Carta Langmuir :

Do livro do Evangelista :

$$\frac{d\sigma}{dt} = k\rho\left(1-\frac{\sigma}{\sigma_0}\right) - \frac{1}{\tau}\sigma$$

onde σ_0 é o número de sítios para adsorção.

se $\frac{\sigma}{\sigma_0} = \sigma_R$

$$\frac{d\sigma_R}{dt} = \frac{k\rho_0}{\sigma_0}\bar{\rho}(\pm d/2,t)(1-\sigma_R) - \frac{1}{\tau}\sigma_R$$

$\sigma_0 \sim \frac{1}{b^2}$

b = tamanho molecular

Como: $K \simeq 10^{-6}\, m/s$, $\rho_0 \simeq 10^{20}\, m^{-1}$, $\sigma_0 \simeq 10^{15}$ $\longrightarrow$ $\frac{k\rho_0}{\sigma_0} \equiv \frac{m/s}{m} = \frac{1}{T_K} \cong \frac{1}{10^{0}} \frac{1}{s}$ ou 10^{-1}

assim

$$\boxed{\frac{d\sigma_R}{dt} = \frac{1}{T_K}\bar{\rho}(\pm d/2,t)(1-\sigma_R) - \frac{1}{\tau}\sigma_R}$$

trocando

$t = \frac{T_D t^*}{4}$

$$\boxed{\frac{d\sigma_R}{dt^*} = \frac{T_D}{4T_K}\bar{\rho}(\pm d/2,t)(1-\sigma_R) - \frac{T_D}{4\tau}\sigma_R} \longrightarrow BC\ 1$$

Eq. Cinética

Eq de Bulk:

$$\boxed{\frac{\partial \bar{\rho}}{\partial t^*} = \frac{\partial^2 \bar{\rho}}{\partial z^2}}$$

$(z = -1 \text{ até } 1)$ (2) Difusão

Conservação:

$$2\sigma + \int_{-d/2}^{d/2} \rho(z,t)\, dz = \rho_0 d$$

$$\left(2\sigma + \int_{-d/2}^{d/2} \bar{\rho} \rho_0 \frac{d}{2} dz = \rho_0 d\right) \cdot \frac{1}{\sigma_0}$$

$$2\sigma_n + \frac{1}{2}\int_{-1}^{1} \left(\frac{\rho_0 d}{\sigma_0}\right) \rho\, dz = \frac{\rho_0 d}{\sigma_0}$$

$$\frac{\rho_0 d}{\sigma_0} = \beta = \text{comprimento reduzido} = \frac{10^{20} \cdot 10^{-6}}{10^{15}} \simeq 10^{-1} \left(10^{0} \text{ depende de } d\right)$$

Logo

$$\boxed{\frac{4\sigma_n}{\beta} + \int_{-1}^{1} \rho\, dz = 2}$$

(3) Conservação

$$D \frac{\partial \rho}{\partial z} = \pm \frac{d\sigma}{dt} \rightarrow 2\frac{D\rho_0}{\sigma_0 d} \frac{\partial \bar{\rho}}{\partial z} = \pm \frac{d\sigma_n}{dt} = \pm \frac{4}{T_D} \frac{d\sigma_n}{dt^*}$$

ou $\frac{\beta}{T_D} \frac{\partial \bar{\rho}}{\partial z} = \pm \frac{2}{T_D} \frac{d\sigma_n}{dt^*} \longrightarrow \boxed{\left.\frac{\partial \bar{\rho}}{\partial z}\right|_{z=\pm 1} = \pm \frac{2}{\beta} \frac{d\sigma_n}{dt^*}}$ BC (4) Corrente

Langmuir com memória

$$\frac{d\sigma}{dt} = k\rho\left(1-\frac{\sigma}{\sigma_0}\right) - \frac{1}{T T_a}\int_0^t e^{-\frac{(t-T)}{T_a}}\sigma(T)\,dT$$

derivando dos dois lados

$$\frac{d^2\sigma}{dt^2} = k\frac{d\rho}{dt}\left(1-\frac{\sigma}{\sigma_0}\right) - \frac{k\rho}{\sigma_0}\frac{d\sigma}{dt} - \frac{1}{T_a}\frac{d\sigma}{dt} + \frac{k}{T_a}\rho\left(1-\frac{\sigma}{\sigma_0}\right) - \frac{\sigma}{T T_a}$$

usando

$\rho = \rho_0\bar{\rho}$ e $\frac{\sigma}{\sigma_0} = \sigma_R$ e multiplicando por $\frac{1}{\sigma_0}$

$$\frac{d^2\sigma_n}{dt^2} = \frac{k\rho_0}{\sigma_0}\frac{d\bar{\rho}}{dt}(1-\sigma_n) - \frac{k\rho_0}{\sigma_0}\bar{\rho}\frac{d\sigma_n}{dt} - \frac{1}{T_a}\frac{d\sigma_n}{dt} + \frac{k\rho_0\bar{\rho}}{\sigma_0 T_a}(1-\sigma_n) - \frac{\sigma_n}{T T_a}$$

usando

$\frac{k\rho_0}{T_0} = \frac{1}{T_k}$ e $t = \frac{t^* T_0}{4}$

$$\frac{16}{T_0^2}\frac{d^2\sigma_n}{dt^{*2}} = \left(\frac{4\,d\bar{\rho}/dt}{T_0 T_k}(1-\sigma_n) - \frac{\bar{\rho}}{T_k}\frac{4}{T_0}\frac{d\sigma_n}{dt} - \frac{4}{T_a T_0}\frac{d\sigma_n}{dt^*} + \frac{\bar{\rho}}{T_k T_a}(1-\sigma_n) - \frac{\sigma_n}{T T_a}\right)\frac{T_0^2}{16}$$

ou

$$\frac{d^2\sigma_n}{dt^{*2}} - \frac{T_0}{4T_k}\frac{d\bar{\rho}}{dt^*}(1-\sigma_n) + \frac{\bar{\rho}T_0}{4T_k}\frac{d\sigma_n}{dt^*} + \frac{T_0}{4T_a}\frac{d\sigma_n}{dt^*} - \frac{\bar{\rho}T_0^2}{16T_kT_a}(1-\sigma_n) + \frac{T_0^2\sigma_n}{16TT_a} = 0$$

$$\boxed{\frac{d^2\sigma_n}{dt^{*2}} - \frac{T_D}{4T_K}\frac{d\bar{\rho}}{dt^*}(1-\sigma_n) + \frac{\bar{\rho}T_D}{4T_K}\frac{d\sigma_n}{dt^*} + \frac{T_D}{4T_a}\frac{d\sigma_n}{dt^*} - \frac{\bar{\rho}T_D^2}{16T_KT_a}(1-\sigma_n) + \frac{T_D^2}{16T_aT}\sigma_n = 0}$$

onde $\bar{\rho} = \bar{\rho}(\pm d/2, t)$

ou

$$\underbrace{\frac{d^2\sigma_n}{dt^{*2}}}_{1} - (1-\sigma_n)\left[\underbrace{\frac{T_D}{4T_K}\frac{d\bar{\rho}}{dt^*}}_{2} + \underbrace{\frac{\bar{\rho}T_D^2}{16T_KT_a}}_{3}\right] + \underbrace{\frac{\bar{\rho}T_D}{4T_K}\frac{d\sigma_n}{dt^*}}_{4} + \underbrace{\frac{T_D}{4T_a}\frac{d\sigma_n}{dt^*}}_{5} + \underbrace{\frac{T_D^2}{16T_aT}\sigma_n}_{6} = 0$$