

Equation of State of Adsorbed Film

- Apply Gibbs Eq. to adsorbed film

$$d\gamma = -\Gamma RT d \ln a_2$$

$$d\gamma = -\Gamma RT d \ln P$$

$$\int_{\gamma_s}^{\gamma_{sv}} d\gamma = -RT \int_0^P \Gamma d \ln P$$

γ_s = surface tension of solid

γ_{sv} = surface tension of solid with adsorbed gas

$$\gamma_{sv} - \gamma_s = -\pi = -RT \int_0^P \Gamma d \ln P$$

$$d\pi = RT \Gamma d \ln P$$

$$\Gamma = \frac{1}{\sigma N_{av}} \quad \sigma d\pi = kT d \ln p$$

$$\text{or } \ln P = \frac{1}{kT} \int \sigma d\pi$$

"Ideal Gas"

$$\pi \sigma = kT \quad \pi = \frac{kT}{\sigma} \quad d\pi = -\frac{kT}{\sigma^2} d\sigma$$

$$\ln P = - \int \frac{d\sigma}{\sigma} = -\ln \sigma + \text{const.}$$

$$P = \frac{k'}{\sigma}$$

$$\theta = \frac{\sigma_0}{\sigma}$$

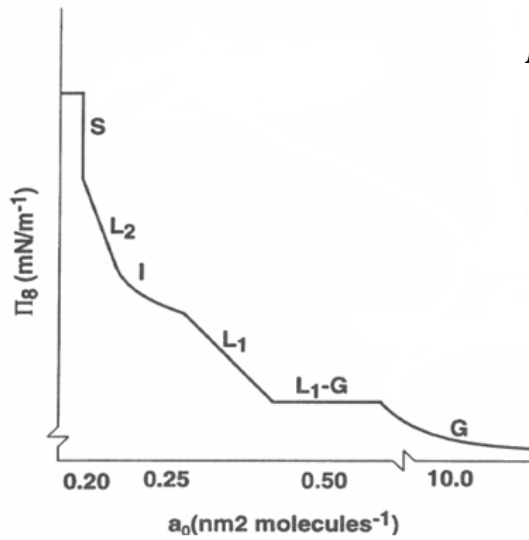
$$\sigma = \frac{\sigma_0}{\theta}$$

$$\theta = k'' P$$

$$\frac{\frac{\text{area}}{\text{molecule}} \text{ in monolayer}}{\frac{\text{area}}{\text{adsorbed molecule}}}$$

Linear Isotherm

but extremely difficult to observe



Liquid Films

$$\pi = b - a\sigma$$

$$d\pi = -a d\sigma$$

$$\sigma d\pi = kT d \ln p$$

$$\frac{kT d \ln P}{\sigma} = -a d\sigma$$

$$kT d \ln P = -a\sigma d\sigma$$

$$\ln P = c - \frac{a\sigma^2}{2kT}$$

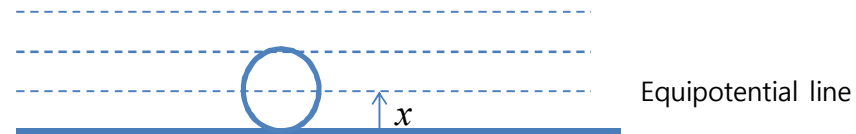
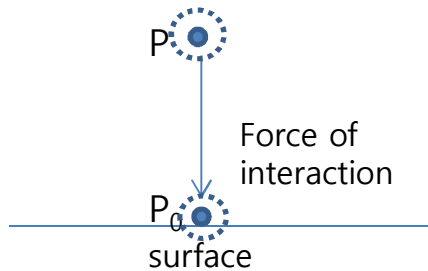
$$\sigma = \frac{S_m m}{v/v_0 N_{av}}$$

$$\ln \frac{P}{P_0} = B - \frac{a}{2kT} \frac{(v_0 S_m m)^2}{(N_{av})^2} \frac{1}{v^2}$$

Harkins – Jura Eq.

