We have arrived isotherm equations which describe adsorption from the two dimensional equation of state via the Gibbs equation (with a saturation limit usually associated with monolayer coverage).

The thermodynamics associated with multilayer condensation will be discussed later.

Now, we transfer our attention to the kinetic approach.

3.5. Kinetic Approach for Isotherms

◆ **A kinetic approach is introduced, and the multilayer adsorption will be taken into account.**

◆ **The derivation assumes that the rates of adsorption and desorption are equal at equilibrium.**

➔ **consider monolayer**

adsorption rate $\propto$ (pressure) × (no. of available sites)

$$R_a = k_a \times P \times S_0$$

desorption rate $\propto$ (no. of sites occupied)

$$R_{d,1} = k_{d,1} \times S_1$$

At equilibrium:

$$k_a \times P \times S_0 = k_{d,1} \times S_1 \quad \ldots\ldots\ldots\ldots\ldots (3)$$

For monolayer adsorption $S_0 + S_1 = S$ substitute into (3)

$$\frac{k_a}{k_d}P = \frac{S_1}{S\text{-}S_1} = \frac{S_1/S}{1-S_1/S} = \frac{\theta}{1-\theta}$$

$k_{d,1} \propto$ (frequency factor) × (Boltzmann factor) $\propto \nu\exp(\frac{-\varepsilon}{kT})$

(per molecule $\frac{\varepsilon}{kT}$ = $\frac{E}{RT}$ per mole)

From kinetic molecular theory

➔ **no. of collisions per unit area per unit time between gas and surface $= Z = (2\pi mkT)^{-1/2}P$** **m: molecular mass**

$$R_a = k_a P S_0 \propto S_0 \sigma^0 Z$$

$$\therefore k_a \propto (2\pi mkT)^{-1/2}\sigma^0$$

Let $K = \frac{k_a}{k_{d,1}} \propto (2\pi mkT)^{-1/2}\frac{\sigma^0}{\nu}\exp(\frac{\varepsilon}{kT})$ **= Langmuir constant**

$$KP = \frac{\theta}{1-\theta} \Rightarrow \theta = \frac{KP}{1+KP}$$

$$\frac{N_A \sigma^0 n}{A_{sp} W} = \theta = \frac{KP}{1+KP}$$

When $\theta = 1$, $(\frac{n}{W})_{sat} = \frac{A_{sp}}{N_A \sigma^0} = \frac{1}{m} \rightarrow \frac{n}{W} = \frac{(K/m)P}{1+KP}$

Let $\frac{p}{n/W} = mp+b$

$$\frac{p}{n/W} = mp+b$$

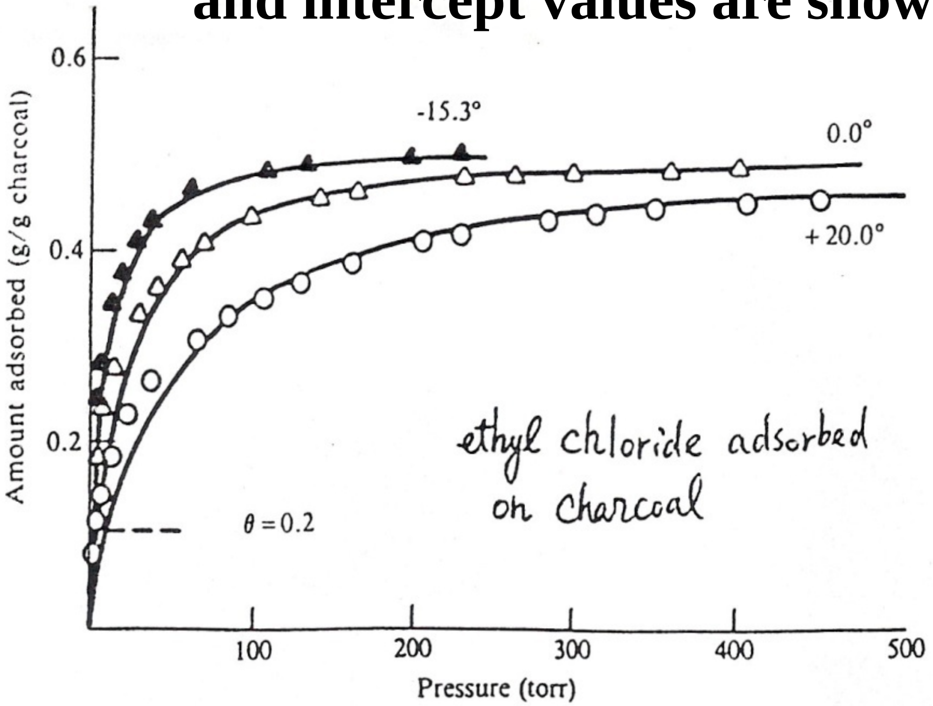
$$\frac{p}{Mn/W} = \frac{m}{M}p + \frac{b}{M}$$

Langmuir equation another form based on q (= $\frac{nM}{w}$)

$$\frac{p}{q} = m'p + b' \quad , \quad \frac{m'}{b'} = K$$

Note for ε: The adsorption sites bind the adsorbate with an energy ε per molecule. This adsorption energy is a characteristic property between the adsorbate and adsorbent. That is, the potential energy of a molecule in the gaseous state is zero, and in the adsorbed state is –ε.

