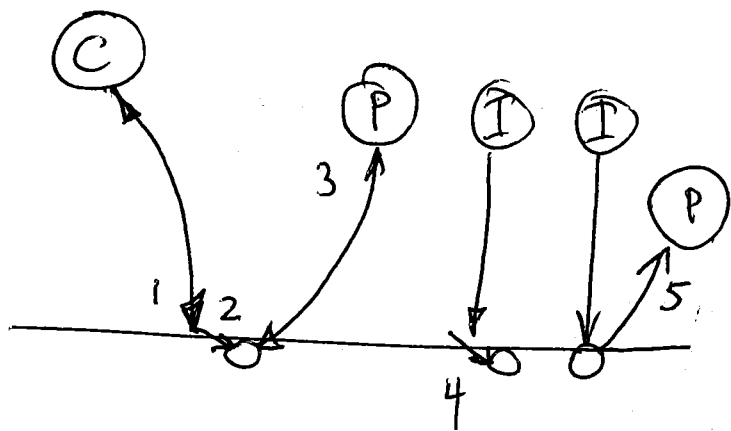


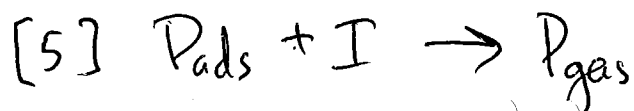
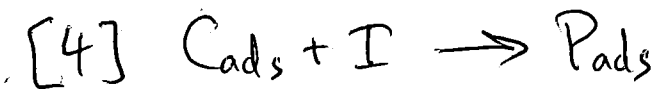
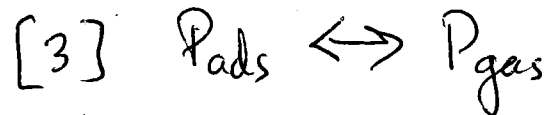
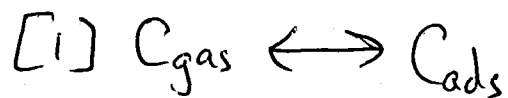


$$\theta_c = \frac{N_c}{N_{\text{site}}} \quad \leftarrow \text{per unit area}$$

$$\theta_p = \frac{N_p}{N_{\text{site}}} \quad \leftarrow \text{possible sites per area}$$

$$\theta = \theta_c + \theta_p$$

surface coverage



$$\frac{dN_c}{dt} = k_{\text{rf}}(1-\theta)F_c - k_{\text{ir}}N_c - k_2N_c - k_4N_cF_I$$

Example 1: Assume [3] fast ([5], negligible) $\Rightarrow \theta_p \ll 1$

$$\frac{dN_c}{dt} = k_{\text{rf}}F_c(1-\theta_c) - k_{\text{ir}}N_c - k_2N_c - k_4N_cF_I = 0 \quad \text{in steady-state}$$

$$k_{\text{rf}}F_c = \theta_c \left[F_c k_{\text{rf}} + N_{\text{site}}(k_{\text{ir}} + k_2 + k_4F_I) \right]$$

$$\theta_c = \frac{1}{1 + \frac{N_{\text{site}}}{k_{\text{rf}}F_c}(k_{\text{ir}} + k_2 + k_4F_I)} = \frac{N_c}{N_{\text{site}}}$$

$$\frac{dx}{dt} = \frac{1}{N} [k_2N_c + k_4N_cF_I] = \frac{(k_2 + k_4F_I)N_{\text{site}}}{\left[1 + \frac{N_{\text{site}}}{k_{\text{rf}}F_c}(k_{\text{ir}} + k_2 + k_4F_I) \right] N}$$

Example 2: Assume σ_c small, but (3) slow
 k_{if} fast ($=1$)

$$\frac{dN_c}{dt} = k_{if} F_c (1 - \theta_p) - k_{tr} N_c - k_2 N_c = 0 \text{ in ss}$$

$$N_c = \frac{k_{if}(1 - \sigma_p) F_c}{k_{ir} + k_2} = \frac{(1 - \sigma_p) F_c}{k_{ir} + k_2}$$

$$\frac{dN_p}{dt} = k_2 N_c - k_5 F_I \theta_p = 0 \text{ in ss}$$

$$\theta_p = \frac{k_2 N_c}{k_5 F_I} = \frac{k_2}{k_5 F_I} \left(\frac{(1 - \theta_p) F_c}{k_{ir} + k_2} \right)$$

$$\frac{k_2}{k_{ir} + k_2} = S_c$$

$$\theta_p = \frac{S_c F_c}{k_5 F_I} (1 - \theta_p)$$

$$\theta_p \left(1 + \frac{S_c F_c}{k_5 F_I} \right) = \frac{S_c F_c}{k_5 F_I}$$

$$\theta_p = \frac{S_c F_c / k_5 F_I}{1 + S_c F_c / k_5 F_I} = \frac{1}{\frac{k_5 F_I}{S_c F_c} + 1}$$

$$\frac{dx}{dt} = \frac{1}{N} k_5 F_I \theta_p = \frac{1}{N} \frac{k_5 F_I}{\frac{k_5 F_I}{S_c F_c} + 1} = \frac{1}{N} \frac{(k_5 F_I)(S_c F_c)}{k_5 F_I + S_c F_c}$$