Plot $\frac{P}{P_0}$ vs $\frac{1}{v^2} \rightarrow$ straight line

Potential Theory (Polani 1914)



Work done to bring the gas molecule to the surface:

$$P - V \text{ Work} = \int_P^{P_0} v dP = \int_P^{P_0} \frac{RT}{P} dP = RT \ln\left(\frac{P_0}{P}\right)$$

Assume potential arises from van der Waals force

$$\epsilon(x) = \int_{\infty}^x F dx = \frac{\epsilon_0}{(a+x)^3}$$

$$RT \ln\left(\frac{P_0}{P}\right) = \frac{\epsilon_0}{(a+x)^3}$$

$$x = -a + \left(\frac{RT \ln(P_0/P)}{\epsilon_0}\right)^{-1/3}$$

$$\text{No. of moles of adsorbed gas} = \frac{v}{v_0} \quad v_0 = \text{molar vol. of gas}$$

$$\text{volume of adsorbed gas (assumed to liquified)} = \frac{v}{v_0} v_l \quad v_l = \text{molar vol. of liquified gas}$$

$$= x \times \text{area} = x \times S_m m \quad m = \text{mass of the solid}$$

$$\frac{v}{v_0} v_l = S_m m \left(-a + \left(\frac{RT \ln(P_0/P)}{\epsilon_0}\right)^{-1/3} \right)$$

$$v = \beta \ln(P_0/P)^{-1/3} - \alpha$$

$$\beta = \frac{S_m m v_0}{v_l} \left(\frac{\epsilon_0}{RT}\right)^{1/3} \quad \alpha = \frac{a S_m m v_0}{v_l}$$

Dubinin-Kaganer-Radushkevich (DKR) Isotherm

- Empirical expression for $\epsilon(x)$

$$x = x_m e^{-b\epsilon^2} \quad x = \text{layer thickness}, \quad x_m = \text{monolayer thickness}$$

$$\epsilon(x) = \left(\frac{1}{b} \ln \frac{x_m}{x} \right)^{\frac{1}{2}} = RT \ln \frac{P_0}{P}$$

$$\ln \frac{x}{x_m} = -B' \left(\ln \frac{P_0}{P} \right)^2 \quad B' = \text{const.}$$

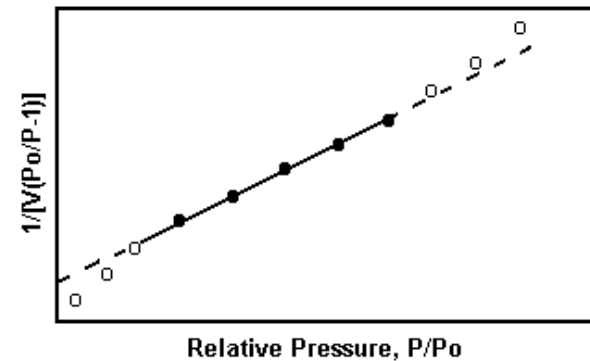
$$\ln \frac{v}{v_m} = -B' \left(\ln \frac{P_0}{P} \right)^2$$

Range of Applicability of Models

- BET: $0.05 < P/P_0 < 0.3$
- H & J: $0.04 < P/P_0 < 0.7$
- Polani: $0.1 < P/P_0 < 0.8$
- DKR: < 0.02

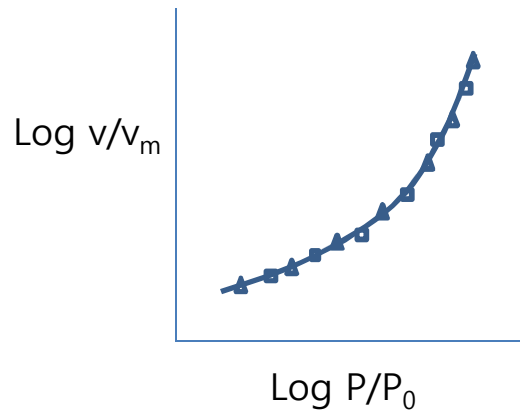
BET

- Never use data points too low in relative pressure (P/P_0).
- Never use data points too high in (P/P_0).



