Adsorption[solid liquid, gas-solid system]

Solid –liquid Separation

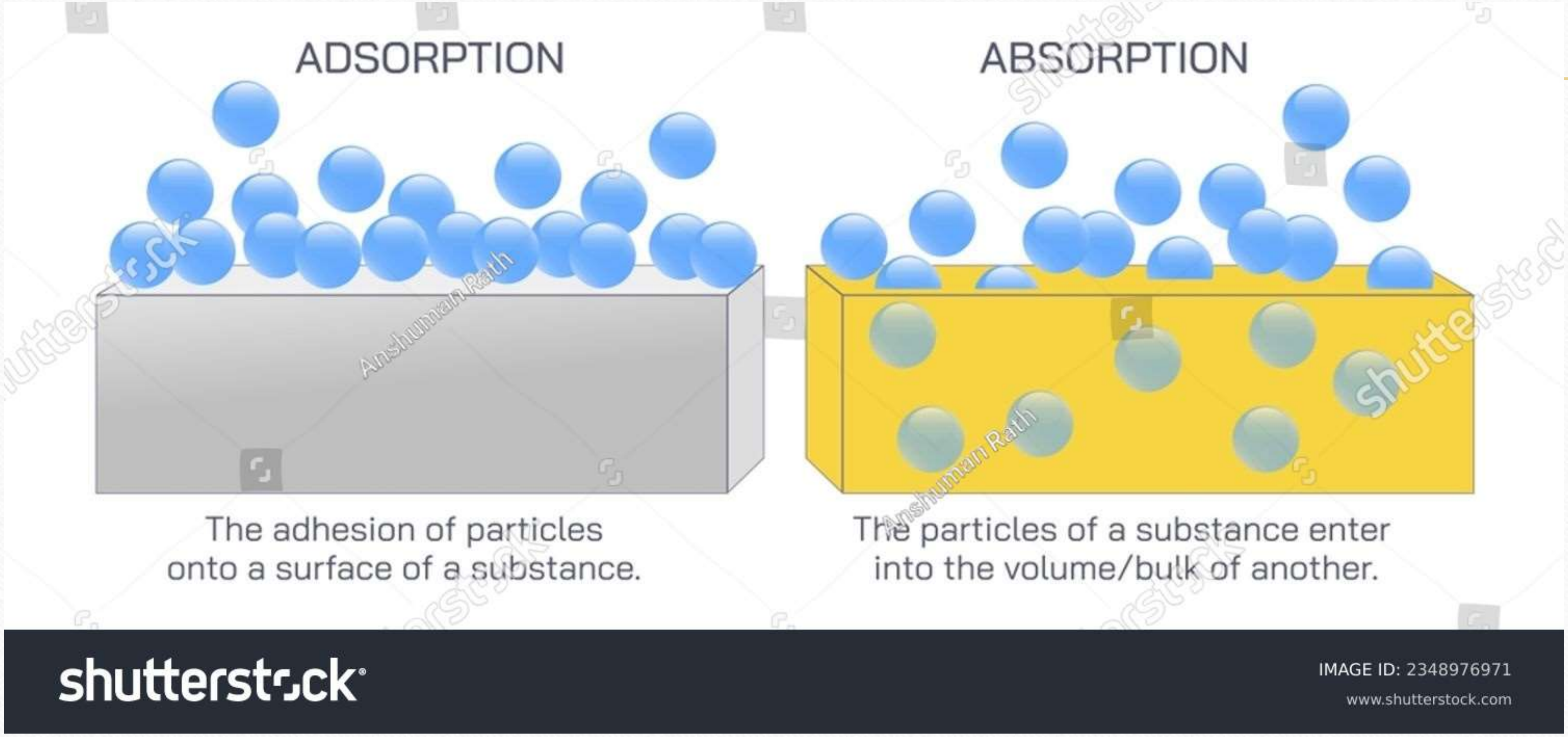
Dataset: Solid –gas system, calculation of specific surface area of an adsorbent

P mm Hg (Pv=760 mm Hg), T=77.4	10	20	40	100	150	200	250	300	350	400	500
q (amount adsorbed per solid)	71.3	142.2	287.7	679.4	1025	1053	1175	1316	1996	3451	5283

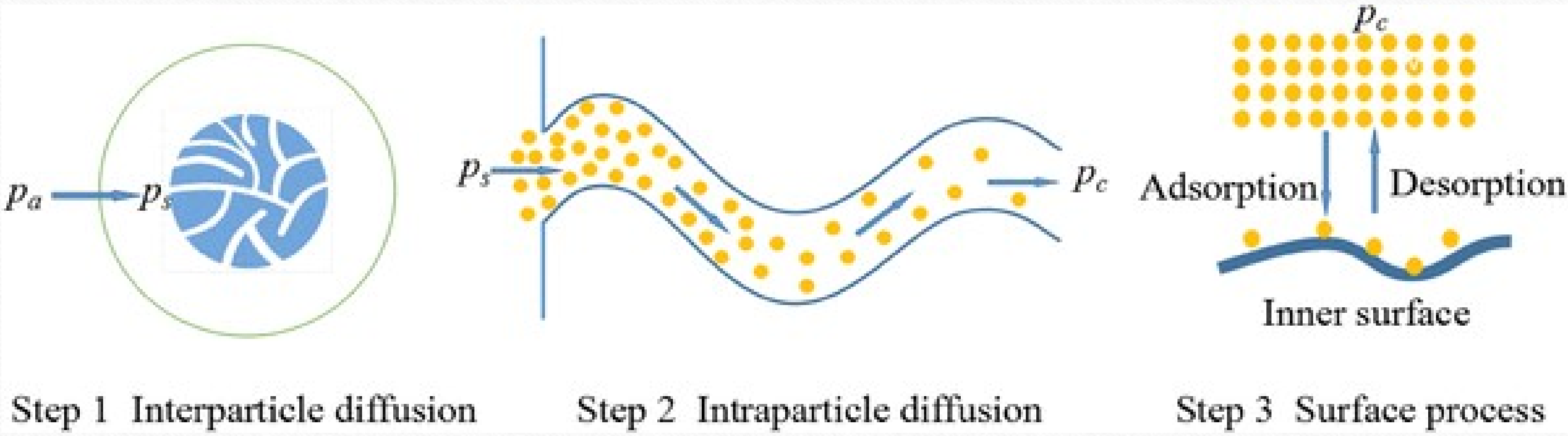
P → Pressure of N_2 (mm Hg)

q → Volume of N_2 adsorbed / 100 gm solid (cm^3).

