

**Mass Transfer Operations-2**  
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**Lecture 24**  
**Adsorption: Types and nature of adsorption, Adsorption isotherm**

Welcome back to Mass Transfer Operations- 2 course. In the last class we discussed on membrane separation processes, now we will start the new topic Adsorption and Ion Exchange.

**Adsorption:**

Adsorption is a unit operation in which one or more components are separated from a mixture of gases using a liquid solvent. In this operation, selective gaseous components exchange their hands with the liquids and dissolve to form a solution. This operation is very important for different industrial applications, such as separation of ammonia from air-ammonia mixture using water in ammonia plant, objectionable  $H_2S$  and  $CO_2$  separation from flue gas using amine as absorbent, etc. Suitable absorption equipment, namely, tray tower, packed column, spray tower, venture scrubber, etc. are generally used to achieve a desired separation. When dissolved gaseous components transfer back to the gaseous phase, is known as stripping which is reverse of absorption operation.

**Adsorbent:** The solid that adsorbs a component is called adsorbent.

**Adsorbate:** The component adsorbed is called adsorbate.

**Sorption:** Selective transfer of molecules of a mixture to the surface or into the bulk of a solid (or liquid) is called sorption.

**Types of Adsorption:**

The types of adsorption namely physisorption and chemisorption are discussed thoroughly. In addition, the nature of adsorbents is also discussed. Single state and multistage adsorption processes are discussed in detailed.

**Physical adsorption or van der Waals adsorption**

Physical adsorption is a reversible phenomenon which is a result of intermolecular force of attraction between molecules of the adsorbent and the adsorbate.  $\Delta H$  varies between 20-40 KJ/mol.

### Chemical adsorption:

- ✓ Chemical adsorption is an irreversible phenomenon which is a result of bond formation between atoms of the adsorbent and the adsorbate.  $\Delta H$  varies between 80-240 KJ/mol.
- ✓ Chemisorption process requires activation energy. Once it is achieved, it releases a higher amount of energy than physisorption because of co-valent bond formation in terms of isosteric heat of adsorption.

### Comparison between physisorption and chemisorption:

| <u><i>Physical adsorption</i></u>          | <u><i>Chemical adsorption</i></u> |
|--|-----------------------------------|
| Weak vander Waals force                    | Chemical bond formation           |
| Favoured at low temperature                | Favoured at high temperature      |
| Activation energy not required             | Activation energy required        |
| Reversible                                 | Irreversible                      |
| Low enthalpy of adsorption                 | High enthalpy of adsorption       |
| Non specific                               | Specific in nature                |
| Multi-molecular layer on adsorbent surface | Mono-layer is possible            |

### Commercial Adsorbents and their Applications:

#### (a) Activated Carbon

- It is a microcrystalline non – graphitic form of carbon.
- Commercially used activated carbon may be of two important types:

### 1. Powdered Activated Carbon (PAC)

**Application** : Decolorization of food products, sugar refining, wine production, water treatment (drinking), refining vegetable oils and fats.

### 2. Granular Activated Carbon (GAC)

**Application** : Solvent recovery from vent gases (like alcohol, ketones etc.), air purification, flue gas desulfurization

## (b) Molecular Sieves (or synthetic Zeolites)

These are crystalline aluminosilicates of metals like sodium, potassium, magnesium or calcium.

- Starting materials for zeolite preparation are sodium aluminate, silicate and hydroxide, alumina tri hydrate ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ), colloidal silica and silicic acid.
- Reaction of ingredients is followed by gel formation under controlled conditions.
- Then gel is crystallized slowly.
- Crystal is filtered, washed, ion exchanged to replace sodium with suitable cation.
- These have both adsorption and catalytic properties.
- Commercial molecular sieves are generally of types A or X.

Type A : 3A, 4A and 5A

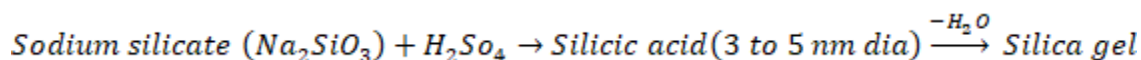
Type X : 10X, 13X

### **Applications:**

- Used for separation of aromatics.
- Used as catalyst – depends upon ability of selective adsorption.
- Used for removal of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  from gas,  $\text{H}_2\text{S}$  from natural gas, mercaptans from petroleum fraction.
- Used for separation of n – paraffins from their branched or cyclic counter parts.

## (c) Silica Gel:

- It is hydrophilic and very polar material due to presence of –OH group.



- Silica gels is of two types :

A type → 2-3 nm; Specific surface area: 650 m<sup>2</sup>/gm

B type → > 7 nm; Specific surface area: 450 m<sup>2</sup>/gm

**Application** : Drying of air and natural gas, drying of liquid hydrocarbons and other gases.

#### **(d) Activated Alumina**

- This is basically a highly porous  $\gamma$  - alumina.  
➤ It is manufactured from precipitated aluminum hydroxide gel.

