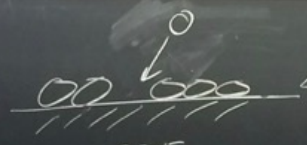
NON CHEMISORPTION

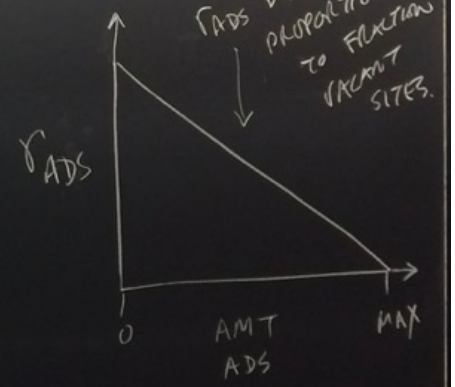
- CAN USE SAME APPARATUS AS BET TO MEASURE # MOLES IN A COMPLETE MONOLAYER



← ONLY ONE MOLECULE ADSORBED PER SURFACE "SITE"

$$A + S \underset{-1}{\overset{1}{\rightleftharpoons}} AS$$

- A: MOLECULE IN FLUID
- S: EMPTY or VACANT SURFACE SITE
- AS: A ABSORBED OVER SURFACE



- WANT TO GET EQN FOR AMT ADS VS CONC OR PRESS OF A @ EQUILIBRIUM

$$r_{ADS} = r_{DES}$$

- USE LANGMUIR MODEL

1) SURFACE COMPOSED OF ARRAY OF IDENTICAL SITES
2) ADS. MOLECULES DISTRIBUTED RANDOMLY OVER SURFACE
3) NO LATERAL (PARALLEL TO SURFACE) INTERACTIONS → ADS & DES k's CONSTANT WITH "COVERAGE"

IRVING LANGMUIR
CIRCA 1920's

RATE OF ADSORPTION IN LANGMUIR MODEL

1) COLLISION RATE, MOL HITTING SURFACE
   DETERMINE FROM "KINETIC THEORY OF GASES"
   e.g., COLLISION RATE = $f(T, P)$

2) FRACTION VACANT SITES → ASSUME ∝ THIS MODEL.

3) PROBABILITY MOLECULE HITTING VACANT SITE WILL ADSORB → "STICKING COEFFICIENT"

$$r_{ADS} = r_{DES}$$

OFTEN k_{ADS}, k_{DES} vs k_1, k_{-1}

$$k_1 P_A [S] = k_{-1} [AS]$$

k_1 = STICKING COEFFIC

ALSO CAN WRITE "SITE BALANCE"
TOTAL # SITES IS CONSTANT

$$[S] + [AS] = [S_{TOTAL}]$$

= AN "ISOTHERM"
BECAUSE T IS CONSTANT

DEFINE FRACTIONAL COVERAGE

$$\theta_A = \frac{[AS]}{[S_{TOTAL}]} \; ; \; \theta_v = \frac{[S]}{[S_{TOTAL}]} \; ; \; \theta_A + \theta_v = 1$$

$$\hookrightarrow \theta_v = (1 - \theta_A)$$

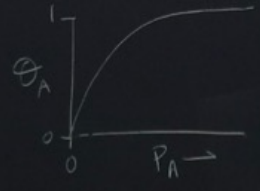
$$k_1 P_A (1 - \theta_A) = k_{-1} \theta_A$$

$$\frac{1 - \theta_A}{\theta_A} = \frac{1}{K_A P_A} \quad \text{WHERE } K_A = \frac{k_1}{k_{-1}} = \frac{k_{ADS}}{k_{DES}}$$

↖ ADS. EQUILIBRIUM CONSTANT FOR A.

ALGEBRA

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A}$$



USE BET APPARATUS BUT NOW USE GAS THAT WILL CHEMISORB (BOND TO) SURFACE, e.g., CO over Pt

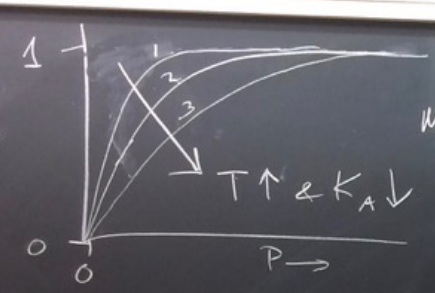
$$\frac{1}{\theta_A} = \frac{n_m}{n} = 1 + \frac{1}{KP}$$

