TITLE OF PROJ. OR STUDY | PROJ. OR STUDY NO.
SUBJECT LHHW Expressions AND DERIVATION | WORKS LECTURE
COMPUTER | DATE 2 APRIL 20 07

Consider Simple Overall Rxn $A \rightleftharpoons B$
over single catalytic site

STEPS ARE ADSORPTION (1), SURFACE RXN (2), DESORPTION (3)
IN SERIES

$$A + S \underset{}{\overset{k_a}{\rightleftharpoons}} A-S$$

$$A-S \underset{}{\overset{k_{SR}}{\rightleftharpoons}} B-S$$

$$B-S \underset{}{\overset{k_d}{\rightleftharpoons}} B + S$$

Can define equil. const.

$$K_A = k_a / k_{-a} = k_{a_A} / k_{d_A}$$

$$K_{SR} = k_{SR} / k_{-SR}$$

$$K_B = k_d / k_{-d} = k_{d_B} / k_{a_B}$$

(FOGLER CONVENTION) written as they occur

THIS is A CLOSED SEQUENCE

A vacant site is occupied by species A, surface reaction to B occurs, B desorbs →
REGENERATING the vacant site "S"

Can WRITE RATES OF EACH STEP AS:

(1) $$r_a = -k_a p_A C_v + k_{-a} C_{A-S} = -k_a \left(p_A C_v - \frac{C_{A-S}}{K_A} \right)$$

(2) $$r_{SR} = -k_{SR} C_{A-S} + k_{-SR} C_{B-S} = -k_{SR} \left(C_{A-S} - \frac{C_{BS}}{K_{SR}} \right)$$

(3) $$r_d = -k_d C_{B-S} + k_{-d} p_B C_v = -k_d \left(C_{B-S} - \frac{p_B C_v}{K_D} \right)$$

- CAN DERIVE GENERAL REACTION RATE USING EQNS 1–3

AND PSSA and SITE BALANCE.

PSSA ON ACTIVE CENTERS ≡ time derivative of active center concentration → 0

THAT IS – we assume CHANGE IN CONC. OF ACTIVE CENTERS IS NEGLIGIBLE COMPARED TO CHANGE IN CONCENTRATION OF MEASURABLES (in this case, A + B)

$$\frac{d(A\text{-}S)}{dt} = -r_a + r_{sr} = 0 \quad (4)$$

$$\frac{d(B\text{-}S)}{dt} = r_{SR} - r_d = 0 \quad (5)$$

$\therefore$ $r_a = r_{sr} = r_d$ AT STEADY-STATE

3 unknowns : C_{A-S}, C_{B-S}, C_V

need 3 eqns to SOLVE USE 4, 5 and one final eqn

SITE BALANCE

$$C_T = C_V + C_{A-S} + C_{B-S}$$

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FIND GENERAL REACTION RATE:

$$r_A = \frac{-C_T\left(p_A - p_B/K\right)}{\left[\left(\frac{1}{K_A k_{sr}} + \frac{1}{k_a} + \frac{1}{K k_d}\right) + \left(\frac{1}{k_{sr} K_A} + \frac{1+K_{SR}}{K k_d}\right) K_A p_A + \left(\frac{1}{K_A k_{SR}} + \frac{1+K_S}{K_S k_a}\right)\frac{1}{K_D} p_B\right]}$$

DERIVATION IS FROM ALGEBRA - BECOMES DIFFICULT AS REACTIONS ARE MORE COMPLEX

OFTEN CAN MAKE USEFUL ASSUMPTION OF RATE LIMITING STEP

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R.L.S. OR RATE DETERMINING STEP

* REACTIONS IN SERIES ARE CONTROLLED BY THE RATE OF THE SLOWEST STEP

(BOOK USES ex. OF RESISTANCES IN AN ELECTRICAL CIRCUIT)

