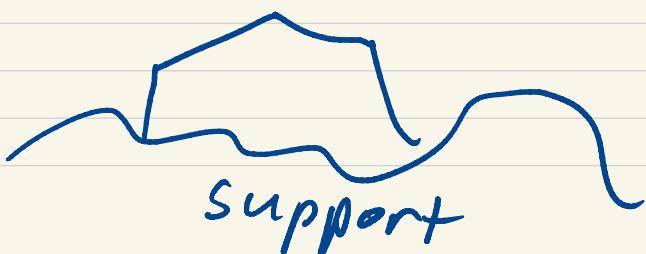


- 1) homogeneous vs heterogeneous catalysts
- 2) examples of classes of heterogeneous reactions
- 3) heterogeneous reactors
- 4) length scales
- 5) supported metal catalysts
 - surface area
 - loading : $m_{\text{cat}}/m_{\text{total}}$
 - dispersion : % accessible V_g
 - particle size :



rate normalization

- pseudo-homogeneous

$$r = \text{moles/vol. time}$$

- mass-normalized

$$r = \text{moles/mass time}$$

- area-normalized

$$r = \text{moles/area.time}$$

- site-normalized

$$r = \text{moles/site.time}$$

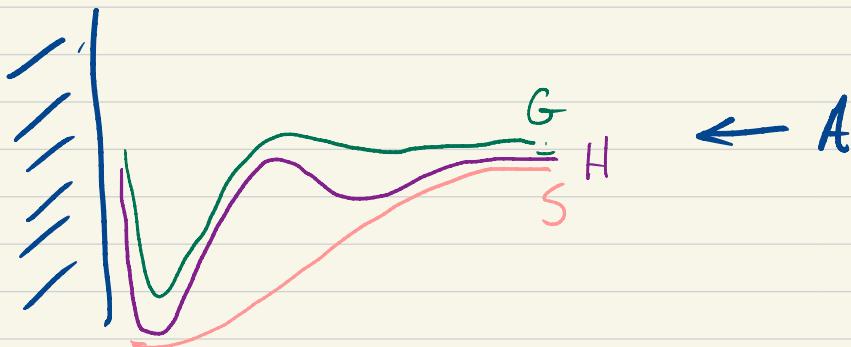
"TOF"

characteristic of catalyst and reaction conditions

hetero cat $\sim 10 \text{ s}^{-1}$

enzymes $\sim 10^6 \text{ s}^{-1}$

Adsorption



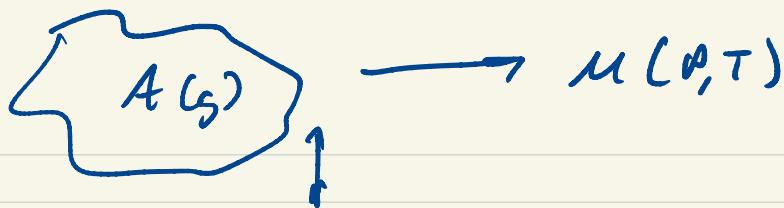
↑
chemical bond
 $\geq 100 \text{ kJ/mol}$
 $\sim 1 \text{ eV}$

↑
physisorption
 $\sim 10 \text{ kJ/mol} - 40$
 $\sim 0.1 \text{ eV}$

S_{trans} : 2D gas depends on adsorbite
: fixed

Typically find that a surface can accommodate a finite # of adsorbates





A — A — A — A

"coverage" $\Theta_A = \frac{\#A}{\# \text{sites}} u(\theta, T)$

"isotherm" describes equilibrium between gas + surface

Langmuir isotherm, GE 1915
 (working on light filaments)
 1932 Nobel prize

Type I: all sites equivalent
 adsorption independent of Θ
 saturates at $\Theta_A = 1$
 "1 monolayer"