Pore size : 1.5 – 6 nm.

Specific surface area : 200 – 400 m<sup>2</sup>/gm

Bulk density : 700 – 900 kg/m<sup>3</sup>

Porosity : 0.4

#### **Application** :

- Dehydrating agent for both gases and liquids.  
➤ Drying of air (air liquefaction plant), hydrocarbons, SO<sub>2</sub>, refrigerants drying of kerosene, gasoline, aromatics.

#### **Characteristics and Properties of Adsorbents:**

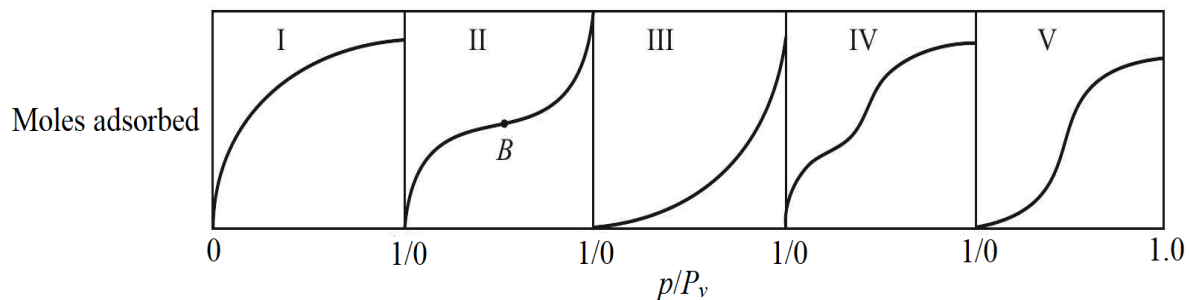
- Selectivity – selectively binding of target components.
- Adsorption capacity – should be high so that adsorbent requirement will be low.
- Reversibility of adsorption – for recovery of adsorbate and reuse of adsorbent.
- Particle size and its distribution.
- Porosity and pore size distribution – high porosity and narrow pore size distribution.
- Specific surface area.
- Structural strength and stability

### Adsorption Equilibria:

- ✓ Adsorption and desorption of molecules occur simultaneously.
- ✓ With fresh adsorbent, rate of adsorption is more than rate of desorption.
- ✓ These rates will be equal and adsorption equilibria is established.
- ✓ At a constant temperature, amount adsorbed per unit mass of adsorbent depends on partial pressure of adsorbent in gas phase (or concentration in case of adsorption from a solution.)
- ✓ The equilibrium relation between the amount adsorbed  $q$  and the concentration  $C$  of the adsorbate or solute at a constant temperature  $T$ , is called **adsorption isotherm**.

$$q = q(C)$$

### Adsorption Isotherms



Type I – favorable :  $O_2$  adsorption on carbon black at  $-183^\circ\text{C}$  on concave downward.

Type II – BET type : multilayer  $\rightarrow$  adsorption of water vapor on carbon black at  $30^\circ\text{C}$ .

Type III – unfavorable : adsorption of  $N_2$  on ice.

Type IV & V – alternating convex and concave (capillary condensation with in pores).

## Langmuir isotherm:

### Assumptions:

- » Molecules are adsorbed at the discrete active sites on the surface.
  - » Each active site adsorbs one molecule only
  - » Adsorbing surface is energetically uniform
  - » There is no interaction among adsorbed molecules
- » Now we will be discussing few of the isotherms these most common isotherm is Langmuir isotherm. So that is widely used, scientist Langmuir actually first observed that type of adsorption behavior and after his name this isotherm is this one termed as Langmuir isotherm but for that say few assumptions are there like this molecules are adsorbed at the discrete active sites on the surface then each active site adsorbs one molecule only and say that is why we can say energetically all the active sites are equivalent like this and adsorbing surface is energetically uniform.
- » There is no interaction among the adsorbed molecules like this but it should not be whenever one molecule will be taking one particular place whenever in the periphery when other molecules will be coming definitely this will interact but we are ignoring that interaction among the adsorbed molecules or adsorbed, so that is why as a result the rate of capture of the molecules of the surface is proportional to the uncovered area so  $1 - \theta$  and the partial pressure of the concentration. So that is why we can say this rate of adsorption process is equal to say  $k_1 p (1 - \theta)$  that is definite one.
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As a result, rate of capture of adsorbate molecules by the surface is proportional to the uncovered area,  $(1 - \theta)$  and partial pressure or concentration of adsorbate.

$$\text{rate of adsorption} = k_1 p (1 - \theta)$$

Rate of desorption is proportional to the fraction of surface covered only.