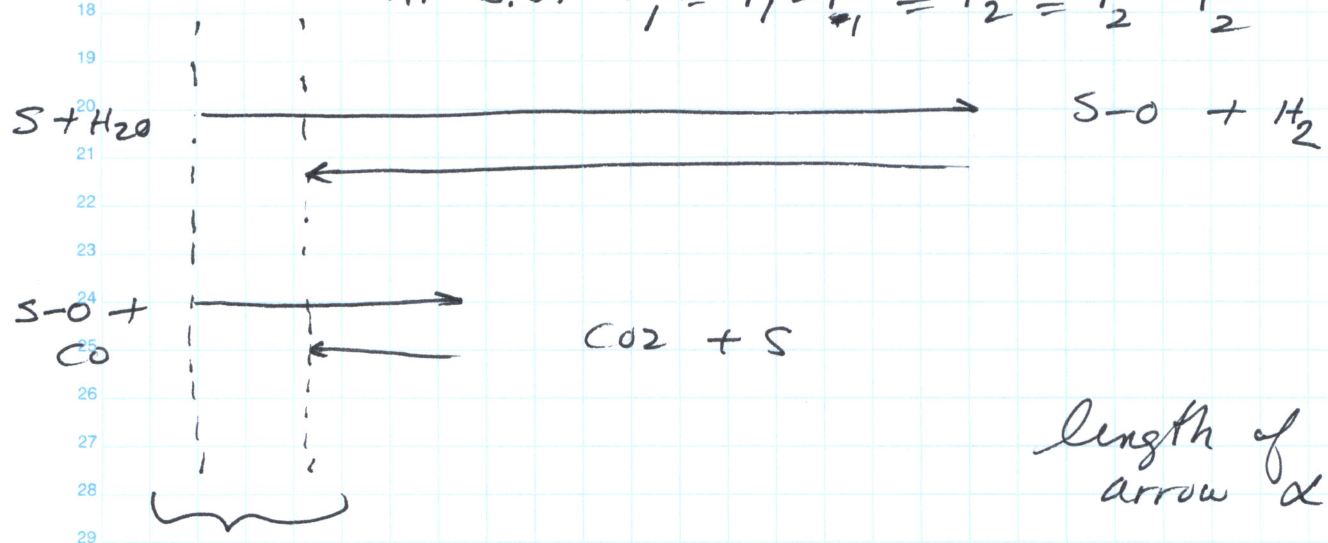
$S + H_2O \rightleftharpoons S\text{-}O + H_2 \quad r_1$

$SO + CO \rightleftharpoons CO_2 + S \quad r_2$

water gas shift rxn

CONSIDER RXNS IN SERIES

AT S.S. $r_1 = \vec{r}_1 - \overleftarrow{r}_1 = r_2 = \vec{r}_2 - \overleftarrow{r}_2$



length of each arrow $\propto$ corres. rate

OBSERVED RATE OVERALL
$r_1 = r_2$

AND

r_1 is close to equilibrium

$$\frac{\vec{r}_1 - \overleftarrow{r}_1}{\vec{r}_1} \ll \frac{\vec{r}_2 - \overleftarrow{r}_2}{\vec{r}_2}$$

Since $\vec{r}_1 \gg \vec{r}_2$

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If R_1 were in equil. $\vec{r}_1 = \overleftarrow{r}_1$
in fact it is in quasi equilibrium compared to rxn 2

SO WE ASSUME IN THIS CASE

$$\frac{\vec{r}_1 - \overleftarrow{r}_1}{\vec{r}_1} \longrightarrow 0 \quad \text{OR} \quad \vec{r}_1 = \overleftarrow{r}_1$$

AND R.D.S is r_2

FOGLER EXPLANATION FOR CAT. RXNS:

if $k_{sr} \ll k_a$ & k_d, AT SS

$$r_{sr} = r_a = r_d$$

$$\frac{r_{sr}}{\underbrace{k_{SR}}_{\text{SMALL}}} = -\left(C_{A-S} - \frac{C_{B-S}}{K_{SR}}\right) \rightarrow \text{Large}$$

$$\left[\frac{r_a}{\underbrace{k_a}_{\text{Large}}} = -\left(p_A C_v - \frac{C_{A-S}}{K_A}\right) \rightarrow \text{SMALL} \cong 0 \qquad \frac{r_d}{\underbrace{k_d}_{\text{Large}}} = -\left(C_{B-S} - \frac{p_B C_v}{K_D}\right) \cong 0\right]$$

USE RLS CONCEPT TO DERIVE ANALTICAL RATE LAWS

PROCEDURE:

1) WRITE DOWN PRESUMED MECHANISM

2) FIND OR ASSUME RATE LIMITING STEP.
(THE (NET) OVERALL RATE IS EQUAL TO THIS STEP.)

3) ASSUME ALL OTHER STEPS IN EQUILIBRIUM.
(USE EQUIL. RELATIONS TO SOLVE FOR UNKNOWNS)

4) WRITE SITE BALANCE

5) ELIMINATE UNKNOWN SURFACE CONCENTRATIONS AND VACANT SITE CONCENTRATIONS TO GET FINAL RATE LAW.