dynamic perspective

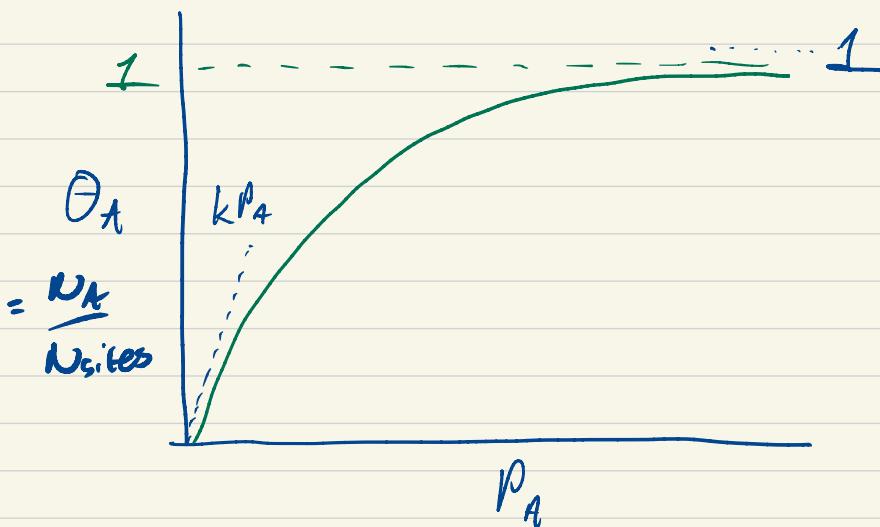
$$r_{\text{ads}} = k_{\text{ads}} \cdot p_A \cdot N \cdot \theta^*$$

$$r_{\text{des}} = k_{\text{des}} \cdot N \cdot \theta_A$$

@ equilibrium $r_{\text{ads}} = r_{\text{des}}$

site conservation $\theta_A + \theta^* = 1$

$$\Rightarrow \boxed{\theta_A = \frac{K \cdot p_A}{1 + K p_A}} \quad K = \frac{k_{\text{ads}}}{k_{\text{des}}}$$
$$= \frac{N_A}{N_{\text{sites}}}$$



example: CO on Ru/Al₂O₃

non-linear fit (est variables)
or linearize

$$\frac{1}{\theta_A} = \left(\frac{1}{K}\right) \cdot \frac{1}{P_A} + 1$$

$$\frac{P_A}{N_A} = \left(\frac{1}{K}\right) \cdot \frac{1}{N_{\text{sites}}} + \frac{P_A}{n_{\text{sites}}}$$

 $\frac{2.89 \mu\text{mol Cu}}{9\text{cat}} \rightarrow 0.0029 \frac{\text{mol Cu}}{\text{mol Ru}}$

0.29% dispersion

$$\frac{S}{V} \sim \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r} \quad r \sim \frac{3}{(S/V)} \sim \frac{3}{0.003}$$

