

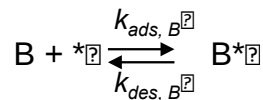
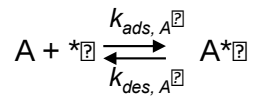
ChE-403 Problem Set 2.2

Week 6

Problem 1

Can you solve the Langmuir isotherm (ϑ_A and ϑ_B) problem when 2 molecules are adsorbing on the surface simultaneously?

This occurs when these two reactions all happen at the same time:



Solution:

Both reaction are assumed to be at equilibrium:

$$\frac{d[A*]}{dt} = 0 = k_{ads,A}[A][*] - k_{des,A}[A*]$$

$$\frac{d[B*]}{dt} = 0 = k_{ads,B}[B][*] - k_{des,B}[B*]$$

$$K_{ads,A} = \frac{[A*]}{[A][*]}$$

$$K_{ads,B} = \frac{[B*]}{[B][*]}$$

$$[*]_0 = [*] + [A*] + [B*] = [*] + K_{ads,A}[A][*] + K_{ads,B}[B][*]$$

$$[*] = \frac{[*]_0}{1 + K_{ads,A}[A] + K_{ads,B}[B]}$$

We can substitute in the $K_{ads,A}$ and $K_{ads,B}$ equations:

$$[A *] = K_{ads,A}[A][*] = \frac{K_{ads,A}[A][*]_0}{1 + K_{ads,A}[A] + K_{ads,B}[B]}$$

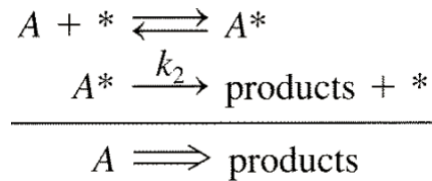
$$\rightarrow \vartheta_A = \frac{[A *]}{[*]_0} = \frac{K_{ads,A}[A]}{1 + K_{ads,A}[A] + K_{ads,B}[B]}$$

Similarly:

$$\vartheta_B = \frac{[B *]}{[*]_0} = \frac{K_{ads,B}[B]}{1 + K_{ads,A}[A] + K_{ads,B}[B]}$$

Problem 2

For the mechanism below:



We had assumed that the first reversible reaction was quasi-equilibrated and that the second was the RDS to calculate the following rate:

$$r = k_2[A^*] = k_2[*]_0 \frac{K_{ads}[A]}{1 + K_{ads}[A]}$$

Can you derive this using the steady-state approximation (SSA)?

Solution:

$$\frac{d[A^*]}{dt} = 0 = k_{ads}[A][*] - k_{des}[A^*] - k_2[A^*]$$

The site balance: $[*] = [*]_0 - [A^*]$

$$k_{ads}[A]([*]_0 - [A^*]) - k_{des}[A^*] - k_2[A^*] = 0$$

$$[A^*] = \frac{k_{ads}[A][*]_0}{k_{ads}[A] + k_{des} + k_2}$$

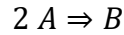
$$[A^*] = \frac{K_{ads}[A][*]_0}{1 + K_{ads}[A] + k_2/k_{des}}$$

$$r = k_2[A^*] = k_2[*]_0 \frac{K_{ads}[A]}{1 + K_{ads}[A] + k_2/k_{des}}$$

Slightly different... but if an equilibrium is assumed for the first reaction then that means that k_{des} and $k_{ads} \gg k_2 \rightarrow \frac{k_2}{k_{des}} \ll 1 \rightarrow$ With this assumption we get the same expression.

Problem 3

Reactant A dimerizes in the presence of Cr/SiO₂. The stoichiometric reaction is the following:

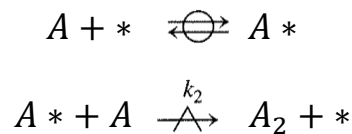


Experimentally, we observe that at a high concentration of A $\frac{d[A]}{dt} \approx -cst1 [A]$ whereas at low concentration of A $\frac{d[A]}{dt} \approx -cst2 [A]^2$.

Can you derive/propose a mechanism and a rate equation that would explain this behavior knowing that adsorbed A (i.e. A*) prefers to react directly with gaseous A instead of another adsorbed A?

Solution:

This mechanism is known as the Rideal-Eley. The proposed mechanism is could be...



We start writing the RDS:

$$r = k_2 [A *] [A]$$

To find an expression for [A*], we use the reaction in equilibrium in the 1st step:

$$K_1 = \frac{[A *]}{[A][*]}$$

With the site balance, we have:

$$[*]_o = [*] + [A *] \rightarrow [*]_o = [*] + K_1 [A][*]$$

We isolate for [*] and substitute in the expression for K₁

$$[*] = \frac{[*]_o}{1 + K_1 [A]} \quad [A *] = K_1 \frac{[*]_o [A]}{1 + K_1 [A]}$$

If we plug into the rate of reaction...

$$r = k_2 K_1 \frac{[*]_o [A]^2}{1 + K_1 [A]}$$

At high concentrations $K_1 [A] \gg 1$ and the rate of reaction becomes..... where $cst1 = k_2$

$$r = k_2 [*]_o [A]$$

At low concentrations $K_1 [A] \ll 1$ and the rate of reaction becomes..... where $cst2 = k_2 K_1$

$$r = k_2 K_1 [*]_o [A]^2$$