_2 & \underset{k_{\mathrm{des},\mathrm{H}_2}}{\overset{k_{\mathrm{ads},\mathrm{H}_2}}{\overset{}{\underset{\mathrm{cu}}{\overset{\mathrm{H}_2}{\overset{\mathrm{cu}}{\underset{\mathrm{H}_2}{\overset{\mathrm{cu}}{\overset{\mathrm{H}_2}{\overset{\mathrm{cu}}{\underset{\mathrm{H}_2}{\overset{\mathrm{cu}}{\overset{\mathrm{H}_2}{\overset{\mathrm{cu}}{\underset{\mathrm{des},\mathrm{H}_2}{\overset{\mathrm{des},\mathrm{H}_2}{\overset{\mathrm{des},\mathrm{H}_2}}}} &\mathrm{Cu}\mathrm{-}\mathrm{H}_2 \end{array}$$

the reaction is a single step as follows:

$$2Cu + H_2 \xrightarrow{k_1} Cu-H + Cu-H$$
 in equilibrium

Is this a ternary collision, and therefore improbable? No, because the 2 Cu surface sites are not separate entities. A  $H_2$  molecule collides with a surface with two adjacent, empty Cu sites.

<sup>©</sup>Copyright Cornell University 2025. All rights reserved. Reproduction or retransmission of this document, in whole or in part, in any manner, without the written consent of T.M. Duncan, is a violation of copyright law.