~1000 atoms

 T -dependence

$$-R \left(\frac{\partial \ln K}{\partial T} \right)_{P_A} = 414^\circ$$

"isosteric" heat
of adsorption

equilibrium perspective $M_A^{gas} = M_A^{ads}$

$$M_A^{gas} = M_A^\circ(T) + RT \ln \frac{P}{P^\circ}$$

$$M_A^{ads} = M_A^\circ(T) + RT \ln \frac{\theta}{1-\theta}$$

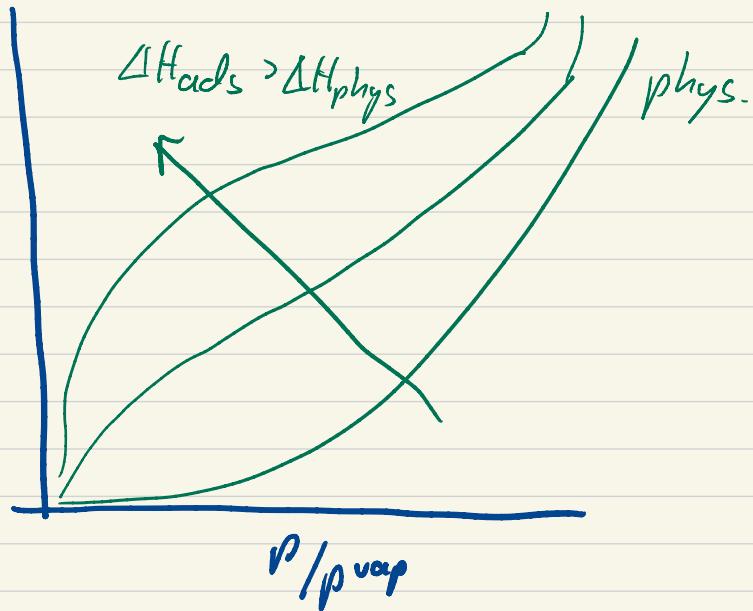
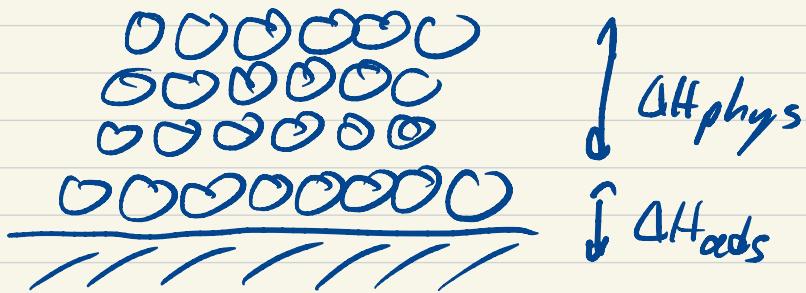
$$-(M_A^\circ - M_A^\circ)/RT = \ln \left(\frac{P}{P^\circ} \right) \left(\frac{\theta}{1-\theta} \right)$$

$$\ln K = \ln \left(\frac{P}{P^\circ} \right) \left(\frac{\theta}{1-\theta} \right)$$

$$K = \left(\frac{P}{P^\circ} \right) \left(\frac{\theta}{1-\theta} \right)$$

$$\Rightarrow Q = \frac{KP/P^\circ}{1+KP/P^\circ}$$

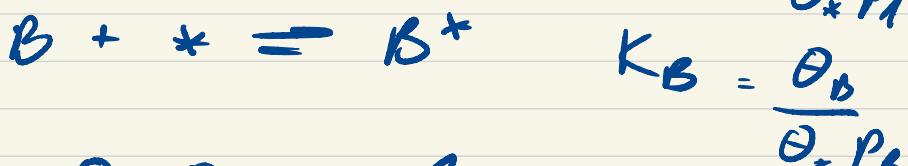
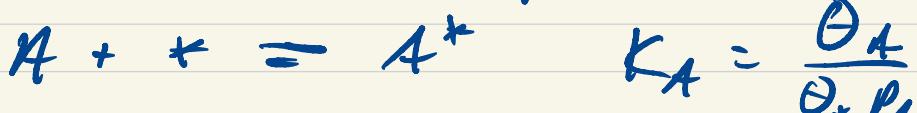
multi-layer adsorption



Often explored using boiling N_2 adsorption to get at total surface area

Brunauer-Emmett-Teller isotherm

competitive adsorption



$$\Theta_A + \Theta_B + \Theta_* = 1$$

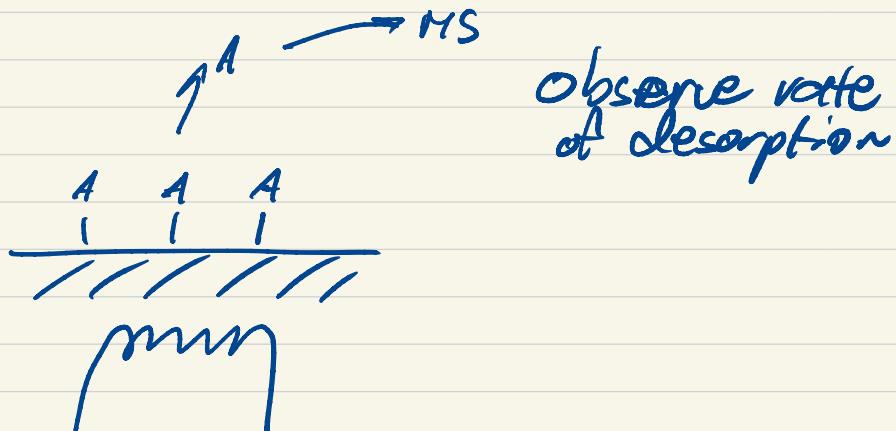
$$\Rightarrow \Theta^* = \frac{1}{1 + K_A P_A + K_B P_B}$$