$$\therefore \text{rate of desorption} = k_2 \theta$$

At equilibrium,  $k_1 p(1 - \theta) = k_2 \theta$

$$\theta = \frac{Kp}{1 + Kp} \text{ where } K = \frac{k_1}{k_2}$$

$\theta = \frac{q}{q_m}$  where  $q$ =amount of gas adsorbed per gm of adsorbent

$q_m$  = maximum quantity of gas adsorbed per gm adsorbent

$$q = q_m \frac{Kp}{1 + Kp}$$

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

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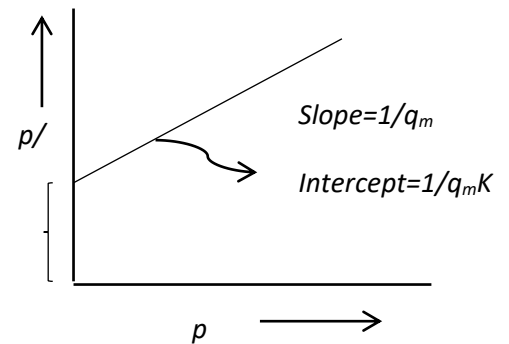
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$$\frac{q}{q_m} = \frac{Kp}{1 + Kp} ; \boxed{q = q_m \frac{Kp}{1 + Kp}}$$

Langmuir Isotherm

$q \rightarrow$  amount adsorbed / gm adsorbent  
 $q_m \rightarrow$  maximum quantity of gas adsorbed / gm

at low  $p$  ;  $Kp \ll 1$

$$\boxed{q = q_m Kp = K_H p}$$

Henry's law

- » Where we can say this  $\theta$  is equal to say  $q$  by  $q_{\text{max}}$  we can say that is equal to capital  $K$  into  $p$  by  $1$  plus capital  $K$  into  $p$  or we can say  $q$  is equal to  $q_{\text{m}}$  into capital  $K$  into  $p$  by  $1$  plus capital  $K$  into  $p$ . So this equation is called say this Langmuir isotherm, where this  $q$ ,  $q$  is equal to we can say this amount adsorbed per unit mass whereas  $q_{\text{m}}$  is the we can say this one maximum capacity. So this  $q$  equal to we can say this one amount adsorbed per gram adsorbent and  $q_{\text{m}}$  is equal to maximum quantity of say gas or adsorbed or whatever may be adsorbed per gram adsorbent okay.
- » So at very low partial pressure or we can say when the adsorbed content is very less then what will happen this in this equation say we can say this  $Kp$  that will be we can say much-much lower than  $1$ . So whenever  $p$  is very less then what will happen this  $q$  will be equal to  $q_{\text{m}}$  so  $Kp$  will be much-much lower than  $1$  means this is then will be like this  $q_{\text{m}}$  into  $k$  into  $p$ , that will be so this  $q_{\text{m}}$  into  $p$  we can convert this into  $K_h$  into  $p$  so I think we know all this-this  $h$  is we can say Henry's Law constant, so this  $K_h$  is this Henry's law constants. So it is like we can say it is a linear one, we can say then we can say so this equation is the form of we can say linear isotherm.
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Low  $p \rightarrow$  linear isotherm  
 \* At large  $p$ ,  $Kp \gg 1$

$$q = q_{\text{m}} \frac{Kp}{1 + Kp} = q_{\text{m}} \Rightarrow \theta = 1$$

$q = q_{\text{m}} \frac{Kp}{1 + Kp} \rightarrow$  Linear form

$$\frac{p}{q} = \frac{1}{q_{\text{m}} K} + \frac{p}{q_{\text{m}}}$$

$\frac{S}{I} = \frac{\frac{1}{q_{\text{m}}}}{\frac{1}{q_{\text{m}} K}} = K$

$\frac{p}{q} \left\{ \begin{array}{l} S = \frac{1}{q_{\text{m}}} \\ I = \frac{1}{q_{\text{m}} K} \end{array} \right.$

- » So we can say whenever at low  $p$  it is a linear form of the linear isotherm okay and say we can say this one at large  $p$  we can say capital  $K$  into  $p$  will be much-much greater than



1 then will be  $q$  will be like this,  $q$  is equal to we can say  $q_m$  into  $K_p$  by  $K_p$  okay, so that will be like this  $q$  will be equal to  $q_m$  that is equal to  $q_m$ .