Difference between Absorption and adsorption



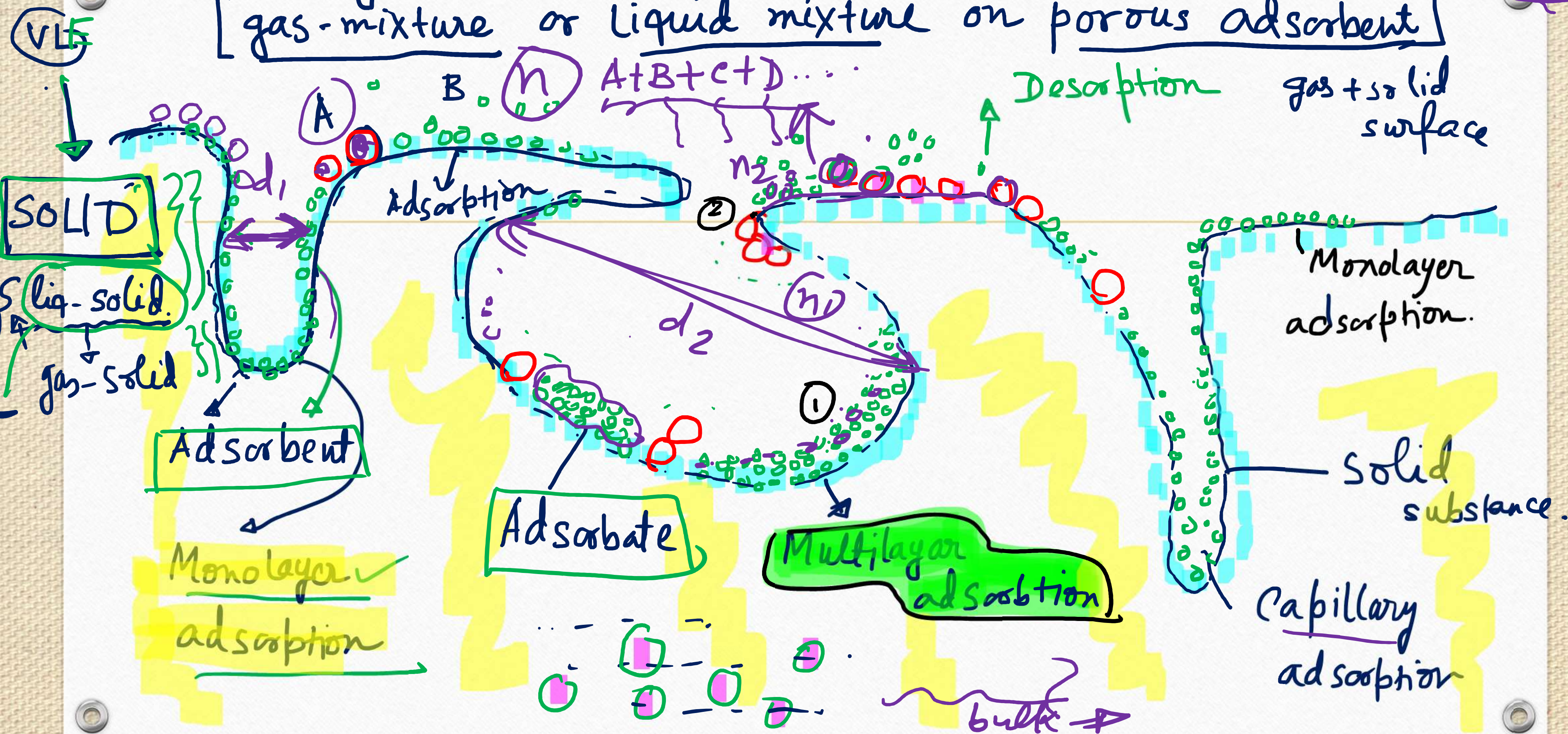
Adsorption



p_a
p_s
p_s
p_c
p_c
Adsorption
Desorption
Inner surface
Step 1 Interparticle diffusion
Step 2 Intraparticle diffusion
Step 3 Surface process

Multilayer adsorption of a binary mixture

[gas-mixture or liquid mixture on porous adsorbent]



ADSORPTION MECHANISM

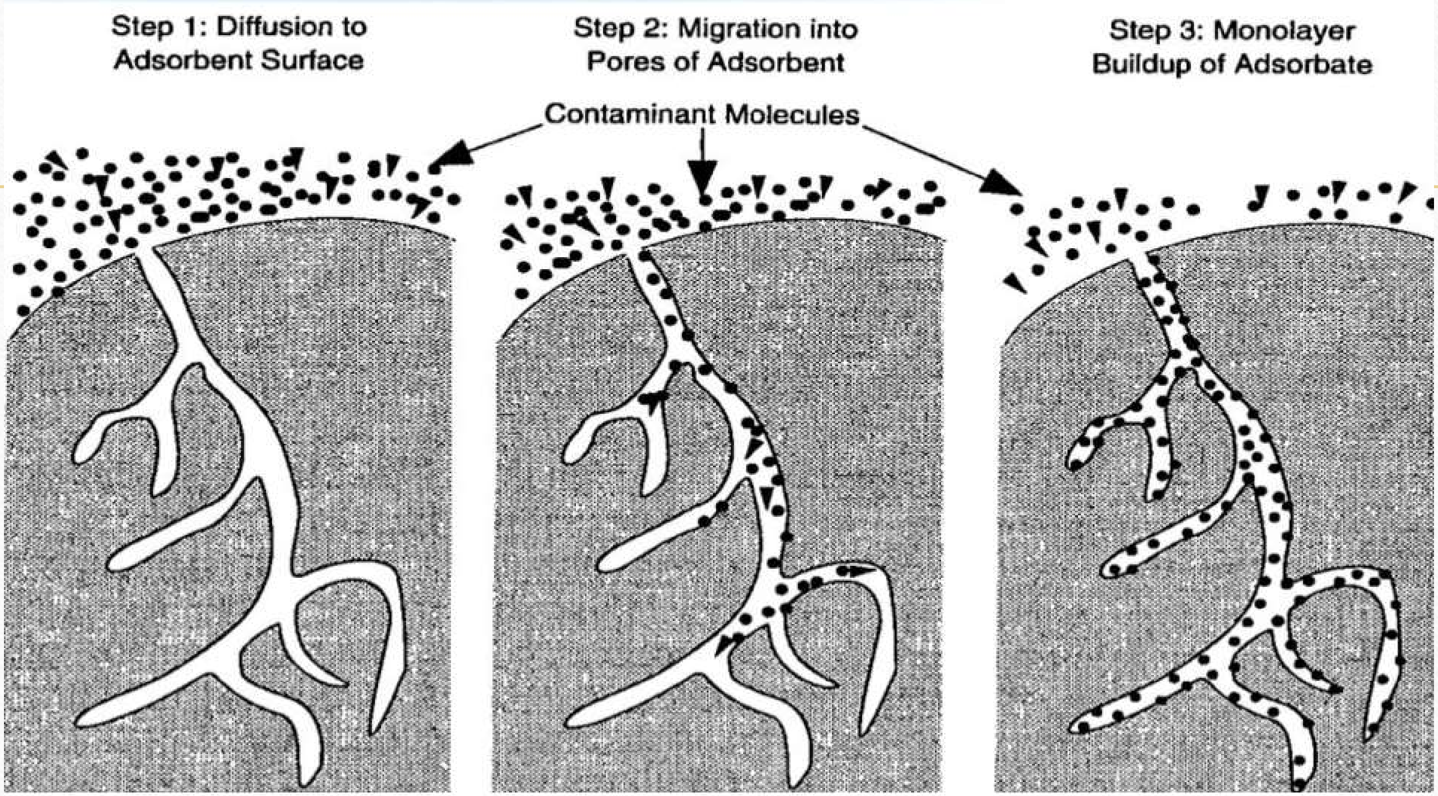
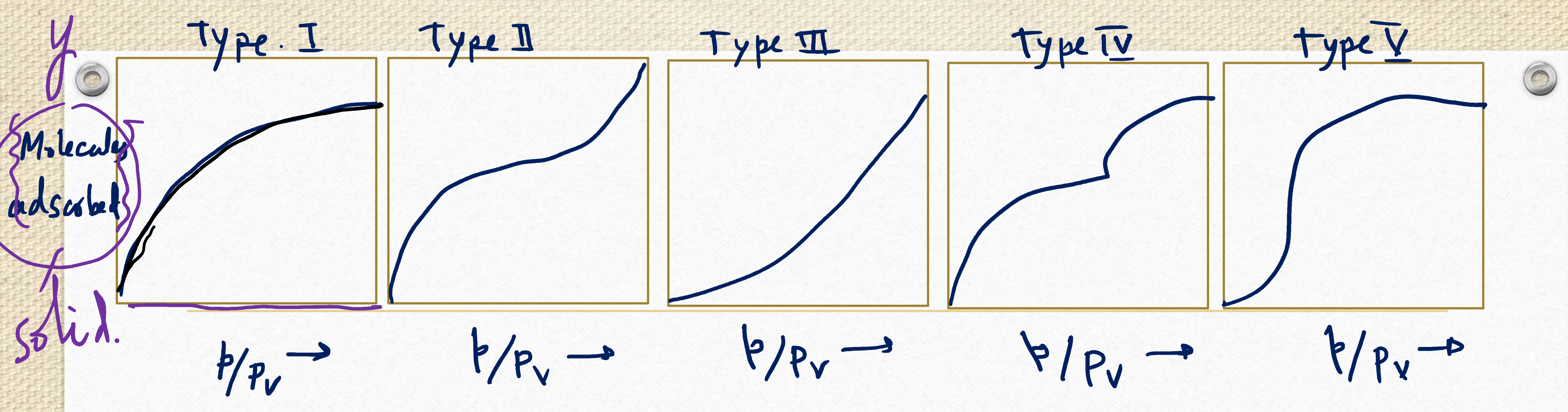