$$\Theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B}$$

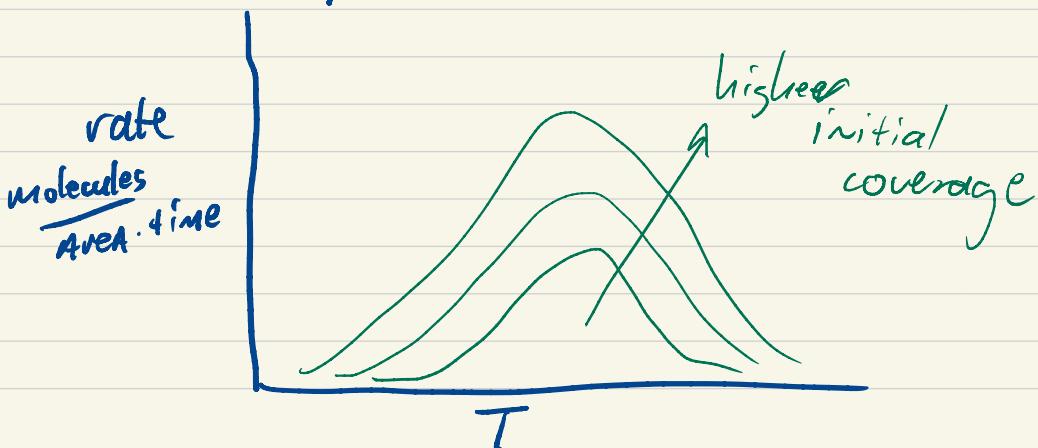
instruments available to measure mass or volume of gas uptake

temperature-programmed desorption

Common way to probe adsorbates
at a surface



- close A @ low T
- ramp T + observe rate of desorption



How to understand?



run under irreversible conditions

$$r_{\text{des}}(\Theta_A, T) = N_{\text{sites}} \cdot \Theta_A \cdot A e^{-E_a(\theta)/k_B T}$$

$$\frac{k_B T}{h} e^{\alpha s^{\ddagger}/k_B T} e^{-\Delta H^{\ddagger}/RT}$$

$$\frac{\text{mole}}{\text{Area} \cdot \text{s}} = \frac{\text{sites}}{\text{Area}} \cdot \frac{\text{ads}}{\text{site}} \cdot \frac{1}{\text{s}}$$

$$\text{Linear } T \text{ ramp} \quad T = T_0 + \beta t$$

To know rate, must know $\Theta_A(T)$

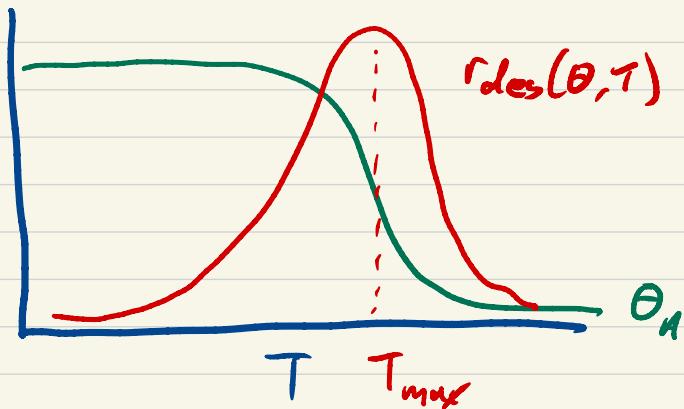
$$\begin{aligned} \frac{d\Theta_A(T)}{dt} &= - \frac{r_{\text{des}}}{N_{\text{sites}}} \\ &= - A e^{-E_a(\theta)/k_B T} \Theta_A \end{aligned}$$

$$dT = \beta dt$$

$$\frac{d\theta_A}{dT} = - \left(\frac{A}{\beta} \right) e^{-E_A(\theta)/k_B T} \theta_A$$

Integrate from $\theta_{A0} \rightarrow 0$

Back substitute to get $r_{des}(Q, T)$



Observe a peak rate.