- » So that is we say whatever  $\theta$  we say this one or so that is will be equal to so we can say this 1, okay. So  $q$  is equal to so  $q$  is equal to  $q_m$  into  $K_p$  by  $K_p$  that will be equal to say  $q_m$  that is we can say this equal to then we can say this one this  $\theta$  will be equal to 1 okay, so  $q$  by  $q_m$  is equal to  $\theta$  is equal to 1. So we can say so that is we can say this one form where will be maximum amount adsorbed per unit mass of this adsorbent will be there is only unit or we can say this one as 1, okay.
- » Now we can rearrange the Langmuir equation say  $q$  is equal to  $q_m$  into capital  $K_p$  by 1 plus  $K_p$  so in the linear form in the say we can say this one in the linear form it will be like this  $p$  by  $q$  is equal to  $1$  by  $q_m$  into  $k$  plus  $p$  by  $q_m$ . So this is the linear just if we do the manipulation we will be getting like this one and then we need to plot this  $p$  by  $q$  versus we can say this one if we plot  $p$  then we will be getting one just it is we can say  $y$  is equal to  $m x$  plus  $c$  so then we can say this intercept that is will be equal to we can say  $1$  by  $q_m$  into  $k$ , this intercept will be  $1$  by  $q_m$  into  $K$  this one,  $m x$  this one and slope this  $m$  will be slope will be say we can say  $1$  by  $q_m$ , okay.
- » So now we have slope by intercept is equal to  $1$  by  $q_m$  divided by  $1$  by  $q_m$  into  $k$  so that is we can say it is coming out as  $1$  by  $q_m$ ,  $1$  by  $q_m$  that is say  $K$ . So slope by intercept actually will give this  $k$  is nothing but  $k_1$  by  $k_2$ , okay. So from there slope by intercept will be getting this capital  $K$  okay, so that will be getting.
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### Freundlich Isotherm

This is an empirical isotherm which assumes that the amount adsorbed at equilibrium has power law dependence on partial pressure (concentration) of the solute,

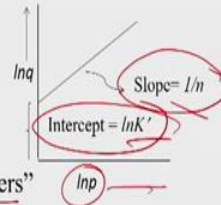
Freundlich isotherm represents,

$$q = K' p^{1/n}$$

$$\ln q = \ln K' + \frac{1}{n} \ln p$$

Two parameter isotherm.  $K'$  and  $n$  are “adjustable parameters”

- Adsorption on surface that is energetically non uniform.
- As a result, heat of adsorption at different sites is not same.

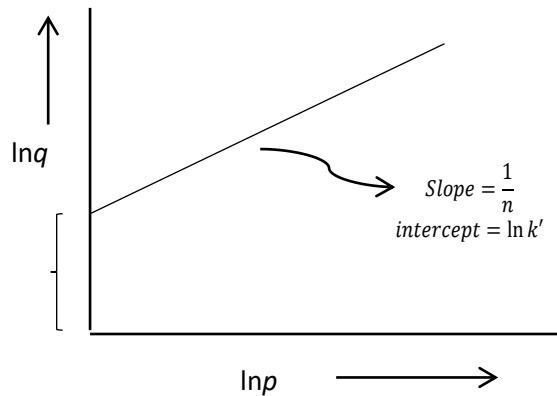


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This is an empirical isotherm which assumes that the amount adsorbed at equilibrium has power law dependence on partial pressure (concentration) of the solute,

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

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



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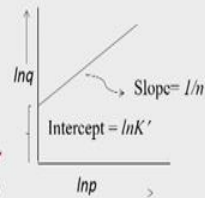
### Freundlich Isotherm

- $n$  varies between 1 and 5. For  $n=1$ , Freundlich equation transform into Henry's equation.

$$q = K_h p^{1/n}$$

- Freundlich isotherm is practically useful and can fit many experimental adsorption data.

- It is thermodynamically inconsistent in the sense that it can not give a finite value of Henry's law coefficient as the concentration/partial pressure tends to zero.



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- » Then third one, this one we can say this for the  $n$  values actually varies between 1 to 5 and for  $n$  is equal to 1 form the equation transforms into Henry's equation that we have seen this one say suppose say  $q$  will be equal to  $k$  into  $p$  because this one  $K_h$  actually is there  $K_h$  into  $p$  to the power 1 by 1 like this will be like this  $q$  is equal to  $K_h$  into  $p$ . So for only isotherm is practically useful and can fit many experimental adsorption rate of points also, will be solving two problems and this will fit this one in a very good extent for so many applications or so for so many industrial this adsorption processes.
- » But it is thermodynamically inconsistent in the sense that it cannot give a finite value of Henry's law coefficient that is  $K_h$  value, this one as concentration or partial pressure tends to 0. Whenever we can say this one  $P$  will be tending to 0 that time actually we can say this one Henry's constant coefficient or  $K_h$  value will not be getting a finite value that is we can say inconsistency in terms of the thermodynamic consideration.
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### Toth Isotherm

This is an empirical isotherm useful for the correlation of equilibrium adsorption data on heterogeneous adsorbents like activated carbon.

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

It is three parameter isotherm,  $q_m$ ,  $b$  and  $n$ .

Valenzuela and Myers (1989) used this isotherm to correlate adsorption data for a large number of systems.