Figure 2.1 : Adsorption mechanism

Adsorption video

https://www.google.com/search?q=adsoption+process++youtube+video&sca_esv=594982741&sxsrf=AM9HkKmb8EpXx3QMIB2HGvhnpzePCAPyLA%3A1704160461988&ei=zWyTZb3-O9O6seMPspOziAw&ved=0ahUKEwj9mOi3zL2DAxVTXWwGHbLJDMEQ4dUDCBA&uact=5&oq=adsoption+process++youtube+video&gs_lp=Egxnd3Mtd2l6LXNlcnAiIGFkc29wdGlvbiBwcm9jZXNzICB5b3V0dWJlIHZpZGVvMgoQIRigARjDBBgKMgoQIRigARjDBBgKSJAbUM8EWN8WcAB4AJABAJgBqgGgAesLqgEEMC4xMLgBA8gBAPgBAcICBxAjGLACGCfiAwQYASBBiAYB&sclient=gws-wiz-serp#fpstate=ive&vld=cid:7b33acf0,vid:xGS-P7YRE5c,st:0

https://www.google.com/search?q=adsorption+youtube+video&sca_esv=594987936&sxsrf=AM9HkKl91vdPeb5W3LHc9ig1TGAb2Wg8Uw%3A1704161597486&source=hp&ei=PXGTZeG3G-3V4-EP5JCs6A0&iflsig=AO6bgOgAAAAAZZN_Tf2YfxzATNmbOZIqValvA9fr8mmW&oq=&gs_lp=Egdnd3Mtd2l6IgAqAggAMgcQIxjqAhgnMgcQIxjqAhgnMgcQIxjqAhgnMgcQIxjqAhgnMgcQIxjqAhgnMgcQIxjqAhgnMgcQIxjqAhgnMgcQIxjqAhgnMgcQIxjqAhgnMgcQIxjqAhgnSIYhUABYAHABeACQAQCYAQCgAQCqAQC4AQHIAQCoAgo&sclient=gws-wiz#fpstate=ive&ip=1&vld=cid:ed54b63b,vid:FcsE22UU18c,st:0



Five basic types of adsorption isotherm.

$p_1/P_v - p_2/P_v$

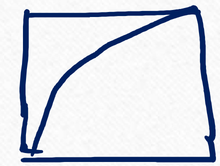
p = adsorbate pressure.

p_3/P_v

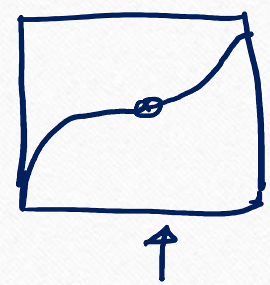
P_v = saturation vapor pressure of the adsorbate.

Type I: Isotherm → formation of mono molecule layer on adsorbate. [Solutes in low concⁿ].

Mono layer



Relatively higher concⁿ of solute loading in solid.



(Eg) O_2 in carbon Black.

Type III. → formation of infinite multilayer -- after having one monolayer.

(Eg.) H_2O vap on carbon black.

Type III : Amount of adsorption increases indefinitely as its relative saturation p/p_v approaches ~1.

Unfavourable →

solute concn is low at a small concn in the fluid.

e.g N_2 adsorption - ice.

Type IV & V : → having the alternative convex and concave region → possibly having capillary condensation in pores.

LangMuir was awarded the Nobel Prize in Chemistry in 1932 for his work in surface chemistry.

Langmuir isotherm: Irving Langmuir

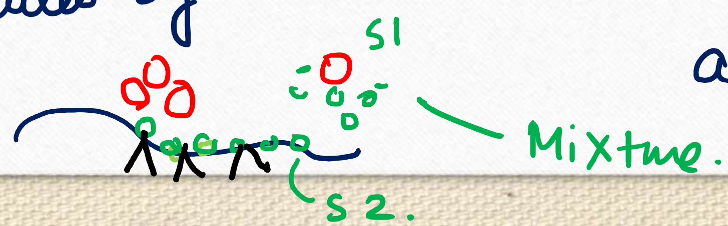
Assumptions: (1) Molecules are adsorbed at discrete active sites on the surface.

(2) Each active site adsorbs one molecule.

(3) The adsorbing surface is energatically uniferm.

(4) There is no interaction among adsorbed molecules.

Rate of capture of adsorbate molecules by surface $\propto$ Fraction of uncovered area $(1-\theta)$ and p.p or conc^n of adsorbate.

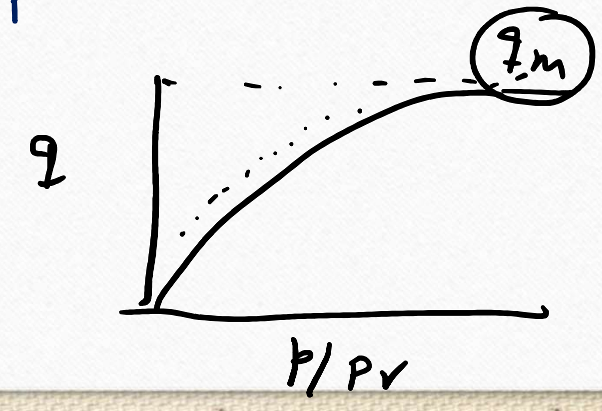


Notations

q = amount of gas or liquid solute adsorbed at equilibrium / gm of adsorbent at pressure P or concn C.

q_m = Maximum quantity of gas or liquid solute adsorbed / gm of adsorbent at saturation.

$\theta = q / q_m$.

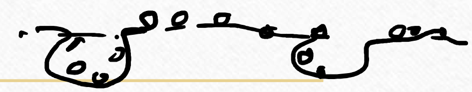


Theoritical Basis.

Rate of capture.

or rate of adsorption $= k_1 p(1-\theta)$.

Rate of desorption $= k_2\theta$.



$$k_1 p(1-\theta) = k_2\theta.$$

$$\Rightarrow \theta = \frac{k_1 p}{k_2 + k_1 p} = \frac{Kp}{1+Kp}$$

$K = k_1/k_2$.

$\theta = q/q_m$. $\Rightarrow$

$$\boxed{q = \frac{q_m K p}{1+Kp}}$$

Langmuir isotherm.

2 parameter

K & q_m.

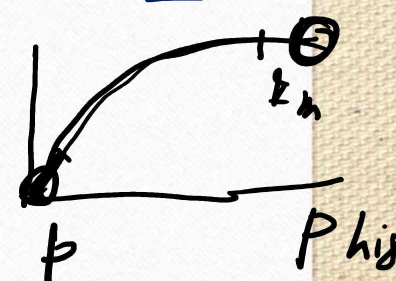
Langmuir isotherm $q = \dfrac{q_m K p}{1+Kp}$.