Thickness Theory

- Characteristic Isotherm



One curve for all solids for a given gas

t-Plot technique (de Boer)

$$\frac{v}{v_m} = \text{no. of monolayer on surface}$$

Film thickness t fixed for fixed $\frac{p}{p_0}$

$$\frac{v}{v_m} = \frac{t}{t_1} \quad t_1: \text{monolayer thickness}$$

$$v_m = \frac{v_0 A_T}{N_{av} \sigma_0} \quad A_T: \text{total surface area } (= S_m m)$$

$$v = \frac{v_m}{t_1} t = \frac{v_0 A_T \cdot t}{N_{av} \sigma_0 t_1} \rightarrow \frac{\text{vol}}{\text{mol}} = \text{molar vol. of the film}$$

i.e., liquid

$$v = \frac{v_0(g)}{v_0(l)} A_T \cdot t$$

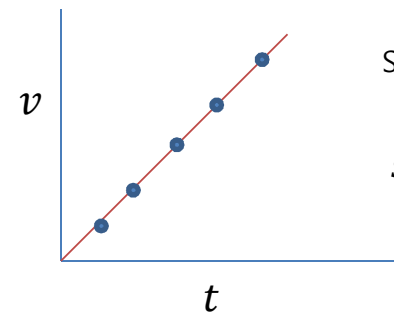
Standard t-values

- N₂ at 78K

P/P ₀	t (Å)
0.1	3.68
0.2	4.36
0.4	5.71
0.6	7.36
0.8	10.57
0.9	14.94

Procedure

- 1) Measure v vs P/P_0
- 2) Obtain t value for P/P_0 each from table
- 3) Plot v vs t



Straight line through origin

$$\text{slope} = \frac{v_0(g)}{v_0(l)} A_T$$

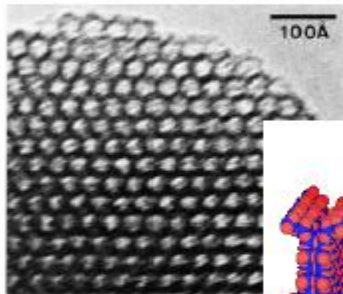
For N₂ at 78 K

$$\text{slope} = 0.0646 A_T \quad \begin{array}{l} \text{for } v \text{ in cm}^3 \\ t \text{ in } \text{Å} \\ A_T \text{ in m}^2 \end{array}$$

Capillary condensation

Capillary condensation

Phenomenon whereby a gas condenses to a liquid-like phase in a pore at a pressure p less than saturation pressure p_0 of the bulk liquid



MCM-41

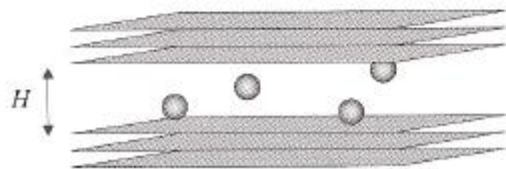
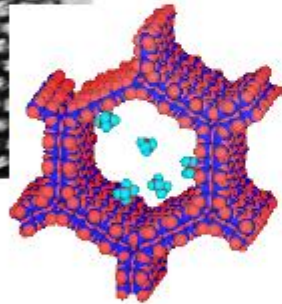
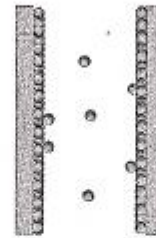
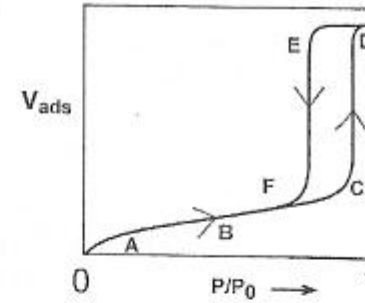
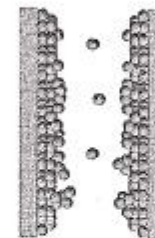


Fig. 3. The slit pore model. Each layer represents a graphene layer.