$$\frac{dr_{des}}{dT} = \dots = 0$$

$$\ln \left(\frac{E_A}{k_B T_{max}^2} \right) = \ln \left(\frac{A}{\beta} \right) - \frac{E_A}{k_B T_{max}}$$

In principle, by determining T_{\max} vs β , can get $\mu + E_a$

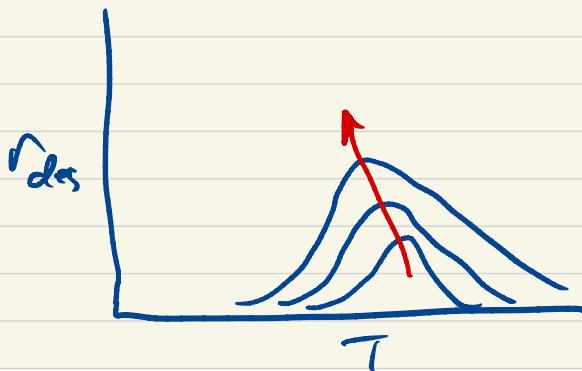
$$\sim 10^{13} \sim BE$$

Desorption can be some other order:

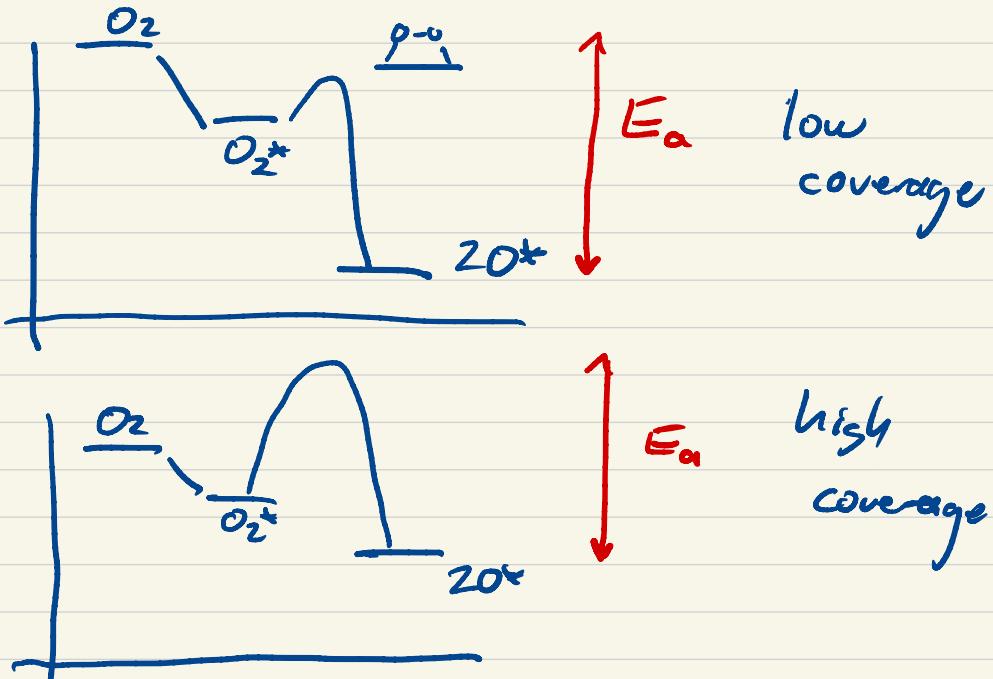


$$r_d = N_s \Theta_A^2 A e^{-E_a/k_b T}$$

Same algorithm, but different sensitivity to Θ_0 .



E_a O_2 desorption Pt(111)



adsorbate - adsorbate
repulsions diminish
binding with
increasing Θ

Will introduce additional
structure to TPD

Surface reactions

Heterogeneous catalytic reaction rates often have complicated suggesting underlying complexity

Langmuir-Hinshelwood model

ex CO oxidation



$$+ \Theta^* + \Theta_{\text{CO}} + \Theta_{\text{O}} = 1$$

Can in principle integrate, eg down length of PFR or CSTR

"microkinetic analysis"