ⓐ If p. pressure of the adsorbate is low $Kp \ll 1$.

$$q = q_m K p = K_H p \longrightarrow$$ [linear isotherm ~ Henry's law]

If p. pressure is high $Kp \gg 1$

$$\Rightarrow \quad q = \frac{q_m \cancel{Kp}}{\cancel{Kp}} = q_m .$$ [saturation].



Experimental data analysis

$$q = \frac{q_m K p}{1+Kp}$$ – Langmuir isotherm

$$\rightarrow \frac{1}{q} = \frac{1+Kp}{q_m K p} = \frac{1}{q_m K p} + \frac{1}{q_m}$$ const.

$$\Rightarrow \frac{p}{q} = \frac{1}{q_m K} + \boxed{\frac{p}{q_m}}$$

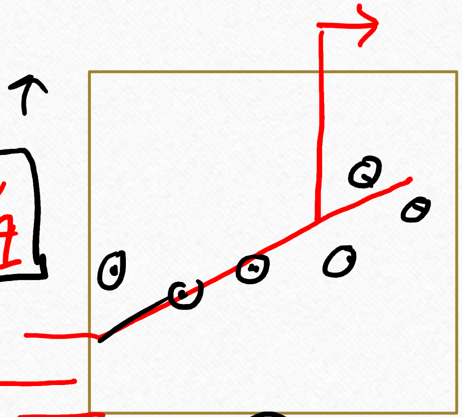
$y = mx + c$

q_m & K can be estimated.

Intercept $= \frac{1}{q_m K}$.

slope. $= 1/q_m$

$\boxed{p/q}$



p

What is isotherm?

The equilibrium relation between amount of gas/liquid (q) mass adsorbed per unit mass of the solid. adsorbent or solute → Adsorption Isotherm.

$q = f(c)$ at constant T.

What is isotere?

Plot of $\ln(c)$ or $\ln(P)$ of solute in fluid/gas vs inverse of absolute temperature $1/T$ for a constant loading of q of the adsorbant., $c = \psi(1/T)$. const q.

$p = \psi'(1/T)$

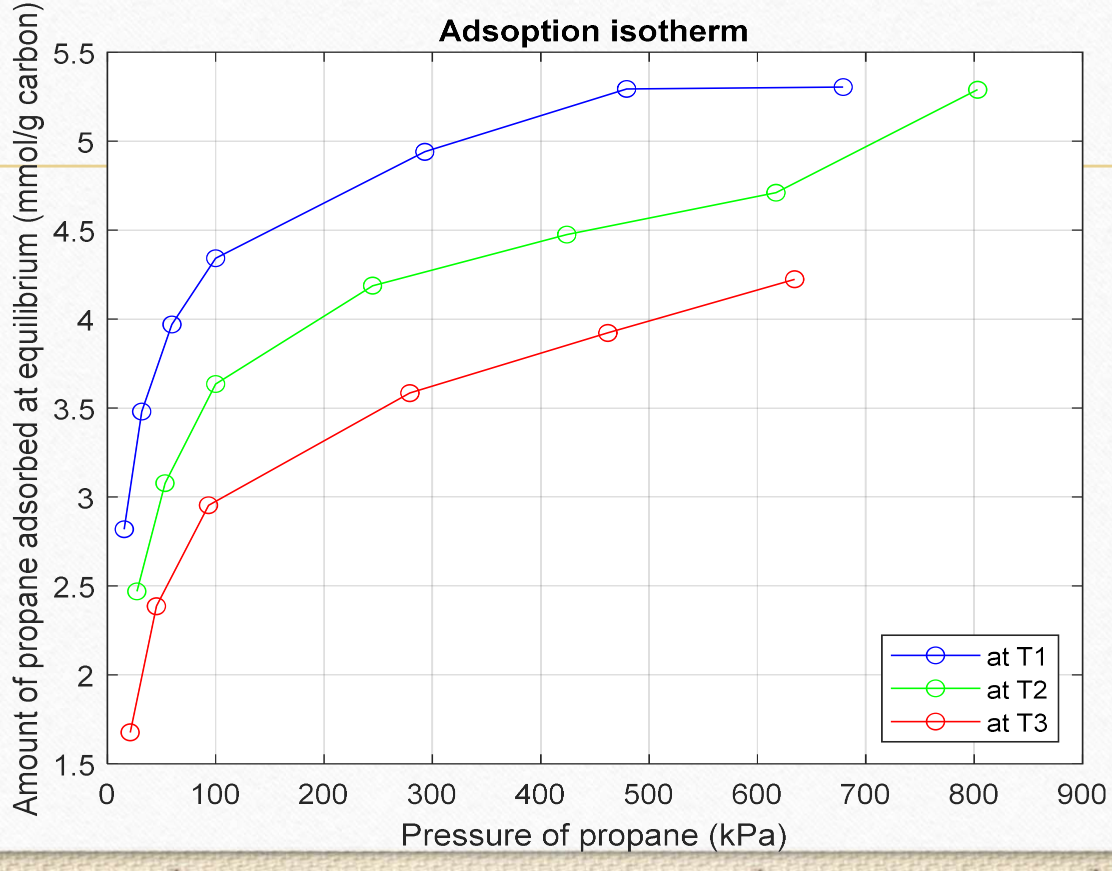
Heat of adsorption

12.4 ***(Fitting of Langmuir isotherm and determination of heat of adsorption)***[2] Ray and Box (*Ind. Eng Chem.*, *42*(1950) 1315) reported the following data on equilibrium adsorption of propane on activated carbon at three different temperatures.

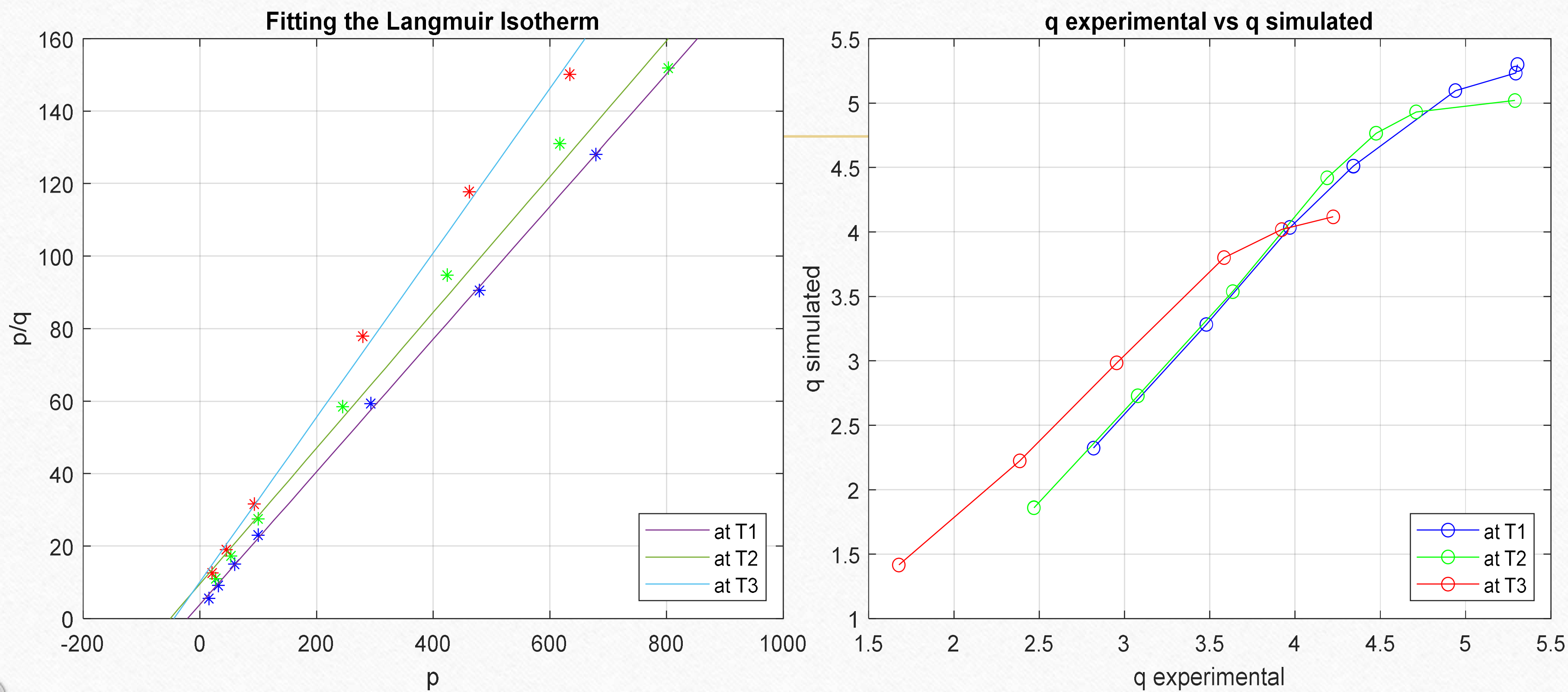
T = 310.9 K		338.7 K		366.5 K	
p (kPa)	q (mmol/g)	p (kPa)	q (mmol/g)	p (kPa)	q (mmol/g)
15.6	2.819	27.2	2.469	21.07	1.677
31.74	3.48	53.2	3.078	45.33	2.386
59.6	3.97	99.97	3.635	93.34	2.954
99.97	4.342	244.8	4.188	279.2	3.584
293	4.94	424	4.475	461.9	3.922
479.2	5.294	617.1	4.71	634.3	4.244
679.1	5.304	803.2	5.289		