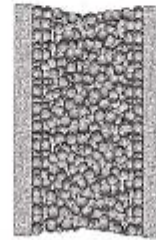
A Monolayer formation



B Multilayer adsorption



C Critical film thickness reached



D Capillary condensation



E Pore evaporation



F multilayer film

The wider the pore size distribution the less sharper is the pore condensation step

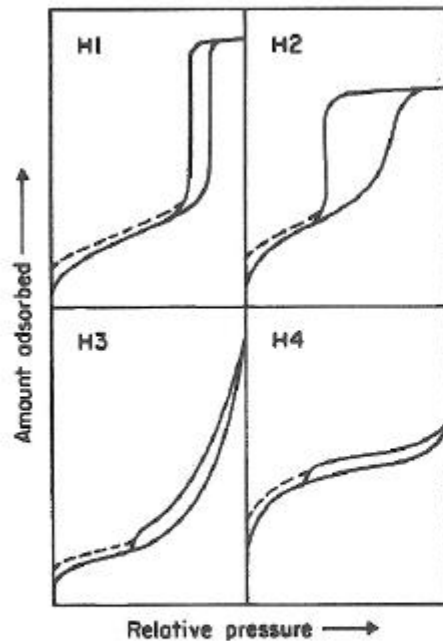


Fig. 3. Types of hysteresis loops

H1 well defined cylindrical pore channels

H2 disordered pores
(pore blocking, percolation phenomena)

H3 non-rigid aggregates of plate-like particles
(slit-shaped pores)

H4 narrow slit pores including pores in the
micropore region

Low pressure hysteresis

no accurate pore size analysis possible!

- Changes in the volume of the adsorbent
 - Swelling of non-rigid pores
- Irreversible uptake of molecules in the pores
- Chemisorption

Kelvin Equation

The relative pressure where the pore condensation occurs depends on the pore radius

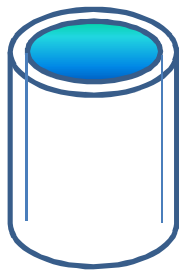
The Kelvin equation provides a correlation between pore diameter and pore condensation pressure

Assumptions

- Pores of cylindrical shape
- No fluid-wall interactions

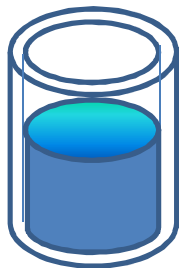
$$\ln \frac{p}{p_0} = \frac{-2\gamma V_l}{r_p RT}$$

γ surface tension of liquid nitrogen
 V_l liquid molar volume
 r_p pore radius
 r_k critical radius
 R universal gas constant
 t statistical thickness



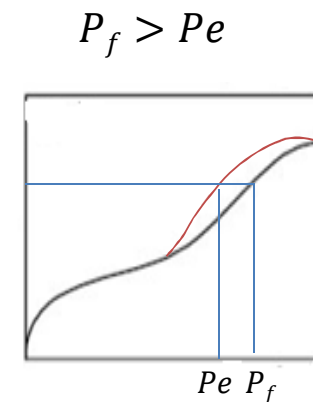
Filling of pores occurs at cylindrical surface

$$\ln \left(\frac{P_f}{P_0} \right) = \frac{-\gamma V_l}{r_p RT}$$

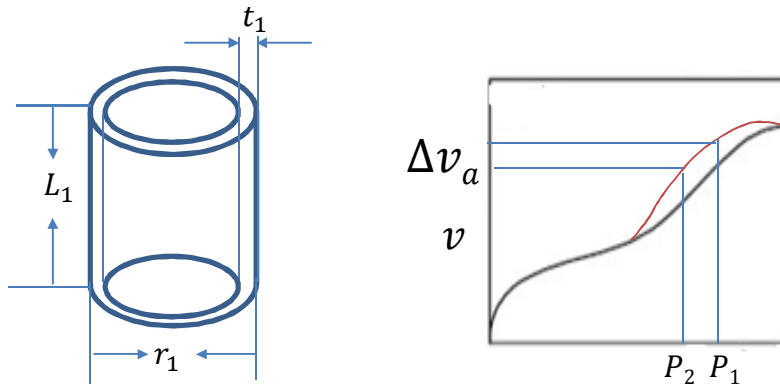


Emptying occurs at spherical meniscus

$$\ln \left(\frac{P_e}{P_0} \right) = \frac{-2\gamma V_l}{r_p RT}$$



Estimation of Pore Size Distribution



at pressure P_1 : $\ln\left(\frac{P_1}{P_0}\right) = \frac{-2\gamma V_l}{(r_1 - t_1)RT}$

