Competitive Molecular Adsorption (Langmuir Model)

For competitive adsorption of two molecules A and B which (i) are both adsorbed molecularly, and (ii) compete for the same adsorption sites, then the Langmuir model can be used to derive a modified adsorption isotherm.

For the molecule A

For the rate of adsorption, R_{ads}

$$R_{ads} \propto P_A \quad \text{and} \quad R_{ads} \propto [\textit{vacant surface sites}]$$

hence $$R_{ads} \propto (1-\theta_A-\theta_B)P_A$$

For the rate of desorption, R_{des}

$$R_{des} \propto \theta_A$$

At equilibrium these rates must be equal (i.e., $R_{\text{ads}} = R_{\text{des}}$), giving

$$(1-\theta_A-\theta_B)b_A P_A = \theta_A \qquad [1]$$

where b_{A} is given by the ratio of the proportionality constants for adsorption and desorption of A.

For the molecule B

The same approach yields:

$$(1-\theta_A-\theta_B)b_B P_B = \theta_B \qquad [2]$$

where b_{B} is given by the ratio of the proportionality constants for adsorption and desorption of B.

Ratioing of equations [1} and [2] gives

$$\frac{b_B P_B}{b_A P_A} = \frac{\theta_B}{\theta_A} \quad \Rightarrow \quad \theta_B = \frac{b_B P_B}{b_A P_A}\theta_A$$

Substitution of this result back into [1] gives

$$(1-\theta_A - \frac{b_B P_B}{b_A P_A}\theta_A)b_A P_A = \theta_A$$

$$\Rightarrow \quad (b_A P_A - b_A P_A \theta_A - b_B P_B \theta_A) = \theta_A$$

$$\Rightarrow \quad (b_A P_A - b_A P_A \theta_A - b_B P_B \theta_A) = \theta_A$$

$$\Rightarrow \quad \theta_A(1 + b_A P_A + b_B P_B) = b_A P_A$$

$$\Rightarrow \quad \boxed{\theta_A = \frac{b_A P_A}{(1 + b_A P_A + b_B P_B)}}$$

and an analagous equation for θ_{B}

(from http://www.chem.qmul.ac.uk/surfaces/scc/)