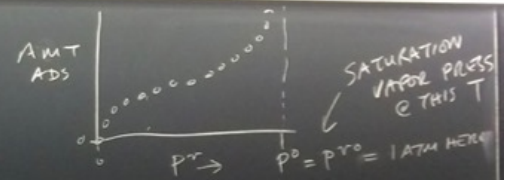


A monolayer is never present in this experiment but we want to determine $n(m)$ mol/g

- PHYSISORPTION OF N_2 VAPOR OVER POROUS SOLID @ 77 K (LIQUID N_2 @ 1 ATM)
- MEASURE AMT. ADS. VS. PRESSURE
- ANALYZE DATA TO GET SURFACE AREA (m^2/g)



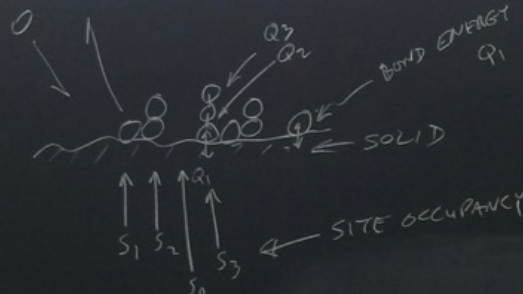
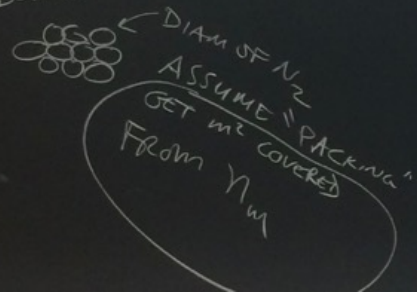
Q_1 A LITTLE STRONGER THAN Q_2, Q_3 etc.
 $Q_2, Q_3, etc \approx$ EQUAL TO $Q_v = \Delta H_{vap}$.

"BET" MODEL \rightarrow "BET METHOD"

- ARRAY OF IDENTICAL SURF. "SITES"
- NO LATERAL (// TO SURF.) INTER-ACTIONS
- $Q_1 > Q_2, Q_3$ etc.
- $Q_2 \approx Q_3 \approx Q_4$ etc = $Q_v = \Delta H_{vap}$.

"MONOLAYER"
 ALL S_1

LOOK DOWN



@ EQUILIBRIUM $r_{ads} = r_{des}$

& DISTRIBUTION OF SITE OCCUPANCY IS CONST.

e.g., # S_0 = CONSTANT, # S_1 = CONSTANT, etc.

for S_1 : $a_1 P S_0 = b_1 e^{-Q_1/RT} S_1$
↑ ADS. RATE CONSTANT $r_{ads} = r_{des}$ ↓ DESORPTION RATE CONST.

for S_2, S_3, S_i : $a_i P S_{i-1} = b_i e^{-Q_i/RT} S_i$

$\frac{S_i}{S_{i-1}} = P \left(\frac{a_i}{b_i} \right) e^{Q_i/RT}$

VAPOR OVER SURFACE OF ITS OWN LIQUID

$a_i P^0 = b_i e^{-Q_i/RT}$

$\frac{1}{P^0} = \left(\frac{a_i}{b_i} \right) e^{Q_i/RT} \Rightarrow \frac{P}{P^0} = P \left(\frac{a_i}{b_i} \right) e^{Q_i/RT}$

DEFINE $X \equiv \frac{\dot{P}}{P^0} = P \left(\frac{a_i}{b_i} \right) e^{Q_i/RT} = \frac{S_i}{S_{i-1}}$ for $i \geq 2$

$Y \equiv P \left(\frac{a_1}{b_1} \right) e^{Q_1/RT} = \frac{S_1}{S_0}$

$C = \frac{Y}{X} \approx e^{(Q_1 - Q_r)/RT}$, SINCE $\left(\frac{a_i}{b_i} \right) \approx \left(\frac{a_1}{b_1} \right)$
↑ ASSUME

- FROM SUMMATION OF $S_0 + S_1 + S_2 + \dots$ WE GET # MOLES ADSORBED @ P = η
- FROM TOTAL # SURFACE SITES GET $\eta_m =$ # MOLES ADS IN HYPOTHETICAL "MONOLAYER"
- SOME ALGEBRA ...

