

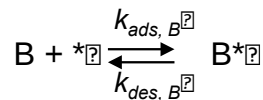
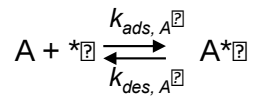
ChE-403 Problem Set 2.2

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:

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

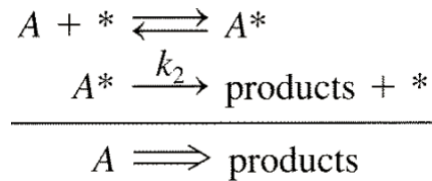
$$\rightarrow \vartheta_A = \frac{[A *]}{[*]_0} = \frac{K_{ads,A}[A]}{1 + K_{ads,A}[A] + K_{ads,B}[B]}$$

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:

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

$$\text{The site balance: } [*] = [*]_0 - [A^*]$$

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

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

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

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

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.