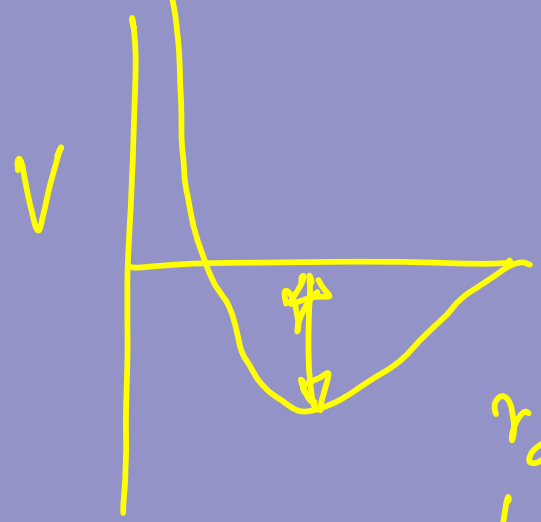
Class 6: Surface chemistry and reactions, and introduction to thermodynamics

$$CO(g) + O_2(g) \xrightarrow{\text{Rh cat}} CO_2(g)$$

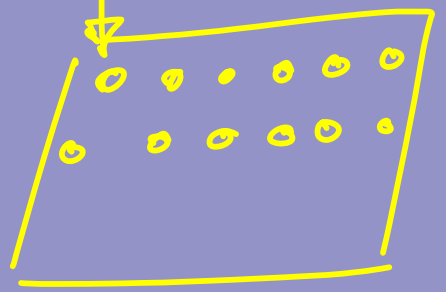
heterogeneous catalyst ↑ automobile exhaust

