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:

$$A + * \underset{k_{des,\,A}}{\overset{k_{ads,\,A}}{\rightleftharpoons}} A*$$

$$B + * \underset{k_{des,\,B}}{\overset{k_{ads,\,B}}{\rightleftharpoons}} B*$$

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:

$$
\begin{array}{rcl}
A + * & \rightleftarrows & A* \\
A* & \xrightarrow{k_2} & \text{products} + * \\
\hline
A & \Longrightarrow & \text{products}
\end{array}
$$

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* $k_{ads} \gg k_2$ → $\frac{k_2}{k_{des}} \ll 1$ → With this assumption we get the same expression.