ChE445_HW5_Winter2020_Solution_and_Code

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0.0.1 HW Assignment 5. Mechanisms of heterogeneous catalytic reactions**

Gas-phase hydrogenation of A to B occurs on a solid catalyst. Two mechanisms were proposed:

Langmuir-Hinshelwood (LH):

$$A + S <=> AS \tag{1}$$
$$H_2 + 2S <=> 2(HS) \tag{2}$$
$$AS + 2(HS) \rightarrow BS + 2S \tag{3}$$
$$BS <=> B + S \tag{4}$$

Eley-Rideal (ER):

$$H_2 + 2S <=> 2(HS) \tag{5}$$
$$A + 2(HS) \rightarrow B + 2S \tag{6}$$

1a. Derive the rate expression for A for the Langmuir-Hinshelwood model. The answer must contain only measurable concentrations of $[A]$, $[H_2]$ and $[B]$, and constants. **25 pts**

1b. Derive the rate expression for A for the Eley-Rideal model (here, with the surface reaction being an RDS). The answer must contain only measurable concentrations of $[A]$, $[H_2]$ and $[B]$, and constants. **25 pts**

1c. Four experiments were conducted in which all three of the components (A, B and hydrogen) were present in the feed. The following reaction rates were obtained:

Run	$[A]$, mol/L	$[B]$, mol/L	$[H2]$, mol/L	$-d[A]/dt$, $mol/(Lh)$
1	0.04	0.02	0.06	0.10
2	0.04	0.04	0.06	0.11
3	0.02	0.02	0.03	0.20
4	0.04	0.02	0.03	0.05

Does $[B]$ affect the reaction rate at other parameters kept constant? What is the apparent order to B for these experiments? **5 pts**

how does $[H_2]$ affect the reaction rate at other parameters kept constant? What is the apparent order to hydrogen for these experiments? **5 pts**

how does $[A]$ affect the reaction rate at other parameters kept constant? What is the apparent order to A for these experiments? **10 pts**

1d. Go back to the derived LH model in question **1a.** Is it consistent with experimental data and under what assumptions (i.e. what terms must be neglected)? What is the most abundant surface intermediate (A, B or hydrogen)? **15 pts**

1e. Go back to the derived ER model in question **1b.** Is it consistent with experimental data and under what assumptions (i.e. what terms must be neglected)? **15 pts**

Answer to Q1:

1a) LH:

$$A + S <=> AS; \quad \theta_A = K_A[A]\theta_s \tag{7}$$
$$H_2 + 2S <=> 2(HS); \quad \theta_H = (K_H[H_2])^{0.5}\theta_s \tag{8}$$
$$AS + 2(HS) \rightarrow BS + 2S; \quad r = k\theta_A\theta_H^2 \tag{9}$$
$$BS <=> B + S; \quad \theta_B = K_B[B]\theta_s \tag{10}$$

Surface balance:

$$\theta_A + \theta_H + \theta_B + \theta_s = 1 \tag{11}$$

$$\theta_s = \frac{1}{K_A[A] + (K_H[H_2])^{0.5} + K_B[B] + 1} \tag{12}$$

$$r = k\theta_A\theta_H^2 = \frac{kK_AK_H[H_2][A]}{(K_A[A] + (K_H[H_2])^{0.5} + K_B[B] + 1)^3} \tag{13}$$

1b) ER:

$$H_2 + 2S <=> 2(HS) \tag{14}$$
$$A + 2(HS) \rightarrow B + 2S \tag{15}$$

$$\theta_H^2 = K_H[H_2]\theta_S^2 \tag{16}$$
$$r = k[A]\theta_H^2 \tag{17}$$

Surface balance:

$$\theta_H + \theta_s = 1 \tag{18}$$
$$\theta_S = \frac{1}{(K_H[H_2])^{0.5} + 1} \tag{19}$$

$$r = \frac{k[A]K_H[H_2]}{(K_H[H_2])^{0.5} + 1)^2} \tag{20}$$

1c)

$[B]$? when $[A]$ and $[H_2]$ are constant: Runs 1 and 4.

$[H_2]$ drops twice, rate drops twice,

$$r \propto [H_2]^1 \tag{21}$$

$[A]$? when $[H_2]$ and $[B]$ are constant: Runs 3 and 4.

$$r_3 \propto [A]_3^a \tag{22}$$
$$r_4 \propto [A]_4^a \tag{23}$$

$$ln\frac{r_3}{r_4} \propto a.ln\frac{[A]_3}{[A]_4} \tag{24}$$
$$ln(4) = a.ln(\frac{1}{2}) \tag{25}$$
$$a = -2 \tag{26}$$

Order to $[A]$ is -2.

1d)

If $K_A[A] >> ((K_H[H_2])^{0.5} + K_B + 1)$

$r = \frac{kK_AK_H[H_2][A]}{K_A^3[A]^3} = \frac{kK_H[H_2]}{K_A^2[A]^2}$

and the rate law matches the reaction order to A, B and H_2.

This assumption means that A is the most abundant surface intermediate ($\theta_A = 1$).

1e)

If $(K_H[H_2])^{0.5} << 1$ then $r = k[A]K_H[H_2]$ matches 1^{st} order to H_2, 0^{th} order to B but doesn't match order to A. The rate law and mechanism are not consistent with experimental data and must be rejected.