Common simplifying assumptions

- ① reactions @ steady state $\frac{d\theta}{dt} = 0$
- ② there exists one rate determining step $\beta \rightarrow 0$
- ③ other steps are at quasi-equilibrium $\rightleftharpoons \beta \rightarrow 1$

$$k_1 P_{CO} \theta_x = k_1 \theta_{CO} \Rightarrow \theta_{CO} = K_1 P_{CO} \theta^*$$

$$k_2 P_{O_2} \theta_x^2 = -k_{-2} \dot{\theta}_o^2 \Rightarrow \theta_o = \theta^* (K_2 P_o)^{1/2}$$

\rightsquigarrow site balance

$$\theta^* + \theta_{CO} + \theta_o = 1$$

$$\theta^* (1 + K_1 P_{CO} + (K_2 P_o)^{1/2}) = 1$$

$$\theta^* = \frac{1}{1 + K_1 P_{CO} + (K_2 P_o)^{1/2}}$$

$$\begin{aligned}
 r_{CO_2} &= k_3 \Theta_{CO} \Theta_O \\
 &= k_3 K_1 P_{CO} \cdot (K_2 P_{O_2})^{1/2} \cdot \Theta_O^{1/2} \\
 &= \frac{k_3 K_1 K_2^{1/2} P_{CO} P_{O_2}^{1/2}}{(1 + K_1 P_{CO} + (K_2 P_{O_2})^{1/2})^2}
 \end{aligned}$$

Limits

$$K_1 P_{CO} \gg 1, (K_2 P_{O_2})^{1/2}$$

$$r_{CO_2} = \frac{k_3 K_2^{1/2} P_{O_2}^{1/2}}{K_1 P_{CO}}$$

inverse in CO, $\Theta_{CO} \rightarrow 1$

"Poisoning" surface

$$(K_2 P_{O_2})^{1/2} \gg 1, K_1 P_{CO}$$

$$r_{CO_2} = \frac{k_3 K_1 P_{CO}}{K_2^{1/2} P_{O_2}} \quad \Theta_O \approx 1$$

Which is it? Depends on
catalyst
reaction conditions

Evaluate in the lab

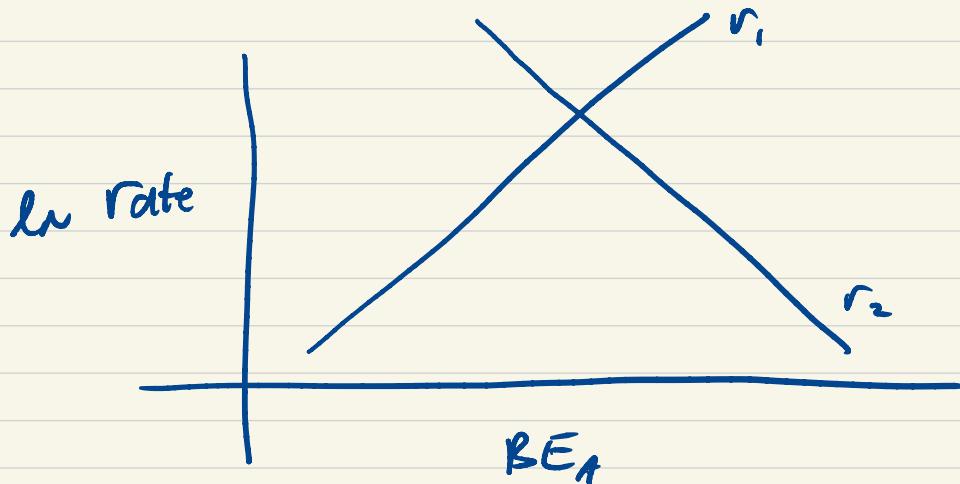
Compute on the computer!!

Example of Hanyu work
 NH_3 oxidation

BEP relations



$$E_{d1} \propto BE_A \quad E_{d2} \propto BE_{A+B} - BE_A$$



"volcano", or Sabatier, plot

Suggests some "optimal" BE_A / optimal material

Long recognized relationship

1) materials

rate normalization

2) ads/desorption, GL
L-H side concept, $\frac{R}{k}$

3) TDD

3) surface reactions

4) L-H mechanism

- pre-equilibrium
- rds

5) scaling

7) structure sensitivity?