EX. The $\frac{p}{q}$ vs. p plots of data in the figure were made, and the slope and intercept values are shown:



Temp (°C)	Slope (g/g)	Intercept (g/g)torr
-15.3	1.9	40
0	2.0	47
20	2.0	88

a. Do the amounts of adsorption at these temperatures reach similar saturation levels?

b. Find the adsorption energy.

[hint: $\ln(KT^{1/2}) = \text{const.} + \frac{\varepsilon}{k}\frac{1}{T} = \text{const.} + \frac{E}{R}\frac{1}{T}$]

Sol.

EX.

Assume two gases A and B individually follow the Langmuir isotherm. Derive an expression for the fraction of surface sites covered by one of the species at equilibrium.

Solution:

$$R_{a,A} = k_{a,A}P_AS_0 = k_{a,A}P_A(S - S_A - S_B)$$

$$R_{d,A} = k_{d,A}S_A$$

$$\rightarrow k_{d,A}S_A = k_{a,A}P_A(S - S_A - S_B)$$

$$\rightarrow \theta_A = K_AP_A(1 - \theta_A - \theta_B) \text{ .... (4)}$$

Similarly => $\theta_B = K_BP_B(1 - \theta_A - \theta_B)$

$$\frac{\theta_A}{\theta_B} = \frac{K_AP_A}{K_BP_B} \rightarrow \theta_B = \frac{K_BP_B}{K_AP_A}\theta_A \quad \text{substitute into (4)}$$

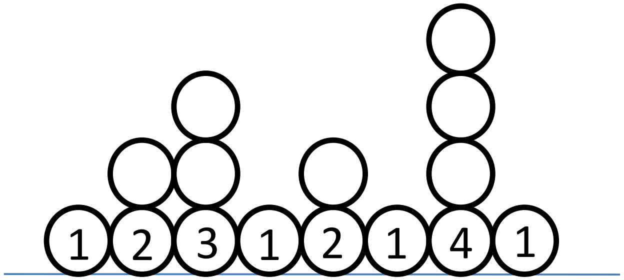
$$\rightarrow \theta_A = \frac{K_AP_A}{1 + K_AP_A + K_BP_B} \quad \text{also, } \theta_B = \frac{K_BP_B}{1 + K_AP_A + K_BP_B}$$

∴ coverage would depend on the partial pressure and the Langmuir constant <u>for each species</u> (competition)

3.6 Multilayer Adsorption: The BET Equation

a surface site may be covered to a depth of more than one molecule

$S = S_0 + S_1 + S_2 + \ldots\ldots = \sum_{i=1}^{n} S_n$ **S_i: no. of sites covered by *i* molecules**



$S_1 = 4 \,,\, S_2 = 2 \,,\, S_3 = 1 \,,\, S_4 = 1$

Consider the composition of the second layer (*i* = 2)

$$R_{a,2} = k_a P S_1$$

$$R_{d,2} = k_{d,2} S_2$$

$$\rightarrow k_a P S_1 = k_{d,2} S_2$$

similarly for 3rd, 4th,….. levels

$$k_a P S_{i-1} = k_{d,i} S_i \quad \text{for } 2 \le i \le n$$

$$k_a P S_1 = k_{d,2} S_2$$

$$k_a P S_2 = k_{d,3} S_3$$

$$\cdot$$

$$\cdot$$

$$k_a P S_{i-1} = k_{d,i} S_i$$

$$\rightarrow S_i = \left(\frac{k_a}{k_{d,i}}\right)^{i-1} P^{i-1} S_1$$

$k_{d,2}$: $\nu \exp\left(-\frac{\varepsilon_v}{kT}\right)$

ε_v = energy of vaporization

also $k_aPS_0 = k_{d,1}S_1$

$$\therefore\ S_i = \left(\frac{k_a}{k_{d,i}}\right)^{i-1}\left(\frac{k_a}{k_{d,1}}\right)P^iS_0$$

No. of sites covered by *i* layers

$$S_i = \frac{k_a^i P^i S_0}{\nu^i\left[\exp\left(\frac{-\varepsilon_\nu}{kT}\right)\right]^{i-1}\exp\left(\frac{-\varepsilon}{kT}\right)}$$

$$= \frac{k_a^i P^i S_0}{\nu^i\left[\exp\left(\frac{-\varepsilon_\nu}{kT}\right)\right]^{i}}\ \frac{\exp\left(\frac{-\varepsilon_\nu}{kT}\right)}{\exp\left(\frac{-\varepsilon}{kT}\right)}$$