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**BET Equation (Braunauer-Emmet-Teller equation)**

The BET equation represents multilayer adsorption equilibria for many systems. The equation is given as

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

$q_m$  = quantity of gas to be adsorbed to form monolayer/gm adsorbent

$$x = \frac{p(\text{partial pressure})}{p^v(\text{vapor pressure of adsorbent})} = \frac{p}{p^v}$$

$c'$  → temperature dependent constant for a particular gas-solid system

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$c' \rightarrow$  temperature dependent constant for a particular gas-solid system

***Assumptions:***

- » Heat of adsorption remains constant till the formation of monolayer is complete.
- » For secondary layer, heat of adsorption is assumed to be equal to heat of liquefaction of adsorbate.

**Determination of specific surface area of solid:**

The projected area,  $\alpha$  of an adsorbed molecule can be calculated from following equation.

$$\alpha = 1.09 \left( \frac{M}{N\rho} \right)^{2/3} \text{ where } M \text{ is molecular weight of adsorbate}$$

N is Avogadro's number

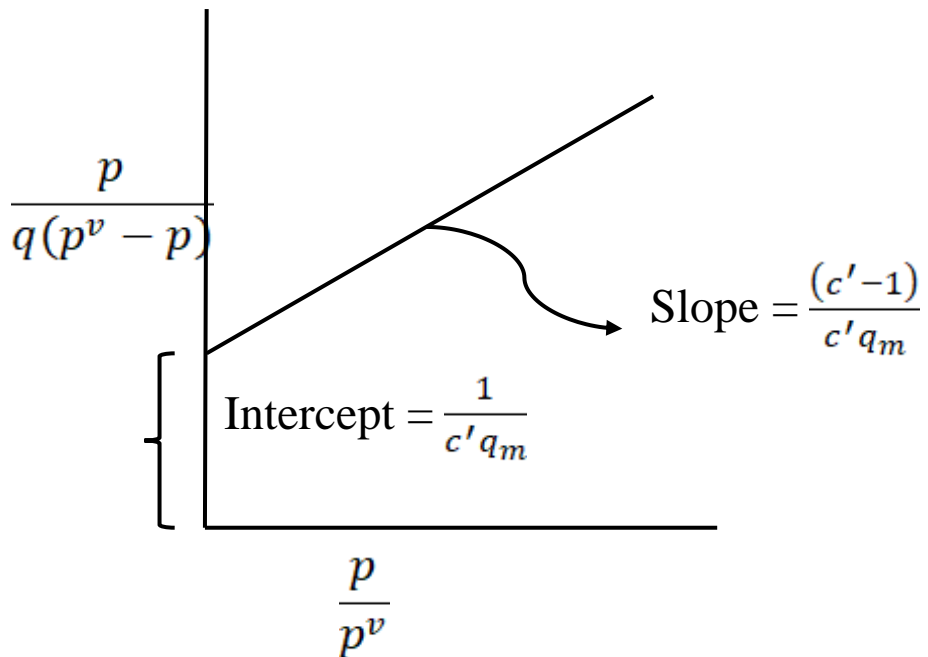
$\rho$  is density of the adsorbate in adsorbed phase

The specific surface area,  $S_g$  is given by

$$S_g = q_m N \alpha$$

To calculate  $q_m$ , putting  $x = \frac{p}{p^v}$  in BET equation.

$$\frac{p}{q(p^v - p)} = \frac{1}{c' q_m} + \frac{(c' - 1)p}{c' q_m p^v}$$



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Specific surface area:  $S_g = q_m \times N_A \alpha$

$$\alpha = \frac{p}{p_v}$$

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- » So and then will be this one the specific surface area we know that we can say this specific surface area  $S_g$  is obtained by using this equation that we have already derived this one, this into alpha where this specific surface area  $S_g$  is equal to  $q_m$  that is how much amount adsorbed for making monolayer,  $n$  is the Avogadro number and alpha is this we can say this one projected area, okay.
- » So now say we need to calculate this  $S_g$  for that actually we need to calculate this  $x$ , will be calculated this  $p$  by  $P_v$  in the this one BET equation.
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#### BET Equation (Braunauer-Emmet-Teller equation)

The BET equation represents multilayer adsorption equilibria for many systems. The equation is given as

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

$q_m$  = quantity of gas to be adsorbed to form monolayer/gm adsorbent

$$x = \frac{p(\text{partial pressure})}{p^v(\text{vapor pressure of adsorbent})} = \frac{p}{p_v}$$

$c'$  → temperature dependent constant for a particular gas-solid system

»

- » So in this BET equation this  $q$  is equal to  $q_m$  into  $c$  prime by  $1 - x$  into  $1 + c$  prime minus  $1$  into  $x$  there will be putting this  $x$  is equal to  $p$  by  $P_v$  okay.