WHERE n = # MOLES A CHEMISORBED
n_m = # MOLES IN MONOLAYER

$$\frac{1}{n} = \left(\frac{1}{n_m}\right) + \left(\frac{1}{n_m K}\right)\frac{1}{P}$$

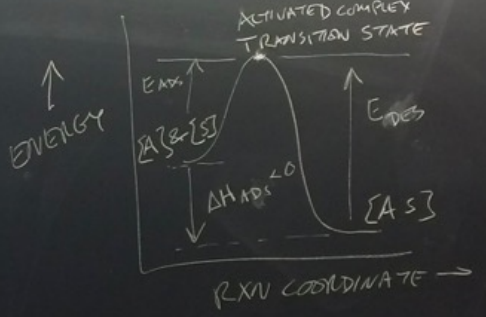
PLOT $\frac{1}{n}$ vs. $\frac{1}{P}$
GET n_m & K_A

$\frac{n}{n_m} = \theta_A$



MOST OFTEN $T_1 < T_2 < T_3$

MOST OFTEN ADS. IS EXOTHERMIC
ADS [AS] AT LOWER ENERGY THAN [A] + [S]



$\Delta H_{ADS} = E_{ADS} - E_{DES}$
↑ ACTIVATION ENERGY

$$\frac{k_{ADS}}{k_{DES}} = \frac{A_{ADS} e^{-E_{ADS}/RT}}{A_{DES} e^{-E_{DES}/RT}}$$

$$K_A = \left(\frac{A_{ADS}}{A_{DES}}\right) e^{-\Delta H_{ADS}/RT}$$

EXCEPTIONS MAY INCLUDE
PROTEIN ADS FROM LIQUID
WITH LARGE CHANGE IN MOLEC.
CONFIGURATION (SHAPE)
& ∴ LARGE CHANGE IN ENTROPY

MEAS. ISOTHERMS @ DIFF. T'S
GET K_A's @ EACH T

$$\ln K = \ln\left(\frac{A_a}{A_d}\right) - \left(\frac{\Delta H}{R_g}\right)\frac{1}{T}$$

→ PLOT ln K vs. $\frac{1}{T}$
& GET ΔH_{ADS}.

- KNOW ASSUMPTIONS IN LANGMUIR MODEL
- BE ABLE TO DERIVE LANGMUIR ISOTHERM EQN
- ANOTHER CASE TO KNOW, ⇝ PREVIOUS CASE, "ASSOCIATIVE ADS." A+S ⇌ AS
  "DISSOCIATIVE ADS"

$A_2 + 2S \underset{-1}{\overset{1}{\rightleftharpoons}} 2\,AS$ ⇝ STILL ASSUME HERE AS DISTRIBUTED RANDOMLY OVER SURFACE, e.g. BY SURFACE DIFFUSION

WANT EQN FOR θ_A vs P_{A_2}

@ EQUIL $r_{ADS} = r_{DES}$

$$k_1 P_{A_2}(1-\theta_A)^2 = k_{-1}\theta_A^2$$

$$\frac{\theta_A^2}{(1-\theta_A)^2} = \frac{1}{K_A P_A}$$

$$\theta_A = \frac{K_A^{1/2} P_A^{1/2}}{1 + K_A^{1/2} P_A^{1/2}}$$

FOR ADS

WANT PROBABILITY THAT A_2 MOLECULE HITS TWO NEIGHBORING VACANT SITES

THAT PROB $\propto \theta_v^2$

FOR DESORPTION

PROB 2 NEIGHBOR A $\propto \theta_A^2$

- ANOTHER CASE TO KNOW

- "COMPETITIVE ADS" → A & B COMPETE FOR SITES.

$$A + S \underset{-1}{\overset{1}{\rightleftharpoons}} AS$$

$$B + S \underset{-2}{\overset{2}{\rightleftharpoons}} BS$$

- SITE BALANCE: $\theta_A + \theta_B + \theta_v = 1$

- @ EQUIL

$$\left.\begin{aligned} k_1 P_A \theta_v &= k_{-1} \theta_A \\ k_2 P_B \theta_v &= k_{-2} \theta_B \end{aligned}\right\} \rightarrow \begin{aligned} \theta_A &= K_A P_A \theta_v \\ \theta_B &= K_B P_B \theta_v \end{aligned}$$

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

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B} \quad \& \quad \theta_B = \frac{K_B P_B}{\text{SAME DENOMINATOR}}$$