Fit the data using Langmuir isotherm and get the correlation coefficients. Determine the isosteric heat of adsorption.

Adsorption of propane at different temperature



Langmuir Isotherm fitting at different temperature



Slope and intercept for Langmuir isotherm

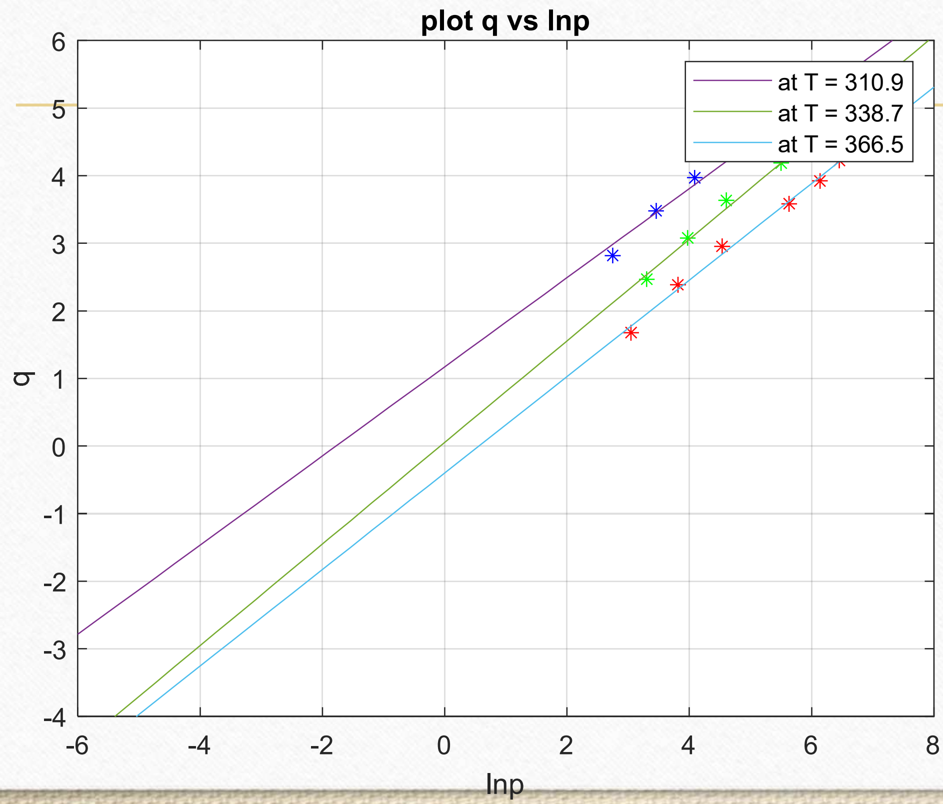
Parameters

qm1 = 5.4631, k1 = 0.0474

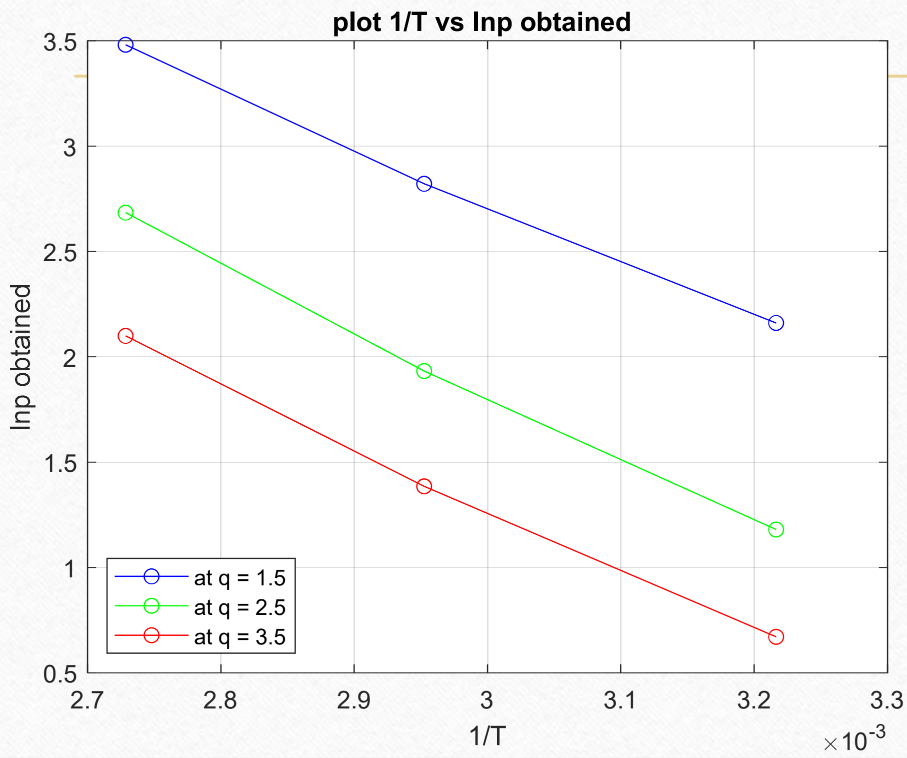
qm2 = 5.3379, k2 = 0.0197

qm3 = 4.4060, k3 = 0.0225

Plot of q vs lnP



Heat of adsoption



determination of heat of adsorption
%from Clausius-Clayperon equation:

delta_H_iso = -R*((T)^2)*d(lnp)/dT = R*d(lnp)/d(1/T)

Ln(P2/P1)= -(delh / R) [(1/T2-1/T1)]

Freundlich isotherm?

SPE.

$\rightarrow q = k' p^{1/n}$ (emperical) $\Rightarrow$

$q = k' C^{1/n}$

↳ concentration.

