

# ChE445\_HW5\_Winter2020\_Solution\_and\_Code

March 13, 2020

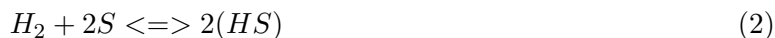
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## 0.0.1 HW Assignment 5. Mechanisms of heterogeneous catalytic reactions\*\*

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

**Langmuir-Hinshelwood (LH):**



**Eley-Rideal (ER):**



**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	$[H_2]$ , 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**

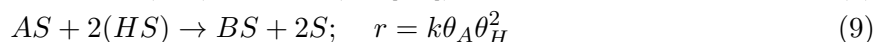
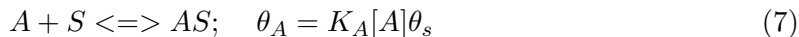
how does  $[A]$  affect the reaction rate at other parameters kept constant? What is the apparent order to  $A$  for these experiments? **10 pts**

**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:**



Surface balance:

$$\theta_A + \theta_H + \theta_B + \theta_s = 1 \quad (11)$$

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

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

**1b) ER:**



$$\theta_H^2 = K_H[H_2]\theta_s^2 \quad (16)$$

$$r = k[A]\theta_H^2 \quad (17)$$

Surface balance:

$$\theta_H + \theta_s = 1 \quad (18)$$

$$\theta_s = \frac{1}{(K_H[H_2])^{0.5} + 1} \quad (19)$$

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

**1c)**

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

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

$$r \propto [H_2]^1 \quad (21)$$

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

$$r_3 \propto [A]_3^a \quad (22)$$

$$r_4 \propto [A]_4^a \quad (23)$$

$$\ln \frac{r_3}{r_4} \propto a \ln \frac{[A]_3}{[A]_4} \quad (24)$$

$$\ln(4) = a \ln\left(\frac{1}{2}\right) \quad (25)$$

$$a = -2 \quad (26)$$

Order to  $[A]$  is  $-2$ .

**1d)**

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

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

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  $(K_H[H_2])^{0.5} \ll 1$  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.