➔ $S_i = x^i c S_0$

where $x = \dfrac{k_aP}{\nu\exp\left(\frac{-\varepsilon_\nu}{kT}\right)} = \dfrac{k_a}{k_{d,i\geq 2}}P$

$$c = \exp\left(\frac{\varepsilon-\varepsilon_\nu}{kT}\right)$$

$$S = S_0 + S_1 + S_2 + \ldots = S_0 + \sum_{i=1}^{n} x^iCS_0$$

n → ∞ as P → P_0 the upper limit

We are interested in the total volume adsorbed (V, measurable) and the volume adsorbed at monolayer coverage (V_m, what we need)

→ Total vol. of gas adsorbed

$$= V = \sum_i^n V_i \propto \sum_{i=1}^n iS_i$$

→ The vol. adsorbed at monolayer coverage

$$= V_m \propto S = S_0 + \sum_{i=1}^n S_i$$

$$\frac{V}{V_m} = \frac{\sum iS_i}{S_0+\sum S_i} = \frac{c\sum ix^i}{1+c\sum x^i} \quad \ldots\ldots\ldots(1)$$

To assist in evaluation of the summation

→ **consider** $\frac{x}{1-x} = x(1+x+x^2+\ldots) = \sum_{i=1}^{n} x^i$ **……(2)**

$x\frac{d}{dx}\sum x^i = x\sum ix^{i-1} = \sum ix^i$ **…………(3)**

substitute (2) and (3) into (1)

$$\frac{V}{V_m} = \frac{cx}{(1-x)\left[1+(c-1)x\right]}$$

and as p → p_0 => V → ∞ **(upper limit)**

i.e., x→1

∴ **x =** $\frac{k_a}{k_{d,i=2}}P$.....(a)

→ **1 =** $\frac{k_a}{k_{d,i=2}}P_0$.....(b)

Therefore $\left(\frac{(a)}{(b)}\right)$ → **x =** $\frac{P}{P_0}$ **= relative pressure**

BET equation: $$\frac{V}{V_m} = \frac{cx}{(1-x)\left[1+(c\text{-}1)x\right]}$$

(V = f ($\frac{P}{P_0}$) , V_m and c are the parameters)

◆ **BET equation describes the volume of gas adsorbed at different values of P/P_0 in terms of two parameters V_m and c**.

3.7. Testing the BET equation

BET equation $\xrightarrow{\text{rearrage}} \frac{1}{V}\frac{x}{1-x} = \frac{c-1}{cV_m}x + \frac{1}{cV_m}$

yield a straight line

ordinate (y-axis) **abscissa (x-axis)**

slope = m = $\frac{c-1}{cV_m}$ **intercept = b =** $\frac{1}{cV_m}$ $V_m = \frac{1}{m+b}$ $c = \frac{m}{b}+1$

◆ **In the following, we shall examine the features of gas adsorption as predicted by the BET theory**.

◆ Discussion on Fig. A (showing general features of BET with different c values)