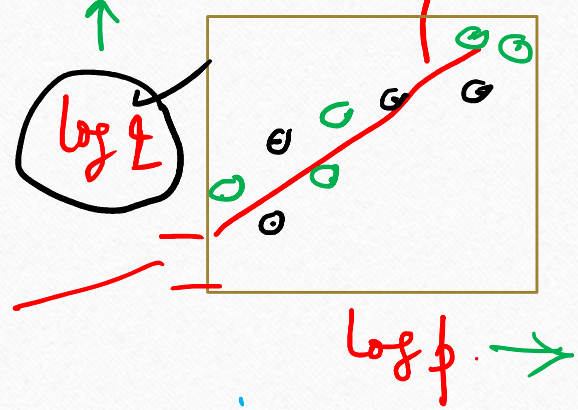
Amount of adsorbed @ eqbm, has power law dependence on the partial pressure of gas solute [concn of liq solute]

k', n → 2 adjustable parameters →

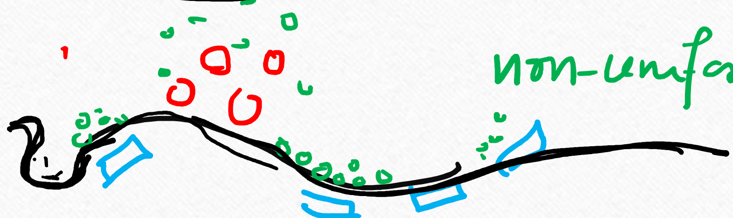
$$\log q = \frac{1}{n}\log p + \log k'$$

slope $= \frac{1}{n}$

intercept $= \log k'$



non-uniformity



// Non-uniform adsorbing surface // different sites are energetically not the same.

Toth isotherm? → Mixture Model →

$$q = \frac{q_m \, p}{(b + p^n)^{1/n}}$$

(Emperical).

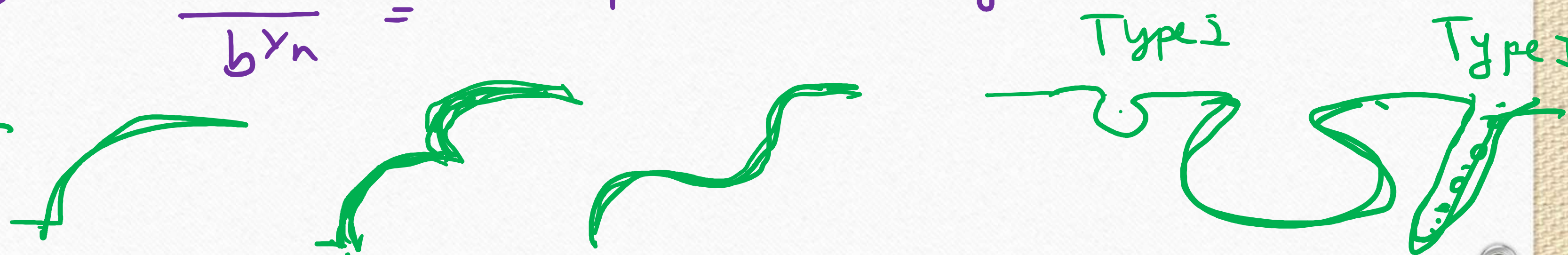
↑ no of parameters.

q_m, b, n three parameter isotherm. [Applicable for heterogeneous adsorption surface]

at low pr, $p^n \to 0$

$$\therefore q = \frac{q_m p}{b^{1/n}} = K p \to \text{Henry's law.}$$

$$\frac{q_m p}{K + P}$$



Sips' isotherm?

3-parameter Model,

$$q = \frac{q_m \left(K'' p\right)^{1/n}}{1+\left(K'' p\right)^{1/n}}$$

statistical.

(Langmuir + Toth)

①

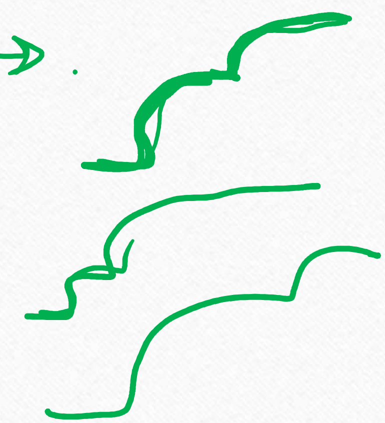
q_m = max^m adsorption capacity

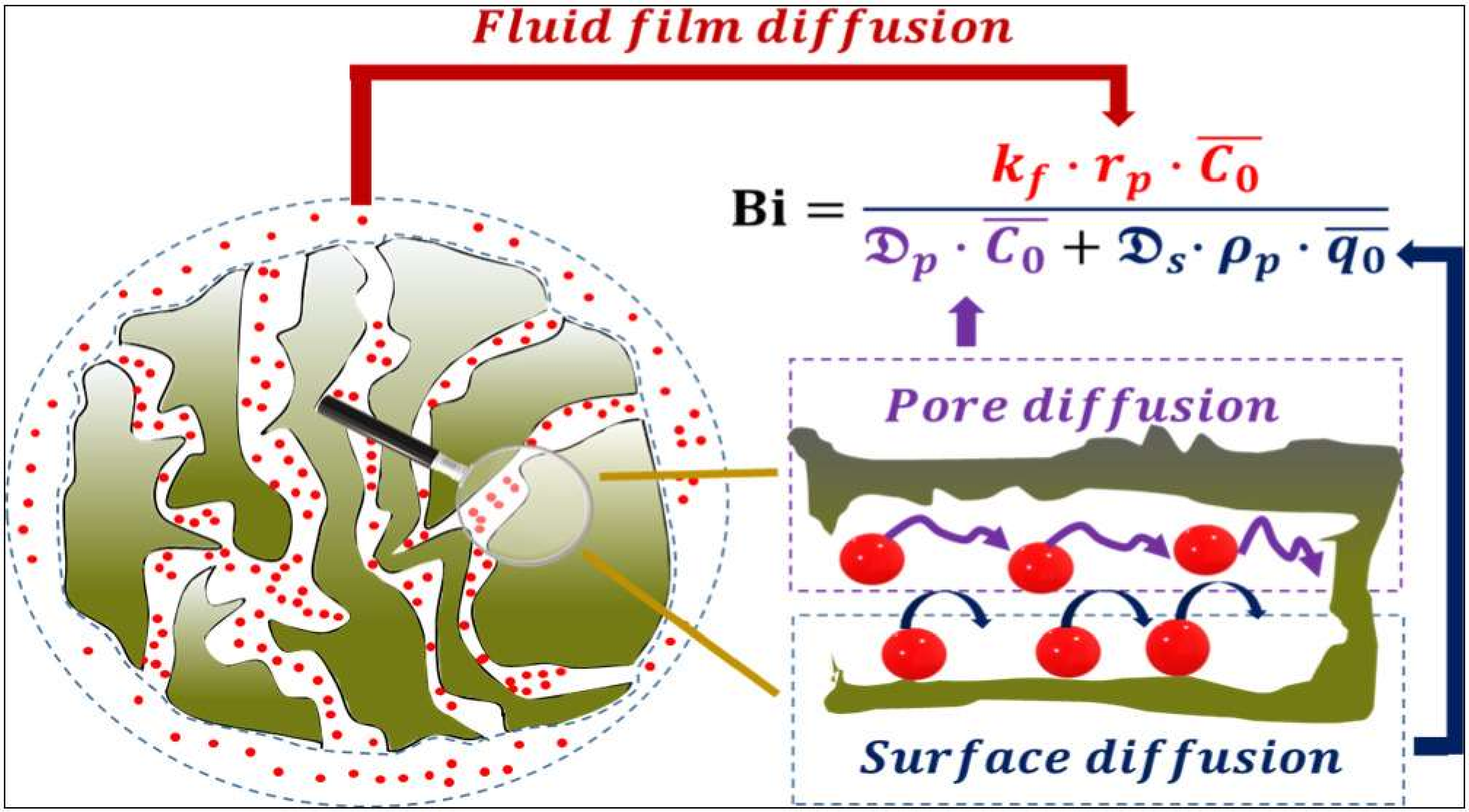
K'' = affinity co-efficient

n = measure of system heterogeneity.