$$CO(ad) + O_2(ad) \rightarrow CO_2(g)$$

Langmuir



$$A(g) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} A(ad)$$



At equilibrium, σ_0

$$r_{ad} = r_{des}$$

$$k_a \sigma_0 [A](1-\theta) = k_d \sigma_0 \theta$$

$$[A] = \frac{p_A}{kT}$$

$$\frac{k_a}{k_d}\frac{1}{k_B T} = b$$

$$[*]_0(\sigma_0) = [A*] + [*]$$

$[*]_0(\sigma_0)$: number of sites

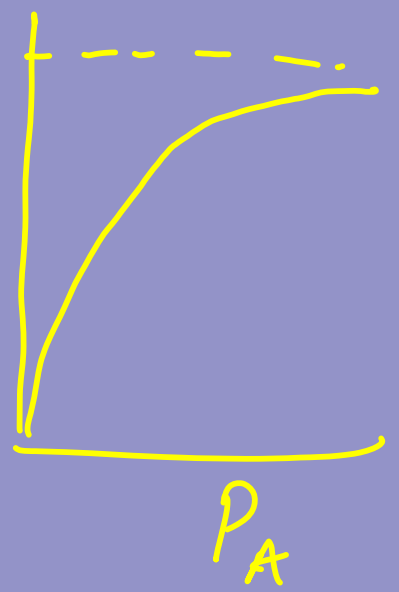
$[A*]$: no. of sites

$[*]$: # free sites

$$[E]_0 = [ES] + [E]$$

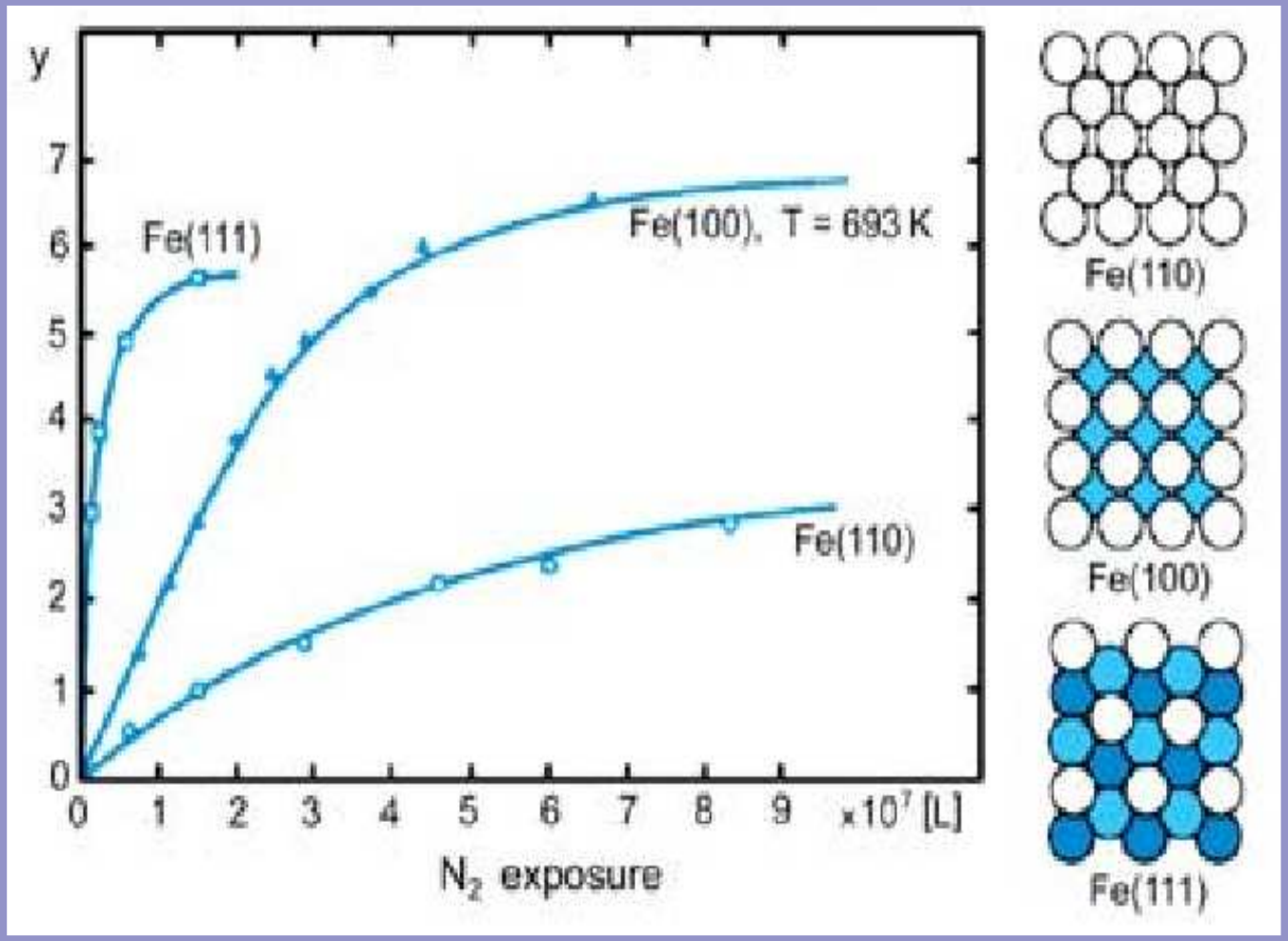
fractional coverage θ

$$\theta = \frac{b P_A}{1 + b P_A}$$



N_2 on Fe

G. Ertl "Nobel" lecture



$N_2 + 3H_2 \rightarrow 2NH_3$

$$H_2 \rightleftharpoons 2H_{ad},$$

$$N_2 \rightleftharpoons N_{2,ad} \rightleftharpoons 2N_s,$$

$$N_s + H_{ad} \rightleftharpoons NH_{ad},$$

$$NH_{ad} + H_{ad} \rightleftharpoons NH_{2,ad},$$

$$NH_{2,ad} + H_{ad} \rightleftharpoons NH_{3,ad},$$

$$NH_{3,ad} \rightleftharpoons NH_3.$$

Dissociative adsorption

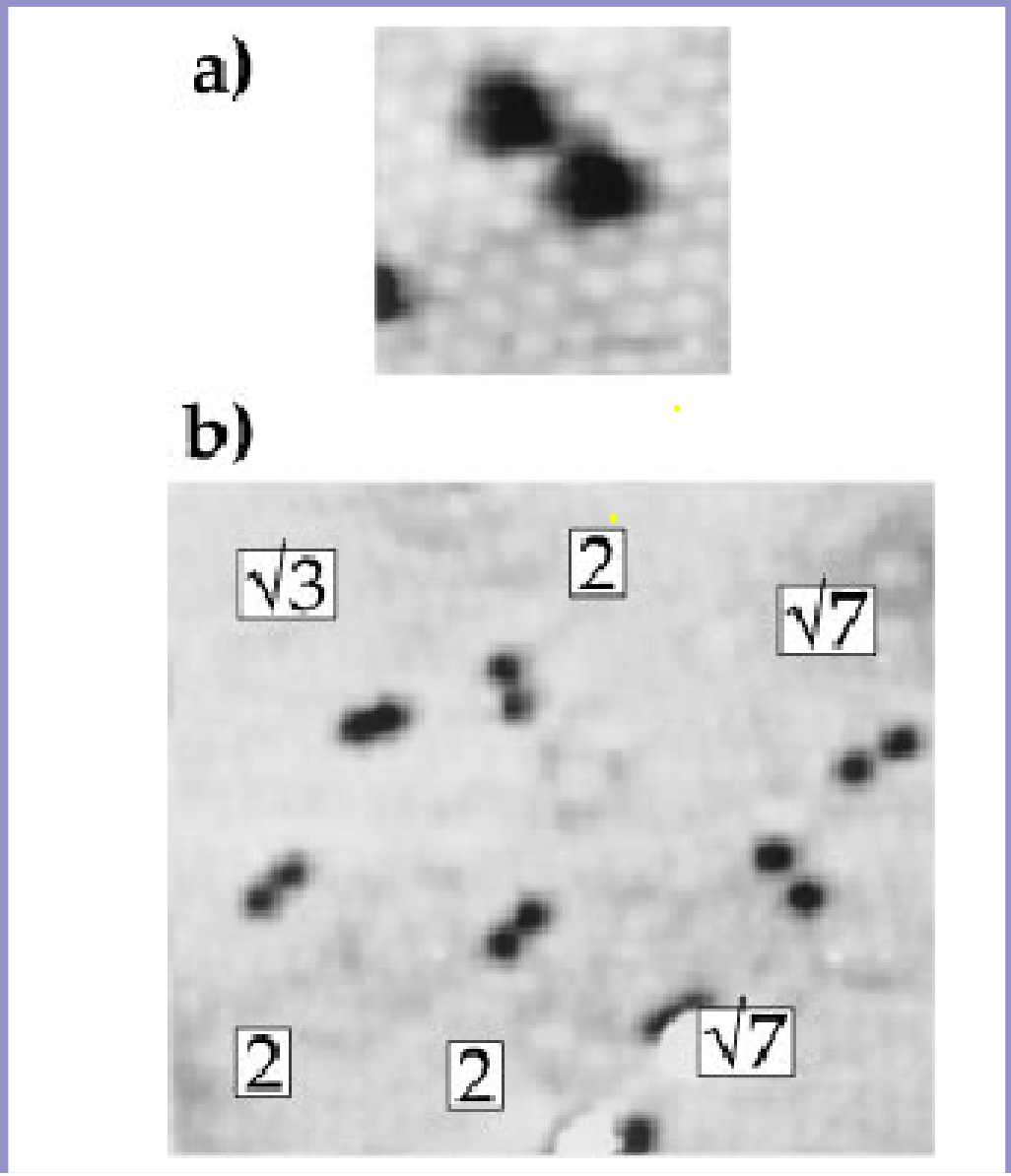
$$A_2\,(g) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} 2A\,(ad)$$

$$r_a = k_a (1-\theta)^2 \sigma_0^2 [A]^2$$

$$r_d = k_d \sigma_0^2 \theta^2$$

$$b = \frac{k_a}{k_a} \cdot \frac{1}{k_B T}$$

$$\theta = \frac{(b P_A)^{1/2}}{1 + (b P_A)^{1/2}}$$



STM picture of O_2 adsorbed on Ru

$$CO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CO_{ad}$$

$$O_2 \xrightarrow{k_3} 2O_{ad}$$

$$O_{ad} + CO_{ad} \xrightarrow{k_4} CO_2$$

$$O_{ad} + CO \xrightarrow{k_5} CO_2$$