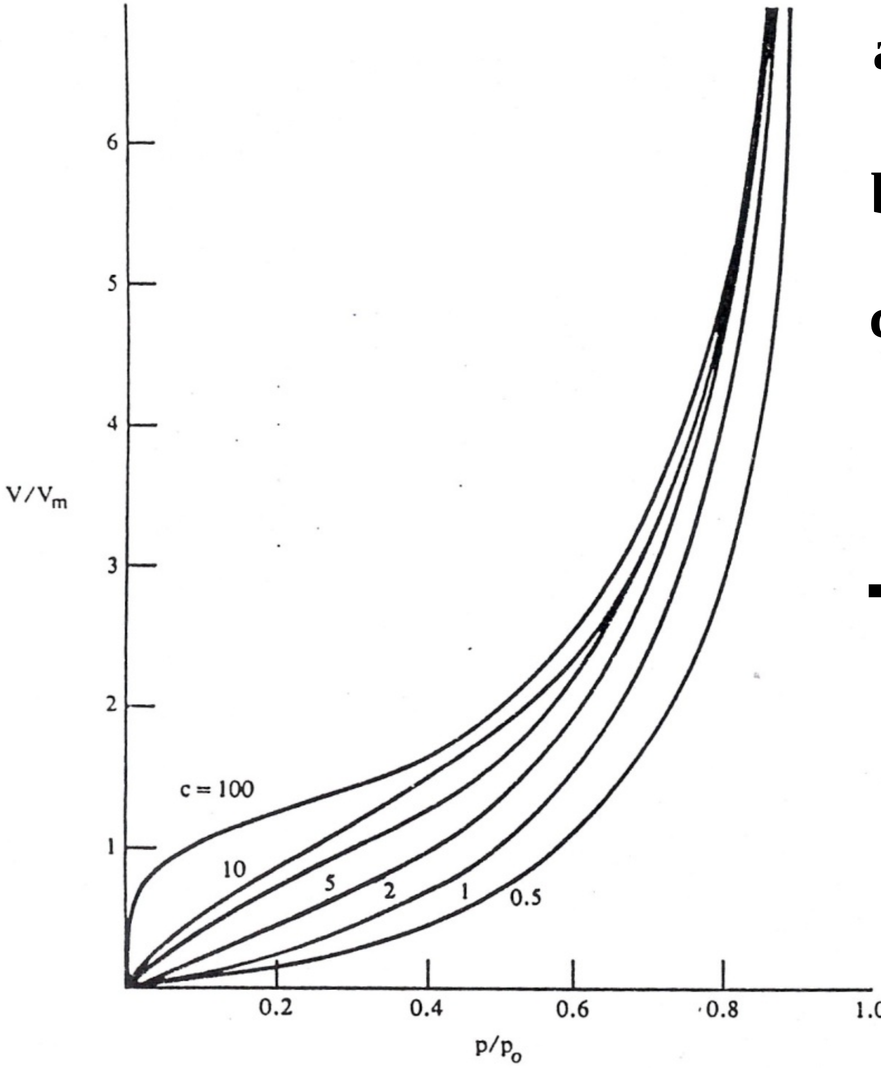


Figure A Plots of V/V_m versus p/p_0 for several values of the parameter c, calculated according to the BET theory by Eq. (90).

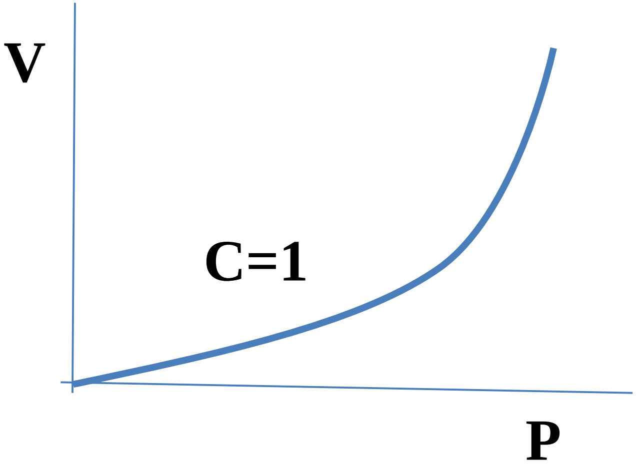
a. rapid increase of $\frac{V}{V_m}$ as $\frac{P}{P_0} \rightarrow 1$

b. shape of curve is sensitive to c value

c. BET eq. encompasses type II and type III isotherms

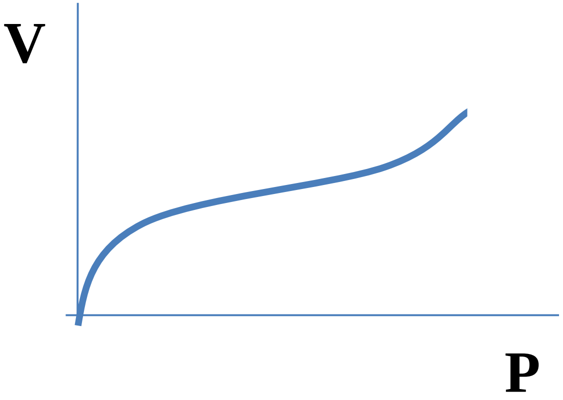
➔ for c ≤ 2, no inflection point

Type III



➔ **for C > 2, inflection becomes increasingly pronounced as c increases**

Type II



Notes:

1. **In view of the wide diversity of curve shapes and the relative insensitivity of adsorption data to the model underlying a particular equation,**

➔ **we expect that the BET equation will fit experimental data successfully.**

2. $c = \exp\left(\frac{\varepsilon - \varepsilon_v}{kT}\right)$ **describes the temperature dependence of adsorption**

One can evaluate $\varepsilon - \varepsilon_v$ from experimental *c*, or vice versa.

c↑ as $(\varepsilon - \varepsilon_v)$↑; when $\varepsilon \gg \varepsilon_v$, we shall observe monolayer adsorption first, followed by multilayer adsorption.

◆ **Discussion on Fig. B:**

N_2 adsorption on nonporous silica (SiO_2) at 77K.