②

③




Fluid film diffusion
$$\mathbf{Bi} = \frac{k_f \cdot r_p \cdot \overline{C_0}}{\mathfrak{D}_p \cdot \overline{C_0} + \mathfrak{D}_s \cdot \rho_p \cdot \overline{q_0}}$$
Pore diffusion
Surface diffusion

Approach. →Multicomponent adsorption isotherm

Use of Langmuir model to describe adsorption equilibrium in a multicomponent system.

adsorbate

$$q_i = q_{im} \frac{b_i p_i}{1 + b_1 p_1 + b_2 p_2 + \dots + b_n p_n}$$

(n components)

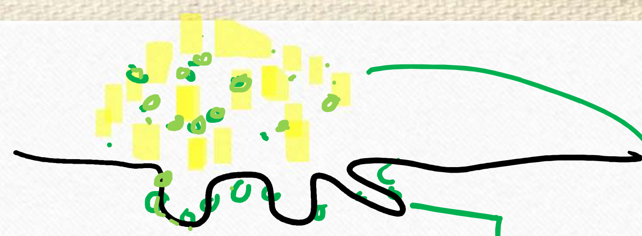
$q_2 = q_3 \dots$

$$q_1 = \frac{q_{1m} b_1 p_1}{1 + \sum b_i p_i}, \qquad q_2 = \frac{q_{2m} b_2 p_2}{1 + \sum b_i p_i}$$

Presence of another component competing for active sites.

Separation factor:

$$\alpha_{12} = \frac{x_1/y_1}{x_2/y_2}$$



x_i = mole fraction of component i in adsorbed phase

y_i = " " " i " fluid phase

(gas/liq)

$\alpha_{12} \Rightarrow$ Relative volatility →

⇓ Distillation.

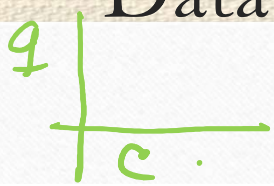
Langmuir Freundlich model

$$q_i = q_{im} \cdot \frac{b_i \boxed{p_i^{n_i}}}{1 + b_1 p_1^{n_1} + b_2 p_2^{n_2} + b_3 p_3^{n_3} \cdots + b_n p_n^{n_n}} \quad (n)$$

Multicomponent adsorption eqbm. {[Higher no of parameters].}

$$\frac{q_{im}\, b_i\, p_i^{n_i}}{1 + \sum_i b_i p_i^{n_i}}$$

Dataset: Solid Liquid system



	Glycine	Phenylalanine	
fluid phase. Concentration of the component [c]	Adsorbed phase Amount adsorbed [q]	fluid phase Concentration of the component [c]	adsorbed phase Amount adsorbed [q]
0.0126	0.794 x 10^{-5}	0.0112	0.6 x 10^{-4}
0.0251	1.41 x 10^{-5}	0.0224	1.2 x 10^{-4}
0.10	5.62 x 10^{-5}	0.0302	1.58 x 10^{-4}
0.1995	11.2 x 10^{-5}	0.0355	1.78 x 10^{-4}

c, P, T

$f(c, P, T) \rightarrow$

$$q = \frac{q_m\, p}{K + p} \quad [L.I]$$

$$q = q_m\, p^{1/n} \quad [F.I]$$

Calculation of specific area of an adsorbent

α = Projected area of an adsorbed molecule $\alpha = \boxed{1.09\left(\frac{M}{N\rho}\right)^{2/3}}$

M = Molecular weight, ρ = density of the adsorbate,

N = Avogadro number,

parameter.

Specific surface area of the adsorbent $= q_m N \alpha$.

q_m = gm mole adsorbed component / gm of adsorbent.

BET's isotherm, Braunauer-Emmet –Teller Equation

BET eqn represent multilayer adsorption eqbm for many system.

[3-parameter models, q_m, c, c']

$$q = q_m \frac{c' x}{(1-x)[1+(c'-1)x]}$$

$c' \rightarrow T$

$x = p/P_v$; q = quantity of component (liquid/gas) adsorbed in gm/gm of adsorbant.

q_m = quantity of component adsorbed to form monolayer on the surface, [gm adsorbed/gm adsorbent].

c' = a temperature dependent constant for a particular gas-solid,

P_v = vapour pr of the adsorbate at at a given temp.

BET equation:

$$q = \frac{q_m c' p/p_v}{(1 - p/p_v)[1 + (c'-1)p/p_v]}$$ - Non-linear.

$$\Rightarrow \left(\frac{p_v - p}{p_v}\right)\left(1 + \frac{(c'-1)p}{p_v}\right) = \frac{q_m c' p}{p_v q}.$$

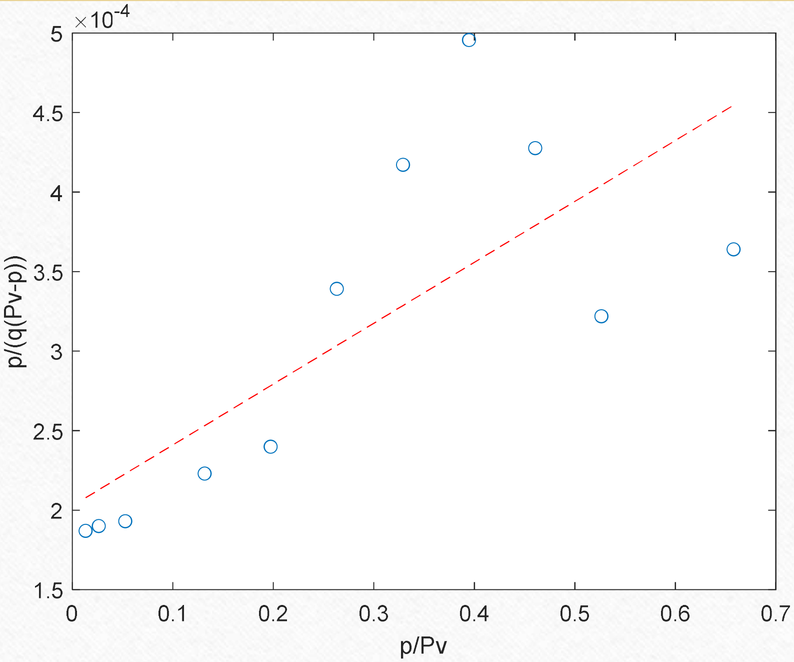
$$\Rightarrow (p_v - p) + \frac{(p_v - p)(c'-1)p}{p_v} = q_m c' p/q.$$ [divide both sides by $(p_v - p) q_m c'$.

$$\Rightarrow \frac{1}{c' q_m} + \frac{(c'-1)}{c' q_m p_v} p = \left[\frac{p}{q(p_v - p)}\right] y$$

$$\Rightarrow \boxed{\frac{p}{q(p_v - p)} = \frac{1}{c' q_m} + \frac{c'-1}{c' q_m p_v} p}$$ — (Can be used in parameter estimation)

In order to fit the BET equation, .

plot $\frac{p}{q(P_v-P)}$ vs p/P_v — should be a st. line for an adsorbate-adsorbent pair.



