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.

Problem 3

Reactant A dimerizes in the presence of Cr/SiO$_2$. The stoichiometric reaction is the following:

$$2\,A \Rightarrow B$$

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…

$$A + * \quad \overset{\ominus}{\rightleftarrows} \quad A\,*$$

$$A * + A \quad \overset{k_2}{\rightarrow\!\!\!\!\!\!\Lambda} \quad A_2 + *$$

We start writing the RDS:

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

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

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

With the site balance, we have:

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

We isolate for [*] and substitude in the expression for K$_1$

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

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 $cst2 = k_2 K_1$

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