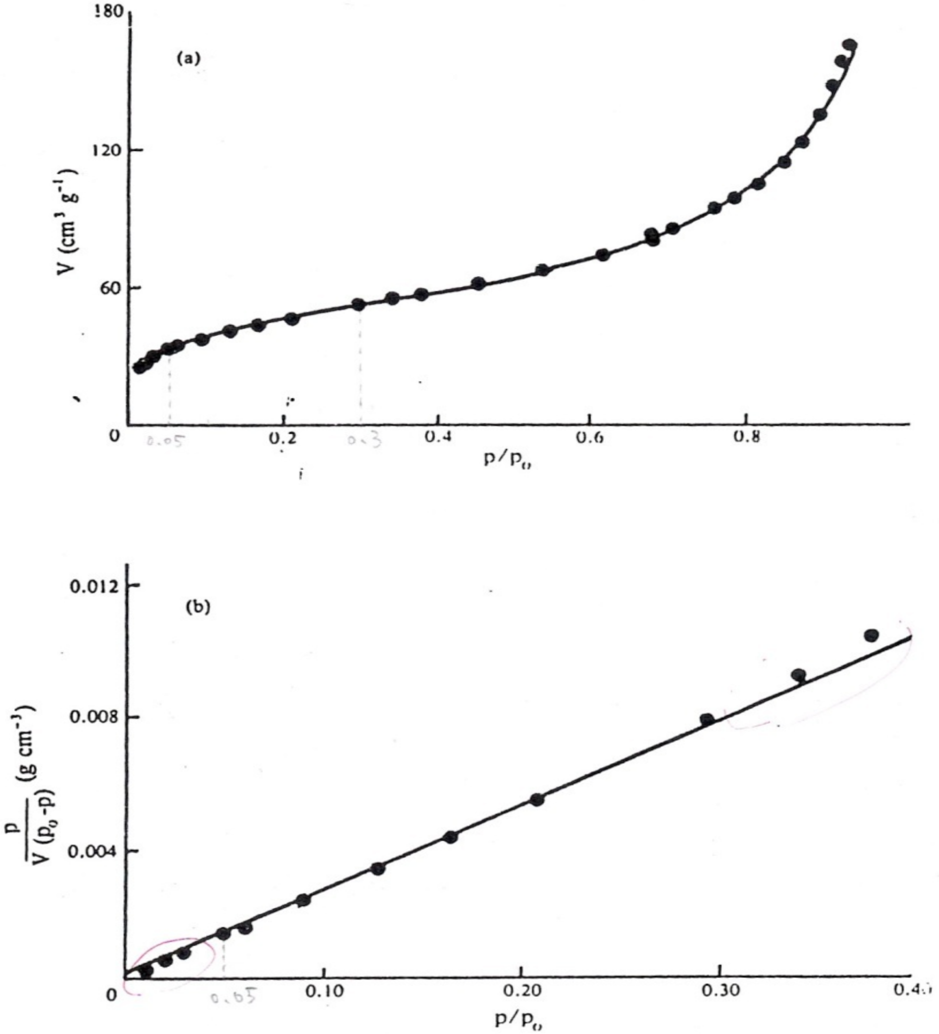


Figure B. Nitrogen adsorption on nonporous silica at 77 K; (a) volume per gram (in cm³ at STP) versus p/p_0 and (b) according to the linear form of the BET equation [Eq. (93)]. [Data from D. H. Everett, G. D. Parfitt, K. S. W. Sing, and R. Wilson, *J. Appl. Chem. Biotechnol.*, *24*:199 (1974).]

(a) adsorption isotherm

$$V \text{ vs. } \frac{P}{P_0}$$

(cm^3g^{-1} STP)

(b) $$\frac{P}{V(P_0 - P)} \text{ vs. } \frac{P}{P_0}$$

($g\ cm^{-3}$)

a. linear BET fit in the range of $0.05 \le \dfrac{P}{P_0} \le 0.3$

b. slope m = 0.0257 $g\ cm^{-3}$ STP
intercept b = 2.85×10^{-4} $g\ cm^{-3}$ STP

$$\therefore V_m = \frac{1}{m+b} = 38.5\ cm^3g^{-1}\ \text{STP}$$

$c = \frac{m}{b} + 1 = 91.2$ **check with Figure A**

c. At p/p_0 below the range of fit, the BET underestimates the adsorption (because adsorption occurs on strong adsorbing sites**).**

At $p/p_0 > 0.3$ the BET overestimates (adsorption may occur on top of adsorbates**)**

d. for $2 \le c \le 500$ (a range applicable to most of the systems)

The BET linear fit occurs in $0.02 \le p/p_0 \le 0.35$, which encompasses the range in which $V = V_m$ occurs.

In applying BET, this is an important region to fit.

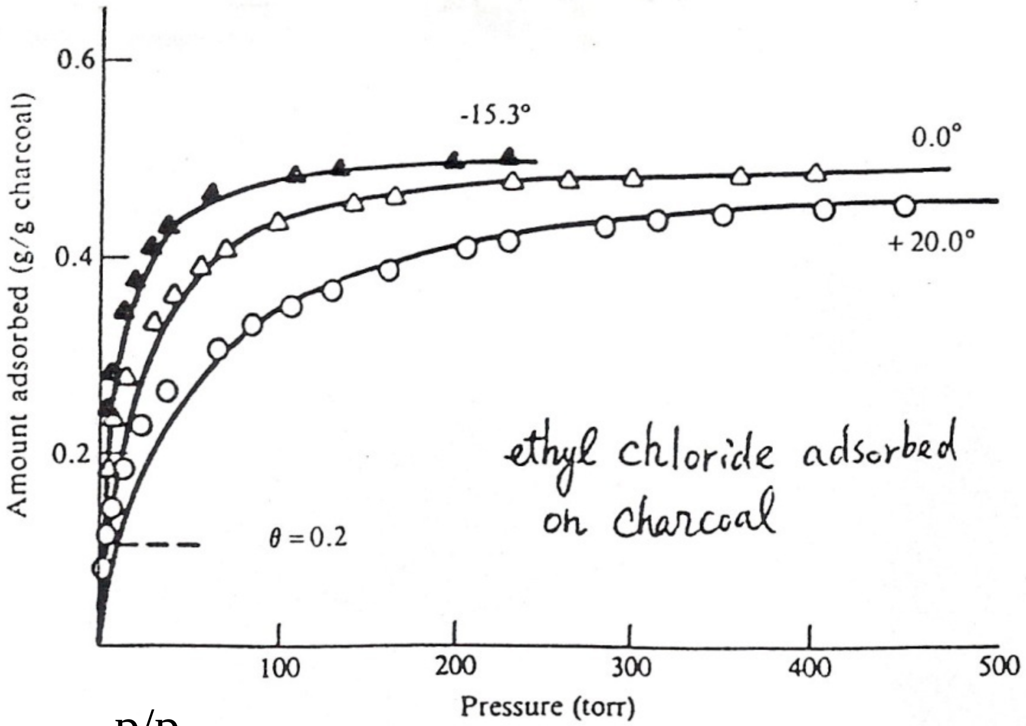
◆ **Another significance of c value when c is large and x small.**