at pressure P_2 : $\ln\left(\frac{P_2}{P_0}\right) = \frac{-2\gamma V_l}{(r_2 - t_2)RT}$

Δv_a = vol of gas desorbed between P_1 and P_2

Pore volume corresponds to

$$\Delta v_c = \Delta v_a \frac{v_0(l)}{v_0(g)}$$

now $\Delta v_c = \pi(r_{1-2} - t_{1-2})^2 L_{1-2}$

$$r_{1-2} = \text{mean pore radius} = \frac{r_1 + r_2}{2}$$

$$t_{1-2} = \text{mean film thickness} = \frac{t_1 + t_2}{2}$$

$$L_{1-2} = \text{total pore length in that range} = \frac{L_1 + L_2}{2}$$

But $\Delta v_{1-2} = \pi(r_{1-2})^2 L_{1-2}$

$$\therefore \Delta v_{1-2} = \left(\frac{r_{1-2}}{r_{1-2} - t_{1-2}}\right)^2 \Delta v_c$$

$$\Delta v_{1-2} = \left(\frac{r_{1-2}}{r_{1-2} - t_{1-2}}\right)^2 \frac{v_0(l)}{v_0(g)} \Delta v_a$$

Procedure

1. Measure Δv_a between P1 and P2 on desorption curve
2. Estimate t_1 and t_2 from de Boer techniques
3. Calculate r_1 and r_2 from Kelvin equation
4. Calculate pore volume between r_1 and r_2 ($= \Delta v_{1-2}$)
5. Pore size distribution

$$\frac{\Delta v_{1-2}}{\sum v_{1-2}}$$

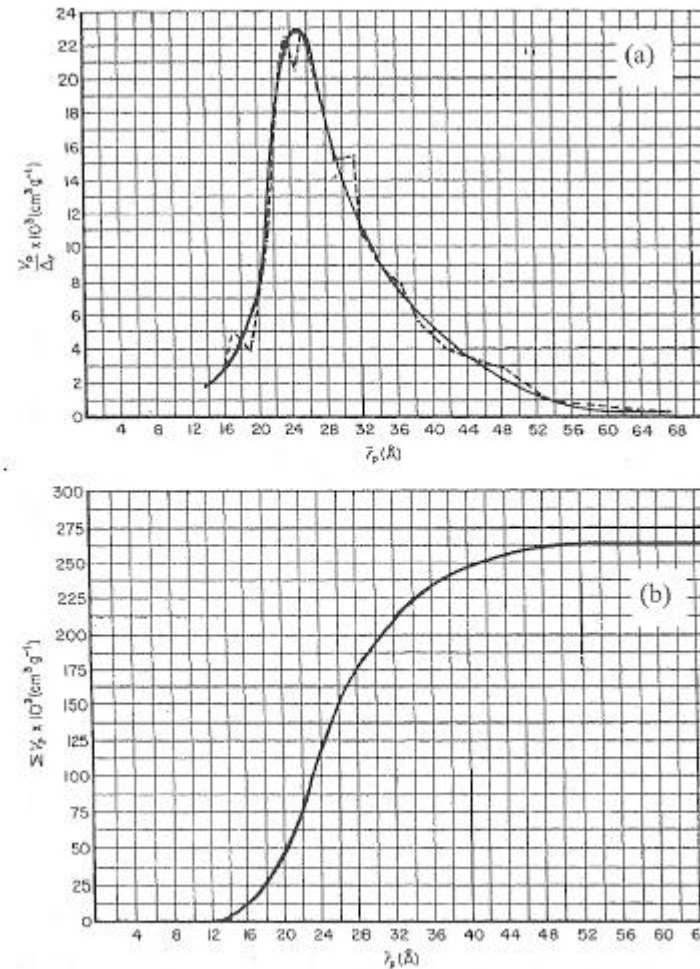
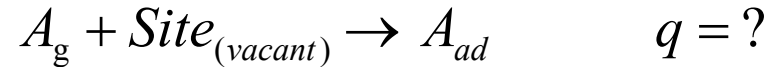