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Specific surface area:  $S_g = q_m \times N_A$

$$x = \frac{p}{P_v}$$

$$\frac{p}{q(p^0 - p)} = \frac{1}{c' q_m} + \frac{(c' - 1)p}{c' q_m p^0}$$

$$S + I = \frac{c' - 1}{c' q_m} + \frac{1}{c' q_m}$$

$$S = \frac{c' - 1}{c' q_m}$$

$$I = \frac{1}{c' q_m}$$

$$S + I = \frac{1}{q_m}$$

$$q_m = \frac{1}{S + I}$$

$$S_g = (q_m) N_A$$

- » So then we will be getting this  $p$  by  $q$  into  $P_v$  minus  $p$  that will be equal to  $1$  by  $c$  prime into  $q_m$  plus  $c$  prime minus  $1$  into  $p$  divided by  $c$  prime into  $q_m$  into vapor pressure, okay. Now we have this one, we have this we can in straight line equation okay, so what we will be doing now? We will be plotting this  $p$  by  $P_v$  versus this  $p$  by  $q$  into  $P_v$  minus  $p$ , so this  $y$  versus  $x$  so  $y$  is equal to say we can say  $m x$  plus  $c$  then we have also now this intercept is equal to we can say intercept is equal to  $1$  by  $c$  prime into  $q_m$  and the slope will be slope is  $c$  prime minus  $c$  by  $c$  prime into  $q_m$ , okay  $q_m$  this  $p$  by  $P_v$ . So then we have this we can say the we will be now doing this one, we will be doing this slope plus intercept.
- » In case of this BET we will be adding this slope and intercept so now we will be getting like this one will be equal to  $c$  prime minus  $1$   $c$  prime into  $q_m$  plus intercept is  $1$  by  $c$  prime into  $q_m$ , that will be giving us  $c$  prime,  $c$  prime this  $1$  by  $q_m$  prime minus this one, so  $1$  by  $q_m$ . So this slope plus intercept will give this  $1$  by  $q_m$  then we can say this  $q_m$  this how much amount of this one solute actually or adsorbed will be forming this monolayer that will be  $1$  by slope plus intercept. So that is we have, now we are able to get this one, okay.
- » So once we get this one, so from there actually we can say this one  $S_g$  will be getting once we have this  $q_m$ . So then we will be getting this suppose this we know this now  $S_g$

is equal to this specific surface area is equal to  $q_m$  will be getting just by this reversing this slope and intercept, slope plus intercept, so we will be getting this we have this  $q_m$  and we know this Avogadro number and then  $\alpha$ . So now we will be able to get this specific surface area okay.

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**Sips Isotherm**

This isotherm equation combines the Langmuir and the Freundlich equation in the following form.

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

$q_m$  = adsorption capacity.

$k''$  = affinity coefficient.

$n$  = gives a measure of system heterogeneity.

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» Now we will be discussing this another isotherm that is Sips Isotherm though it is not widely used but in some cases we can say this one if we combine the Langmuir and Freundlich isotherm we will be getting one another isotherm, this is we can say also empirical isotherm,  $q$  is equal to  $q_m$  into  $k''p$  to the power  $1/n$  by  $1 + (k''p)^{1/n}$  where this  $q_m$  is the we can say this one adsorption maximum, adsorption capacity  $k''$  is affinity coefficient and  $n$  gives the measure of the system heterogeneity that is also we can say this one constant for a particular system, so it is one empirical isotherm.

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### Heat of Adsorption:

Three types: Now we will be discussing about the heat of adsorption, so there are three different types of heat of adsorption values. One is the differential heat of adsorption then second one is integral heat of adsorption and third one is isosteric heat of adsorption out of these we will be more interested in the isosteric heat of adsorption.

So in case of the differential heat of adsorption rate of change of the integral heat of the adsorption with adsorbent loading will be there for the case of the integral heat of adsorption, total enthalpy change from 0 adsorbent loading to the final loading at temperature T will be there and for isosteric heat of adsorption similar electronic arrangements of the chemical compounds that is active sites are energetically homogeneous we assume this one and heat of adsorption independent of adsorbent loading and when the temperature will be changing for calculating this isosteric heat of adsorption we need to change the temperature from T1 to T2 and that time actually will be getting this one. Will be calculating the from the thermodynamic consideration, okay. So that will be doing like this one using this Clausius Clapeyron equation.

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Exothermic process:  $\Delta G = \Delta H - T\Delta S$

Clausius-Clapeyron Equation

$$(\Delta H)_{\text{isosteric}} = -RT^2 \frac{d \ln p}{dT} = R \frac{d \ln p}{d(1/T)}$$
$$d \ln p = \frac{(\Delta H)_{\text{isosteric}}}{R} d\left(\frac{1}{T}\right)$$

The graph shows  $\ln p$  on the y-axis and  $1/T$  on the x-axis. A straight line with a negative slope is drawn through two points corresponding to temperatures  $T_1$  and  $T_2$ . The slope of this line is labeled as  $S = \frac{(\Delta H)_{\text{isosteric}}}{R}$ .

