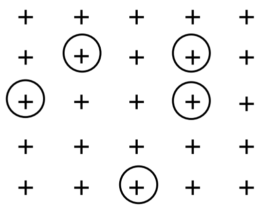
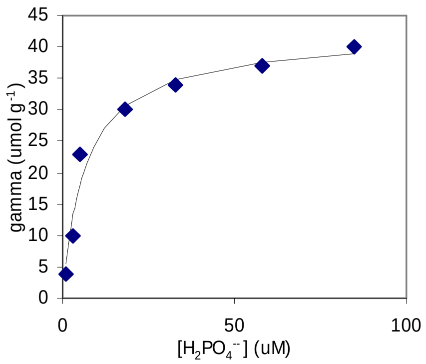
Monolayer Adsorption



occupied: $\theta_A = 5/25$

free: $(1 - \theta_A) = 20/25$



$[A]_\sigma \equiv n_{A\sigma}/\sigma$

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free binding sites: $[B]_\sigma \equiv n_{B\sigma}/\sigma$

maximum: $[B]_{o\sigma} \equiv n_{Bo}/\sigma$

$[B]_{o\sigma} = [B]_\sigma + [A]_\sigma$

$[A]_{max\sigma} = [B]_{o\sigma}$

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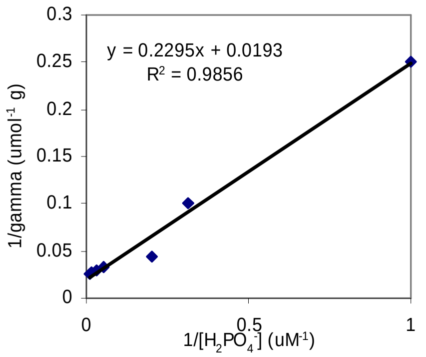
fractional coverage: $\theta_A = \dfrac{[A]_\sigma}{[A]_{max\sigma}}$

$[A]_\sigma = [A]_{max\sigma}\,\theta_A = [B]_{o\sigma}\,\theta_A$

$$A\,(g) + B_\sigma \underset{k_d}{\overset{k_a}{\rightleftarrows}} A_\sigma$$



$$\frac{d\,[A]_\sigma}{dt} = k_a[B]_\sigma P_A - k_d[A]_\sigma$$

$$\frac{d\,[A]_\sigma}{dt} = k_a[B]_{o\sigma}(1 - \theta_A)P_A - k_d[B]_{o\sigma}\theta_A$$

$$\frac{d\,\theta_A}{dt} = k_a(1 - \theta_A)P_A - k_d\theta_A$$

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equilibrium: $\theta_A = \dfrac{k_a\,P_A}{k_d + k_a\,P_A}$

$b \equiv \dfrac{k_a}{k_d}$ $\qquad \theta_A = \dfrac{b\,P_A}{1 + b\,P_A}$

$$\frac{1}{\theta_A} = \frac{1 + b\,P_A}{b\,P_A} = \frac{1}{b\,P_A} + 1$$

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surface loading: $\Gamma = n_{Amax}/m = n_{Bmax}/m$

$$\Gamma_{A\sigma} = \Gamma_{max\sigma}\frac{b\,P_A}{1 + b\,P_A} \qquad \frac{1}{\Gamma_{A\sigma}} = \frac{1}{\Gamma_{max\sigma}}\left(\frac{1}{b\,P_A} + 1\right)$$

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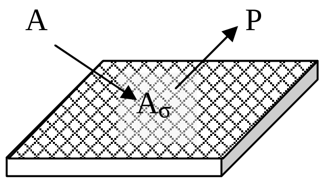
fraction free: $1 - \theta_A = \dfrac{1}{1 + b\,P_A}$

Surface Catalysis



(1) adsorption on the catalyst surface
(2) the chemical reaction
(3) desorption of the products

Assume the product is very weakly adsorbed:

$$A\,(g) + B_\sigma \underset{k_d}{\overset{k_a}{\rightleftarrows}} A_\sigma \xrightarrow{k_\sigma} P\,(g) + B_\sigma$$

Assume surface adsorption steps are in equilibrium, rapid pre-equilibrium mechanism; $k_a, k_d >> k_\sigma$:

$$\frac{1}{\sigma}\frac{d\xi}{dt} = k_\sigma [A]_\sigma$$

$$\frac{1}{\sigma}\frac{d\xi}{dt} = k_\sigma [B]_{o\sigma}\,\theta_A$$

Single monolayer:

$$\frac{1}{\sigma}\frac{d\xi}{dt} = k_\sigma [B]_{o\sigma} \frac{b_A P_A}{1 + b_A P_A}$$

Assume the moles of A on the surface are small compared to the moles of reactant in the gas phase:

$$\frac{1}{V}\frac{d\xi}{dt} = -\frac{dP_A}{dt} = \frac{dP_P}{dt}$$

$$-\frac{dP_A}{dt} = [k_\sigma\,\sigma/V\,[B]_{o\sigma}] \frac{b_A P_A}{1 + b_A P_A}$$

$$-\frac{dP_A}{dt} = k \frac{b_A P_A}{1 + b_A P_A} \qquad k = [k_\sigma\,\sigma/V\,[B]_{o\sigma}]$$

$$-\frac{dP_A}{dt} = k\,b_A P_A \qquad \text{(monolayer, weakly adsorbed)}$$

$$k_{obs} \equiv k\,b_A$$

$$-\frac{dP_A}{dt} = k \qquad \text{(monolayer, strongly adsorbed)}$$