Figure 8.1 (a) Pore size distribution curve from table 8.1. Raw data: -----; smoothed data: —————; (b) Cumulative pore volume plot from table 8.1.

Heat of Adsorption



If dn_s moles of gas transferred to surface giving an amount dQ of heat

$$q = \frac{dQ}{dn_s} = \text{differential heat}$$

$$\text{or } Q = \frac{1}{n_s} \int_0^{n_s} q dn_s = \text{Integral heat}$$

$$\text{if } q \neq f(n_s) \quad Q = q$$

If the adsorbent and the enclosed vessel is inert and $T = \text{const.}$

$$dQ = dU + PdV + \gamma dA$$

where $U = U_g + U_s$ g : bulk gas, s : surface

$$V = V_g + V_s$$

If total volume and solid surface area are constant

$$dQ_{V,A,T} = dU_g + dU_s$$

$$\frac{dQ_{V,A,T}}{dn_s} = \frac{dU_g}{dn_s} + \frac{dU_s}{dn_s}$$

$$\begin{aligned} q_{V,A,T} &= - \left(\frac{\partial U_g}{\partial n_g} \right)_{V,A,T} + \left(\frac{\partial U_s}{\partial n_s} \right)_{V,A,T} \quad (dn_s = -dn_g) \\ &= -\bar{E}_g + \left(\frac{\partial U_s}{\partial n_s} \right)_{V,A,T} \\ &= q_d \end{aligned}$$

$q_d = q_{V,A,T} = \text{differential calorimetric heat of adsorption}$

$$\text{Integral Heat } Q_d = \frac{1}{n_s} \int_0^{n_s} q_d dn_s$$

$$dQ_{P,A,T} = dU_g + dU_s + PdV_g + PdV_s$$

$$\text{But } dU_s = TdS_s - PdV_s + \mu_s dn_s$$

$$\begin{aligned} dQ_{P,A,T} &= d(U_g + PV_g) + TdS_s + \mu_s dn_s \\ &= dH_g + TdS_s + \mu_s dn_s \end{aligned}$$

$$\text{at equilibrium } \mu_g = \mu_s = \left(\frac{\partial G_g}{\partial n_g} \right) = \bar{G}_g = \bar{H}_g - T\bar{S}_g$$

$$dH_g = \left(\frac{\partial H_g}{\partial n_g} \right) dn_g = \bar{H}_g dn_g = -\bar{H}_g dn_s$$

$$dS_s = \bar{S}_s dn_s$$

$$\begin{aligned} dQ_{P,A,T} &= -\bar{H}_g dn_s + TdS_s + \bar{H}_g dn_s - T\bar{S}_g dn_s \\ &= T(\bar{S}_s - \bar{S}_g) dn_s \end{aligned}$$

$$\begin{aligned} dq_{P,A,T} &= T(\bar{S}_s - \bar{S}_g) \\ &= dq_{ST} \quad \text{isotheric heat of adsorption} \end{aligned}$$

$$dG_s = -S_s dT + V_s dP + \gamma dA + \mu_s dn_s$$

$$d\mu_s = -\bar{S}_s dT + \bar{V}_s dP + \left(\frac{\partial \gamma}{\partial n_s}\right) dA + \left(\frac{\partial \mu_s}{\partial n_s}\right) dn_s$$