So like this if we say the adsorption process is exothermic process so we can say  $\Delta G$  will be equal to  $\Delta H - T\Delta S$  okay, so where  $\Delta G$  will be actually negative okay so then using this Clausius Clapeyron equation will be getting this  $\Delta H$  that is well known isosteric will be

equal to minus  $RT^2 \frac{d \ln p}{dT}$  is equal to  $R$  into say if we enter this one inside this  $dT$  so  $R$  into  $\ln p$  by  $d \ln p$ , so this negative will be coming along with  $T^2$ .

So we can say this  $d \ln p$  will be  $\Delta h_{\text{isosteric}}$  by  $R$  into  $d \ln p$  okay. So will be doing one thing say will be changing the temperature from  $T_1$  to  $T_2$  suppose if we plot now  $\ln p$  by  $T$  so differential one of the  $\ln p$  by  $T$  so we will be getting like this, say we can say so increasing the temperature or we can say this one if we decrease this  $\ln p$  by  $T$ , so we can say this one suppose this is for  $T_1$  and this is for  $T_2$ , so for this we will be getting one  $p$  and for this one will be this  $p$ .

So differential of  $\ln p$  will be plotting here suppose  $\ln p$  is plotted here so differential of  $\ln p$  will give this one differential  $\ln p$  by  $T$  like this, so this is we can say this one for this is  $\ln p$  by  $T_1$ , this is  $\ln p$  by  $T_2$ . So this is  $\ln p$  by  $T_1$ , this is  $\ln p$  by  $T_2$  so will be getting that type of things or straight line, this slope will be like this  $\Delta h_{\text{isosteric}}$  by  $R$ .

So from here actually will be getting this  $R$  is the universal gas constant, so will be getting this  $\Delta h_{\text{isosteric}}$  from this equation or from this experimentation. So if we change the temperature from  $T_1$  to  $T_2$  and if we plot  $\ln p$  by  $T$  versus  $\ln p$  by  $T_2$  and differential one with this differential logarithm pressure will be getting this we can say straight line and the slope will give the we can say this enthalpy values, isosteric heat of adsorption process.

### **Selection of Adsorbents:**

- a) Ease of separation: If relative volatility of component in a mixture is close to unity, one specific component can be separated easily by adsorption.
- b) Solute Concentration: A low concentration of target component in feed can be easily separated by adsorption.
- c) Process Condition: Adsorption is effective if product is susceptible to thermal damage.
- d) Adsorbent criteria: Adsorption capacity, mass or volume of solute adsorbed/unit mass of adsorbent.

### **Problem 1:**

The following data have been collected on equilibrium adsorption of nitrogen on an oxidation catalyst at 77.4K, the normal boiling point of nitrogen. Determine the specific surface area of catalyst by BET technique.

$p^v = 760 \text{ mm Hg}$  at 77.4K. For liquid nitrogen,  $\rho = 0.808 \text{ gm/cc}$

| $P$ (Pressure of $N_2$ , mm Hg) | $V$ (Volume of $N_2$ adsorbed, $\text{cm}^3$ at NTP per 100 g solid) |
|---------------------------------|--|
| 10                              | 71.3   |
| 20                              | 142.2  |
| 40                              | 287.7  |
| 100                             | 679.4  |
| 150                             | 1025   |
| 200                             | 1053   |
| 250                             | 1175   |
| 300                             | 1316   |
| 350                             | 1996   |
| 400                             | 3451   |
| 500                             | 5283   |

| $P$ (Pressure of $N_2$ , mm Hg) | $\frac{p}{p^v}$ | $\frac{p}{v(p^v - p)}$ |
|---------------------------------|-----------------|------------------------|
| 10                              | 0.0132          | 0.0187                 |
| 20                              | 0.0263          | 0.019                  |
| 40                              | 0.0526          | 0.0193                 |
| 100                             | 0.1316          | 0.0223                 |
| 150                             | 0.1974          | 0.024                  |

|     |        |        |
|-----|--------|--------|
| 200 | 0.263  | 0.025  |
| 250 | 0.329  | 0.028  |
| 300 | 0.3947 | 0.03   |
| 350 | 0.4605 | 0.0293 |
| 400 | 0.5263 | 0.0322 |
| 500 | 0.6579 | 0.0364 |

### Solution:

Now we will be solving one problem very simple problem like the following data have been collected on equilibrium adsorption of the nitrogen on an oxidation catalyst at 77.4 kelvin. The normal boiling point of the nitrogen then now we need to determine the specific surface area  $S_g$  of the catalyst by BET technique where this vapor pressure is given the 760 millimeter mercury at 77.4 kelvin. For liquid nitrogen density is given as 0.808 gram per cc.