$\frac{X}{\eta(1-X)} = \frac{1}{C \eta_m} + \left(\frac{C-1}{C \eta_m} \right) X \Rightarrow$ DO EXPERIMENTS MEAS η vs. P

$X = \frac{P}{P^0}$

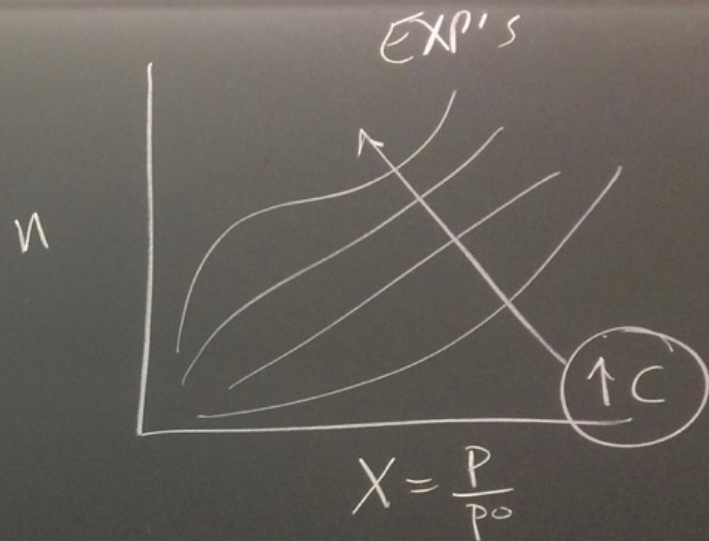
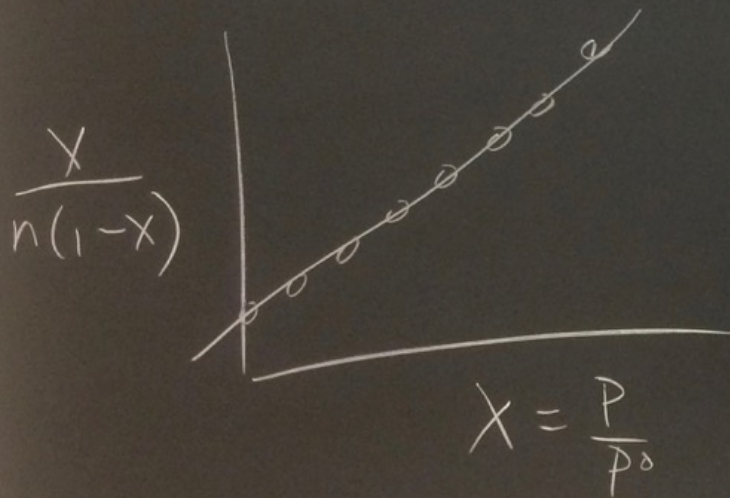
GO HAVE TABLE OF X & η VALUES

PLOT $\frac{X}{n(1-X)}$ vs. X

$$\text{INTERCEPT} = \frac{1}{c n_m}$$

$$\text{SLOPE} = \left(\frac{c-1}{c n_m} \right)$$

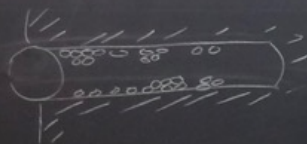
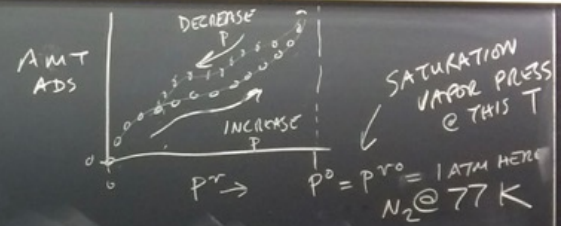
ALGEBRA \rightarrow GET c & n_m VALUES