- Go BACK TO $A \rightleftharpoons B$
- Assume Surface reaction Limited
- $r_{A_{NET}} = r_{SR} = -k_{Sr}\left(C_{A-S} - \dfrac{C_{B-S}}{K_{SR}}\right)$

> need expressions for unknowns C_{A-S} + C_{B-S}

- Adsorption A + Desorption of B are in equil:

$$K_{A_{ADS}} = \frac{C_{A-S}}{p_A C_V} \qquad K_{B_{DES}} = \frac{p_B C_V}{C_{B-S}}$$

SOLVE for C_{A-S} + C_{B-S}

$$C_{A-S} = K_A p_A C_V \qquad C_{B-S} = \frac{p_B C_V}{K_B}$$

- WRITE SITE BALANCE, SUBSTITUTE

$$C_T = C_V + C_{A-S} + C_{B-S}$$

$$= C_V + K_A P_A C_V + \frac{p_B C_V}{K_B}$$

$$= C_V\left(1 + K_A p_A + \frac{p_B}{K_B}\right)$$

$$C_V = \frac{C_T}{(1 + K_A p_A + p_B/K_B)}$$

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$$r_{A_{NET}} = -k_{SR}\left(K_A p_A C_V - \frac{p_B C_V}{K_B K_{SR}}\right)$$

SUBST for C_V

$$r_{A_{NET}} = \frac{-k_{SR} K_A C_T \left(p_A - p_B / K_A K_B K_{SR}\right)}{\left(1 + K_A p_A + p_B / K_B\right)}$$

$$K \equiv \frac{p_B^{eq}}{p_A^{eq}} = \frac{C_{B-S} K_B K_A \cancel{C_V}}{\cancel{C_V}\, C_{A-S}}$$

$$p_B = \frac{C_{B-S} K_B}{C_V} \qquad p_A = \frac{C_{A-S}}{K_A C_V}$$

SUBST EQUIL RXNS.

$$\frac{C_{B-S}}{C_{A-S}} = k_{SR} \quad \text{SO} \quad K = K_A K_B K_{SR}$$

$$r_{A_{NET}} = \frac{\overbrace{-k_{SR} K_A C_T}^{k_s'} \left(p_A - p_B / K\right)}{\left(1 + K_A p_A + p_B / K_B\right)}$$

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Compare to LHHW Charts from Froment + Bischoff

Convention used:

$$K_A = \frac{\text{"surface"}}{\text{"free"}} \qquad K_B = \frac{\text{"surface"}}{\text{"free"}}$$

OR WRITE ALL STEPS AS ADSORPTION STEPS

So

$$K_A = \frac{C_{A-S}}{C_v\, p_A} \quad + \quad K_B' = \frac{C_{B-S}}{C_v\, p_B}$$

Then

$$r_{A_{Net}} = \frac{-\,k_{SR} K_A C_t \left(p_A - p_B/K\right)}{\left(1 + K_A p_A + K_B' p_B\right)}$$

PROBABLY MORE LIKE LITERATURE CASES you've seen researching your project.

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$$O_2 + 2S \rightleftharpoons 2\,S\text{-}O$$

$$S\text{-}O + SO_2 \overset{2}{\rightleftharpoons} SO_3 + S \qquad r.d.s$$

$$K_1 = \frac{(C_{S-O})^2}{p_{O_2} C_V^2} \longrightarrow C_{S-O} = (K_1 p_{O_2})^{1/2} C_V$$

$$r = k_2 C_{S-O} p_{SO_2} - \frac{k_2}{K_2} p_{SO_3} C_V$$

$$= k_2 (K_1 p_{O_2})^{1/2} p_{SO_2} C_V - \frac{k_2}{K_2} p_{SO_3} C_V$$

$$= k_2 K_1^{1/2} C_V \left(p_{O_2}^{1/2} p_{SO_2} - \frac{1}{K_1^{1/2} K_2} p_{SO_3} \right)$$

SITE BALANCE :

$$C_T = C_V + C_{S-O} = C_V \left(1 + (K_1 p_{O_2})^{1/2}\right)$$

$$C_V = \frac{C_T}{\left(1 + (K_1 p_{O_2})^{1/2}\right)}$$

$$r = \frac{k_2 K_1^{1/2} C_T \left(p_{O_2}^{1/2} p_{SO_2} - \frac{p_{SO_3}}{K_1^{1/2} K_2} \right)}{\left(1 + (K_1 p_{O_2})^{1/2}\right)}$$

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$$K_{rxn} = \frac{f_{SO_3\,eq}}{f_{SO_2} f_{O_2\,eq}^{1/2}} = K_1^{1/2} K_2$$

so

$$r = \underbrace{k_2 K_1^{1/2} C_T}_{k_2'} \frac{\left(f_{O_2}^{1/2} f_{SO_2} - \frac{f_{SO_3}}{K} \right)}{\left(1 + (K_1 f_{O_2})^{1/2} \right)}$$