$$\frac{V}{V_m} = \frac{cx}{(1-x)[1+(c\text{-}1)x]} = \frac{cx}{1+cx}$$

$$\frac{V}{V_m} \cong \theta \text{ (low } P/P_0 \text{)} \rightarrow \theta = \frac{cx}{1+cx}$$

BET → Langmuir

EX 3.4



Temp (°C)	Slope (g/g)	Intercept (g/g)
-15.3	1.9	0.040
0	2.0	0.047
20	2.0	0.088

The $\frac{p/p_0}{q}$ vs. p/p_0 plots of data in the figure were made, and the slope and intercept values are shown:

Find the adsorption energy according to BET eq., energy of vaporization for ethyl chloride is 23 kJ/mol.

[hint: c large and x small, c = exp $\left(\frac{\varepsilon-\varepsilon_v}{kT}\right)$ $\frac{V}{V_m}=\theta=\frac{cx}{1+cx}$ **]**

Sol.

3.8 Specific Surface Area: The BET equation

- **The BET permits us to extract V_m from multilayer adsorption data.**

➔ We use V_m for A_{sp} determination on the basis of:

$$V_m = \left(\frac{n}{w}\right)_m \left(22,414\frac{cm^3}{mol}\right) = \frac{A_{sp}}{N_A\sigma^0}(22,414)$$

$$\therefore A_{sp}\left[\frac{m^2}{g}\right] = \frac{V_m N_A \sigma^0}{22,414}$$

We need to know σ^0.

- **Assumptions to determine σ^0**

1. All adsorbate molecules are in liquid-phase at the same temp.

2. Adsorbed material has the same density.

3. Molecules are closely packed .

IUPAC standard N_2 at 77K , $\sigma^0 = 16.2$ Å^2

standard samples: silica and carbon black

For data in Figure B $V_m = 38.5 \ \frac{cm^3}{g}$ STP N_2

$$A_{sp} = \frac{(38.5\frac{cm^3}{g})(6.02\times10^{23}\frac{1}{mol})(16.2\times10^{-20}m^2)}{22,414\frac{cm^3}{mol}} = 168 \ \frac{m^2}{g}$$

EX 3.5

The following data give the volume at STP of nitrogen and argon adsorbed on colloidal silica at -196˚C: V@STP(cm³/g)

P/P_0	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5	0.6	0.7	0.8	0.9
Nitrogen	34	38	43	46	48	51	54	58	58	61	68	77	89	118
Argon	23	29	32	38	41	43	45	50	54	55	62	69	79	93

Using 16.2 Å² as the area occupied by a nitrogen molecule on the surface, determine the surface area of the silica by BET method. What value of the molecular surface area is required to give the same BET area for the argon data?

3.9. Heat of Adsorption (Non-ideality of solid surface)

We will follow the Clapeyron eq. in thermodynamics to calculate heat of adsorption from the isotherms.

at equilibrium

$$G_g = G_s \qquad dG_g = dG_s$$

$$dG = -SdT + VdP + \Sigma\mu_i dn_i$$

assuming no change in adsorption amount

$$-S_s dT + V_s dP = -S_g dT + V_g dP$$

$$\rightarrow \quad \left(\frac{\partial P}{\partial T}\right)_{n_s} = \frac{S_g - S_s}{V_g - V_s}$$

if the adsorption process is reversible,

$$S_g - S_s = \frac{q_{st}}{T}$$

q_{st} = isosteric heat of adsorption

$$\left(\frac{\partial P}{\partial T}\right)_{n_s} = \frac{q_{st}}{T(V_g - V_s)}$$