Linear Regression:

Polyfit function

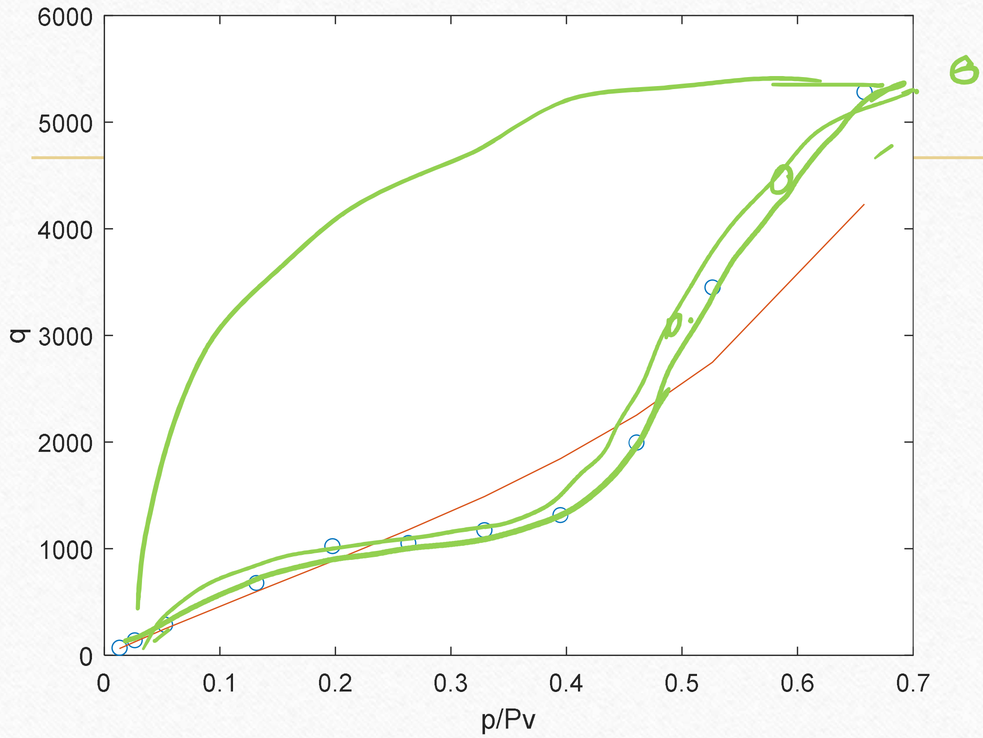
Dataset: Solid –gas system, calculation of specific surface area of an adsorbent

P mm Hg (Pv=760 mm Hg), T=77.4	10	20	40	100	150	200	250	300	350	400	500
q (amount adsorbed per solid)	71.3	142.2	287.7	679.4	1025	1053	1175	1316	1996	3451	5283

$P \rightarrow$ Pressure of N_2 (mm Hg)

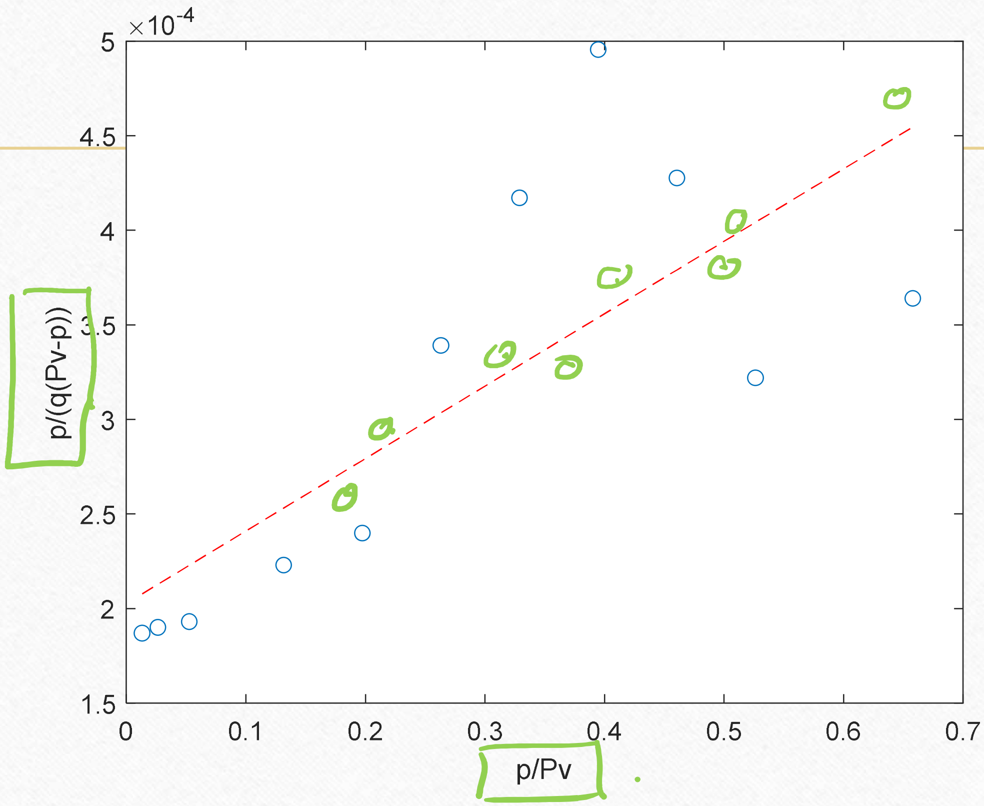
$q \rightarrow$ Volume of N_2 adsorbed / 100 gm solid (cm^3).

BET's isotherm, Braunauer-Emmet –Teller Equation



Model fitting to adsorption process

Plotting for straight line form



Amount adsorbed experimental vs. amount adsorbed theoretical

goodness of fit / quantify.

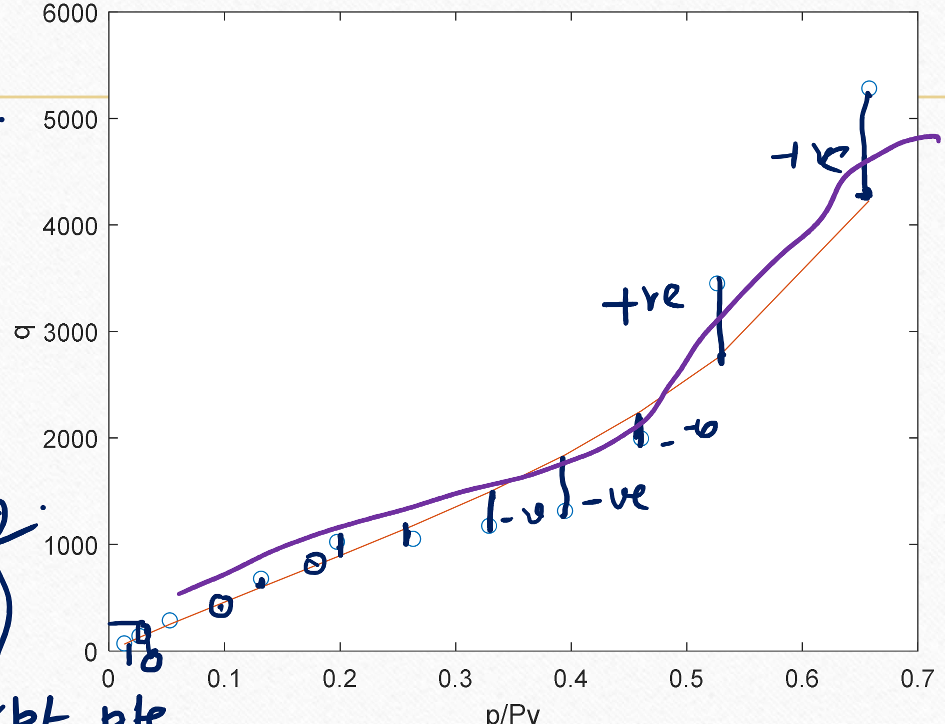
12 pts $n=12$.

x_{1exp} (y_{1exp})

x_{1exp} (y_{1sim})

$$\sum_{i=1}^{n}\left(y_{exp_i} - y_{sim_i}\right)^2.$$

n = no of expt pts.



RMSE

Root mean square error.

RMSE | Model 1.

$$= \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(y_{exp_i} - y_{sim_i}\right)^2}$$

RMSE | Model 2.

Plotting of amount absorbed vs p. pressure