const. n_s and A $d\mu_s = -\bar{S}_s dT + \bar{V}_s dP$

also $d\mu_g = -\bar{S}_g dT + \bar{V}_g dP$

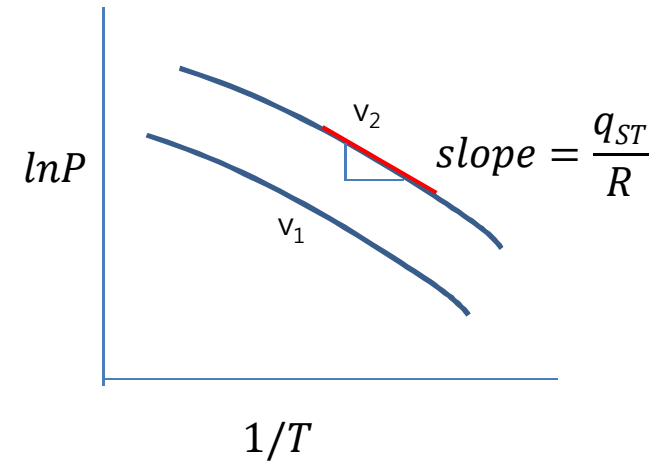
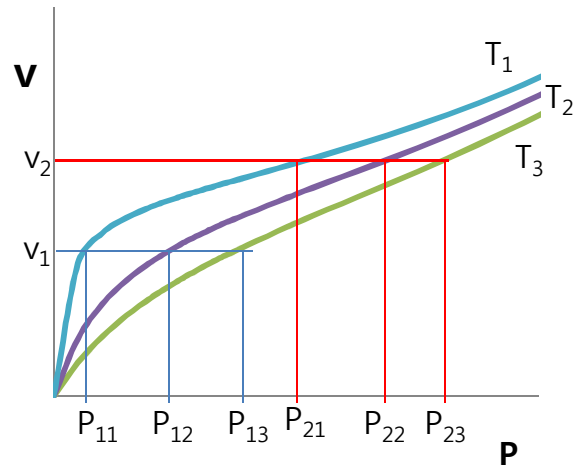
at equil. $d\mu_s = d\mu_g$

$$\therefore dP = \left(\frac{\bar{S}_g - \bar{S}_s}{\bar{V}_g - \bar{V}_s}\right) dT$$

If $\bar{V}_g \gg \bar{V}_s$ and since $P\bar{V}_g = RT$

$$\left(\frac{\partial \ln P}{\partial T}\right) = \frac{\bar{S}_g - \bar{S}_s}{RT} = -\frac{q_{ST}}{RT^2} \quad \text{or} \quad \left(\frac{\partial \ln P}{\partial \left(\frac{1}{T}\right)}\right)_{n_s, A} = \frac{q_{ST}}{R}$$

\therefore Plot of $\ln P$ vs $\frac{1}{T}$ at fixed n_s and A should have slope $\frac{q_{ST}}{R}$



Relationship between q_d and q_{ST}

$$dQ_{P,A,T} = dU_g + dU_s + PdV_g + PdV_s = q_{ST}dn_s$$

$$dQ_{V,A,T} = dU_g + dU_s = q_d dn_s$$

$$\therefore q_{ST}dn_s = q_d dn_s + PdV_g + PdV_s$$

If gas is ideal and $V_g \gg V_s$ $PV_g = ngRT$

at const. T and P , $PdV_g = RTdn_g = -RTn_s$

Thus, $q_{ST} = q_d - RT$

Heterogeneous Surfaces

- Suppose adsorption sites have distribution of energy such that

$f(E)dE =$ fraction of sites which have energy E to $E + dE$

if sites act independently

Should get equilibrium adsorption each level

$$d\theta = \theta'(E, P, T)f(E)dE$$

$\theta' =$ adsorption equation, eg. Langmuir

$$\theta = \int_0^{\infty} \theta'(E, P, T)f(E)dE$$

$$\text{if } \theta' = \frac{K(E)P}{1 + K(E)P}$$

$K(E) = K_0 e^{E/RT}$: Arrhenius

$f(E) = \alpha e^{-E/RT}$: Boltzman

Result is

$\theta = aP^{1/n}$ *Fruendlich Isotherm*