Assumptions: **a.** $V_g >> V_s$

b. $V_g = \dfrac{RT}{P}$

c. q_{st} **independent of T**

$$\left(\frac{\partial P}{\partial T}\right)_{n_s} = \frac{P}{RT^2} q_{st}$$

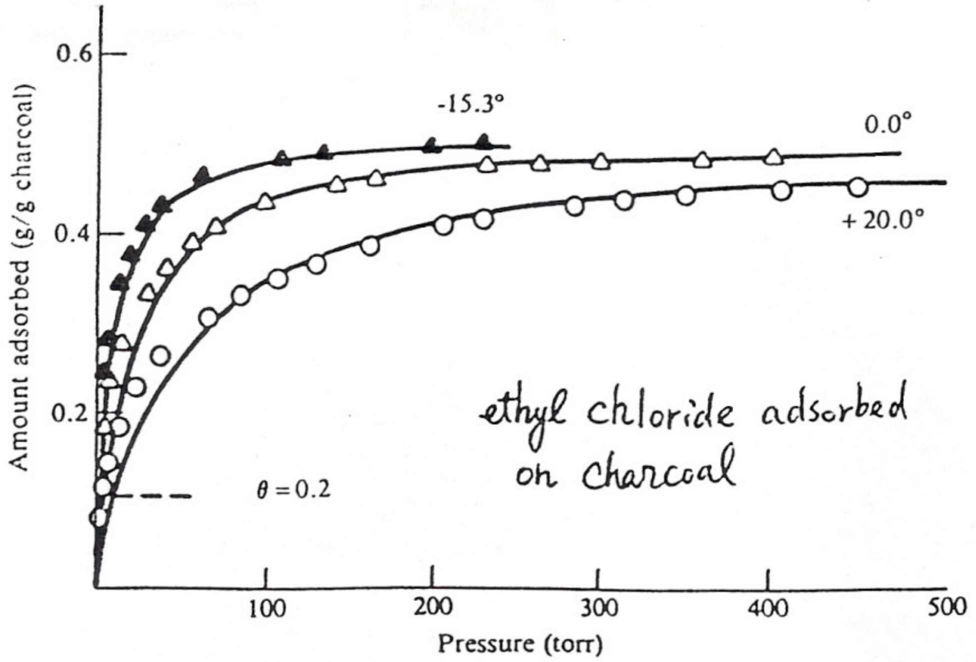
integration→ $\ln\left(\dfrac{P_1}{P_2}\right) = -\dfrac{q_{st}}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

or $\dfrac{dP}{dT} = \dfrac{q_{st} P}{RT^2}$

$$\frac{dP}{P} = \frac{q_{st}}{R} \cdot \frac{dT}{T^2} = -\frac{q_{st}}{R} d\left(\frac{1}{T}\right)$$

$$\ln P = -\frac{q_{st}}{R}\frac{1}{T} + \text{const.} \qquad \ln P \text{ vs. } \frac{1}{T} \rightarrow \text{slope} = -\frac{q_{st}}{R}$$

Ex. 3.3 & 3.4



e.g. at $\theta = 0.2$

T	-15.3	0	20
P	0.2	0.63	2.4

$$\ln P \text{ v.s. } \frac{1}{T} \rightarrow \text{slope} = -\,5330\text{ K}$$

$$\therefore q_{st} = 44.3\ \frac{kJ}{mol}$$

a graph of $\ln P$ vs. $\frac{1}{T}$, is linear with a slope of $-\frac{q_{st}}{R}$

values of q_{st} for data shown in Ex 3.3 and 3.4

θ	0.06	0.08	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
q_{st} ($kJmol^{-1}$)	56.9	47.3	46.4	44.4	41.4	40.2	40.2	40.0	38.1	37.2

- **BET or Langmuir model assumes that a single energy applied to all adsorption sites.**
- $q_{st}\big|_{\theta=1} \approx$ **adsorption energy obtained from BET (estimated near monolayer).**

- **Isosteric heat of Langmuir Isotherms**

Langmuir

$$\theta = \frac{KP}{1+KP} \rightarrow KP = \frac{\theta}{1-\theta} \rightarrow P = \frac{1}{K}\frac{\theta}{1-\theta}$$

$$\ln P = -\ln K + \ln\frac{\theta}{1-\theta} \qquad \left(\frac{d\ln P}{d(\frac{1}{T})}\right)_{\theta} = -\frac{q_{st}}{R} = -\frac{E}{R} \qquad \therefore \quad q_{st} = E = \text{const.}$$

Further Discussion of Isosteric Heat with Different Equations of State

- $\pi\sigma = kT \xrightarrow{\text{Gibbs}} \theta = m'P$ **Henry's law**

- **no molecular area**
- **no lateral interaction**

The picture from kinetic approach

$$k_a S P = k_d S_1$$

$$\left(\frac{k_a}{k_d}\right) P = \theta$$

$$m' = \frac{k_a}{k_d} \propto \exp\left(\frac{E}{RT}\right) \qquad \ln P = -\ln m' + \ln \theta$$

$$\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_\theta = -\frac{q_{st}}{R} = -\frac{E}{R} \qquad \therefore \quad q_{st} = \text{const}$$