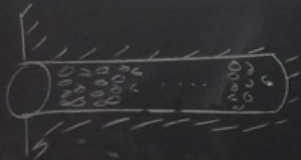
- NOW SLOWLY DECREASE P & MEASURE HOW MUCH IS ADSORBED @ EACH P

- HYSTERESIS \rightarrow WHY? \rightarrow HAVE MORE ADS @ SAME P

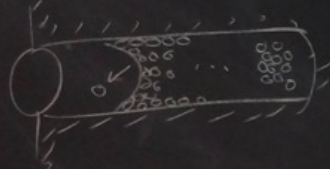
- CONSIDER POROUS SOLID MODELED AS HAVING CYLINDRICAL PORES OF DIFF. SIZES



\leftarrow PICTURE AS WE $\uparrow P$ & MEAS AMT ADS



\leftarrow PICTURE NEAR $X = \frac{P}{P^0} = 1$ PORE FILLED WITH LIQUID N_2

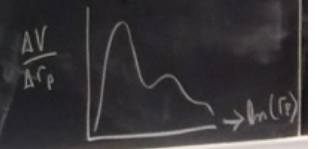


\leftarrow AS P IS \downarrow WE GET PORE EMPTYING AS N_2 VAPOR DESORBS FROM CURVED LIQUID SURF. OR 'MENISCUS'

\rightarrow IF CAN MEASURE, THEN GET # MOLE & (LIQUID) PORE VOLUME IN MAT'L FOR PORES THIS SIZE

WHY? USE TO ESTIMATE DIFFUSION COEFF IN POROUS MAT'L

ANALYZE DATA TO GET PORE VOLUME VS. PORE RADIUS DISTRIBUTION



@ EQUIL

$\overline{\Delta G}^v = \overline{\Delta G}^l$

PARTIAL MOLAR GIBBS FREE ENERGY OF VAPOR & LIQ EQUAL.

WORK TO CREATE A CURVED SURFACE

$\Delta P = \frac{2\gamma}{r}$ ← "SURFACE TENSION"

← RADIUS OF CURVED SURFACE

← DIFF. IN P ACROSS CURVED SURF.

EQUATION OF YOUNG & LAPLACE

- FOR LIQUIDS, $\overline{\Delta G}^l = \overline{V}^l \Delta P = \frac{2\gamma V^l}{r}$

- FOR VAPOR - MODEL AS IDEAL GAS

$\overline{\Delta G}^v = \int_{p_0}^p V^v dp = \int \left(\frac{RT}{P}\right) dp = RT \ln\left(\frac{P}{P_0}\right)$

← VAPOR PRESS OF LIQ. WITH CURVED SURF.

← STAB. V.P. OVER FLAT LIQ. SURFACE

COMBINE - KELVIN EQN

$-RT \ln\left(\frac{P}{P_0}\right) = \frac{2\gamma V^l}{-r_m} = \frac{2\gamma \overline{V}^v r}{r_{pore}}$

$P < P_0$

← RADIUS OF MENISCUS

$r_m < 0$ FOR LIQ. THAT "WETS" PORE WALLS

← "CONTACT ANGLE"

← PORE RADIUS

FOR LIQUID N_2 IN MOST POREOUS MAT'L

$\theta \approx 0^\circ ; \therefore \cos\theta = 1$

$-r_m = r_{pore}$

FOR N_2 @ 77 K

@ $\frac{P}{P_0} = 0.5$ $r_{pore} = 1.4$ nm

SOLVE FOR r_{pore} FROM (P/P_0)

← Δ AMT ADS

← Δ AMT → VOL. OF PORES THIS SIZE

ALSO READ notes at ReactorLab.net, Resources, Grad CRE Notes, Adsorption and Pore size distribution