$$O_2 + 2CO_{ad} \xrightarrow{k_6} 2CO_2$$

Langmuir - Hinshelwood mechanism (both reactants adsorbed)

Eley - Rideal mechanism

Langmuir - Hinshelwood mechanism

$$A(ad) + B(ad) \xrightarrow{k_2} C$$

$$\frac{d[C]}{dt} = k_2 \theta_A \theta_B$$

$$\theta_A = \frac{b_A P_A}{1 + b_A P_A + b_B P_B}$$

$$\theta_B = \frac{b_B P_B}{1 + b_A P_A + b_B P_B}$$

$$\frac{d[C]}{dt} = k_2$$

$$A(ad) + B(g) \rightarrow C$$

Eley-Rideal

$$\frac{d[C]}{dt} = k_2 \theta_A \cdot [B]$$

$$\theta_A = \frac{b P_A}{1 + b_A P_A + b_B P_B}$$

$$[B] = b P_B$$

Thermodynamics (P, V, T)

"classical"

"Statistical mechanics"

1) The internal energy change accompanying the conversion 1 mol of liquid water at the boiling point into steam is zero.

(2) Other things being the same, it takes longer to heat air in a closed vessel than in an open one.

(3) The conversion of liquid water to ice at 263 K is thermodynamically forbidden because the entropy change is negative.

4 The large and negative ΔG when hydrogen reacts with oxygen to give water at room temperature and pressure suggests that the reaction is spontaneous. However, a mixture of hydrogen and oxygen is stable for long periods without the formation of water.

5 The first law of thermodynamics implies that the temperature of two bodies at different temperatures when equilibrium is achieved after they are in thermal contact will become equal.

1) You can't win

2) You can't break even

3) You can't quit the game.