- $\pi(\sigma-\sigma^0) = kT \rightarrow m'P = \frac{\theta}{1-\theta}\exp\frac{\theta}{1-\theta}$ **Volmer eq'n**

$$\ln P = -\ln m' + \ln\frac{\theta}{1-\theta} + \frac{\theta}{1-\theta}$$

$$\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_\theta = -\frac{q_{st}}{R} = -\frac{E}{R} \qquad \therefore \quad q_{st} = \text{const}$$

❖ $(\pi + \frac{a}{\sigma^2})(\sigma-\sigma^0) = kT \quad \rightarrow \quad m'P = \frac{\theta}{1-\theta}\exp(\frac{\theta}{1-\theta})\exp(-\frac{2a\theta}{\sigma^0 kT})$

$$\left(\frac{d\ln P}{d(\frac{1}{T})}\right)_\theta = -\frac{q_{st}}{RT} = -\frac{E}{R} - \frac{2a}{\sigma^0 k}\theta \quad \rightarrow q_{st} = E + \frac{2aN_A}{\sigma^0}\theta$$

- **If the interaction (lateral) is attractive, a is positive, which lead to a linear increase of q_{st} with coverage.**

- **If the interaction is repulsive, a is negative, q_{st} decrease with θ.**

It is not necessary that the repulsive interaction is the cause for the q_{st} decrease. Surface heterogeneity may also lead to the q_{st} decrease (because hot spots covered first).

The effect of surface structure

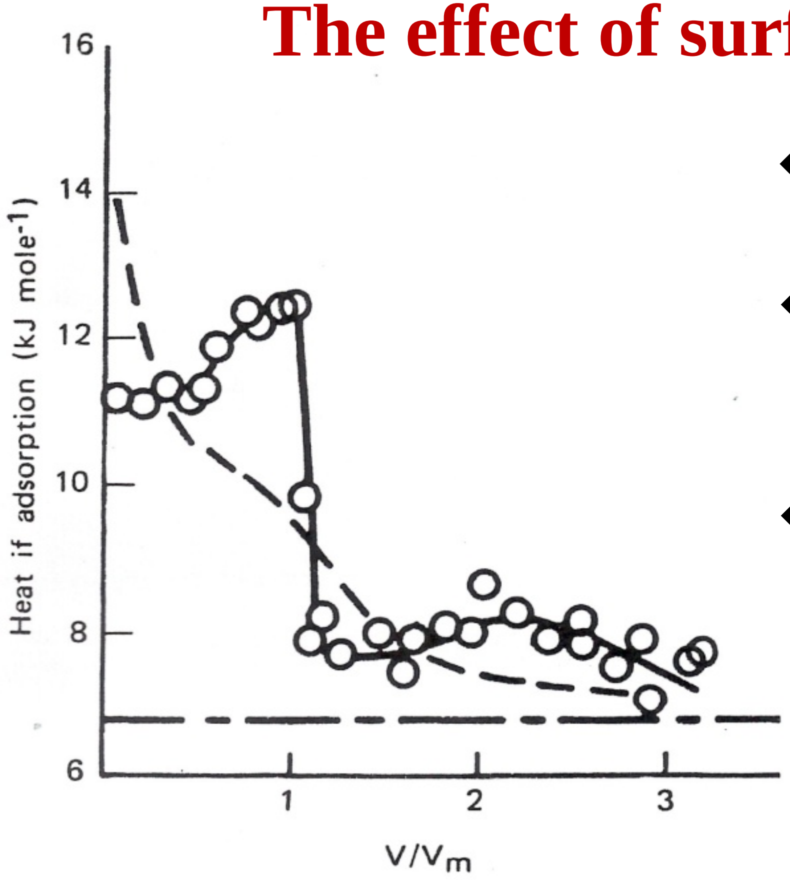


Figure Calorimetric heats of adsorption as a function of coverage for argon on carbon black at 78 K. The dashed line represents untreated black; the solid line is after graphitization at 2000°C. The horizontal line is the heat of vaporization of argon. [Reprinted from R. A. Beebe and D. M. Young, *J. Phys. Chem.*, *58*:93 (1954), copyright by the American Chemical Society.]

- **broken line: untreated black**
- **solid line: heat treated at 2000°C in an inert atmosphere**
- **horizontal line: heat of vaporization of argon**

(1) Untreated black: heat of ads. decreases with V/V_m, indicating the surface heterogeneity (functional groups, ether, carbonyl, hydroxyl and carboxyl…). The heterogeneity is smeared out as coverage increases.

Graphitized black: reduction of oxygen-containing groups leads to sharpening of both the basal and prismatic crystallographic planes. Heat is quite constant at low coverage and the value is high.

(2) For graphitized black , there is a sharp discontinuity at monolayer coverage ($\frac{V}{V_m}$ =1), beyond which $Q_{ads} \approx Q_{vap}$

At $\frac{V}{V_m} < 1$, Q_{ads} increases with $\frac{V}{V_m}$.

This is probably due to lateral interaction between molecules.