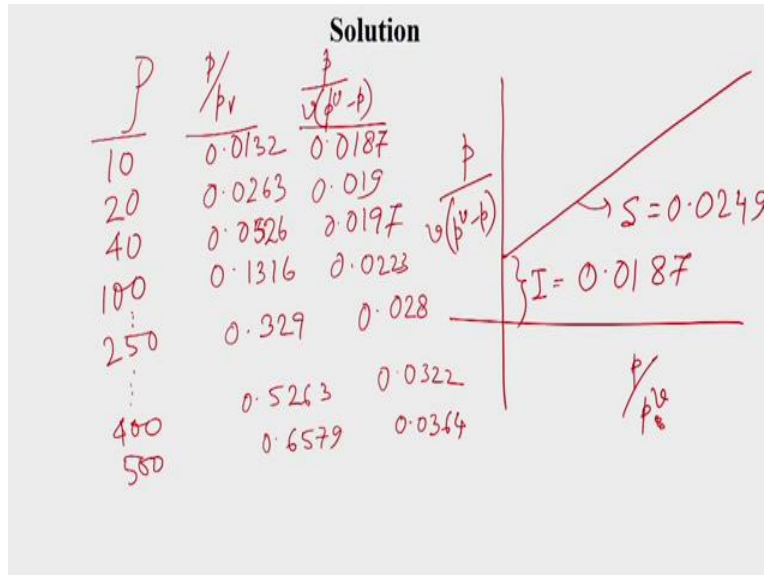
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| <i>P (Pressure of <math>N_2</math>, mm Hg)</i> | <i>V (Volume of <math>N_2</math> adsorbed, <math>cm^3</math> at NTP per 100 g solid)</i> |
|--|--|
| 10 ✓   | 71.3 ✓   |
| 20   | 142.2  |
| 40   | 287.7  |
| 100  | 679.4  |
| 150  | 1025   |
| 200  | 1053   |
| 250  | 1175   |
| 300  | 1316   |
| 350  | 1996   |
| 400  | 3451   |
| 500 ✓  | 5283 ✓   |

Okay, so this is a very simple problem for that the pressure as well as this volume these are given. Suppose this pressure is suppose 10 millimeter mercury then volume is 71.3 this we can say centimeter cube per 100 gram solid. So that way upto this 500 this millimeter mercury pressure the volume is given. So we have this pressure versus volume is there so from there

actually we will be getting all the other parameters for BET surface BET this one adsorption isotherm. For that will be doing we need to get finally what is the  $S_g$  value?

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So will be doing this one very systematically will be doing like this say we may be requiring few points but for the betterment of the result, we can do this one suppose this  $P$  like this  $P$  is 10 then we say  $p$  by  $P_v$  will be 0.0132 and say  $p$  by  $v$  into  $P_v$  minus  $p$  will be say 0.0187 like  $y$  number will be having this 20 then it will be like this 0.0263 then it will be 0.019.  $S_p$  when it is 40, so it is 0.0526 then it is 0.0193 okay.

So whenever the pressure is increasing to 100, so it will be like 0.1316 then this parameter  $p$  by  $v$  into  $P_v$  minus  $p$  will be 0.0223. So this way we can say for say let us say 250, we can calculate others also for 250 that  $P$  by  $P_v$  will be 0.329 and  $v$   $p$  by  $v$  into  $p_v$  minus  $p$  will be 0.028 so like this one if we say 400 will be getting 0.5263 and  $p$  by  $v$  into  $P_v$  minus  $p$  will be 0.0322 for 500 will be getting 0.6579 and this  $p$  by  $v$  into  $P_v$  minus  $p$  will be 0.0364.

Now will be plotting this one, in the say  $p$  by  $v$  into  $P_v$  minus  $p$  versus  $p$  by  $p_v$ . So now will be getting one equation straight line, so where actually will be getting this we need this slope, this slope will be actually from this graph if we use this graph paper then from there will be calculating but here actually we are putting this value 0.0249 and intercept actually you will be equal to 0.0187.

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**Solution**

$$q_m = \frac{1}{S+I} = \frac{1}{0.0249 + 0.0187} = 22.94 \frac{\text{cm}^3}{\text{gm}}$$

$$\alpha = 1.09 \left( \frac{M}{M_0} \right)^{\frac{2}{3}} = 1.09 \left( \frac{28}{6.023 \times 10^{23} \times 0.808} \right)^{\frac{2}{3}}$$

$$= 1.625 \times 10^{-15} \text{ cm}^2$$

$$S_g = \left( \frac{q_m N}{V} \right) \alpha = \frac{22.94 \times 6.023 \times 10^{23}}{1.625 \times 10^{-15}} \times 1.625 \times 10^{-15}$$

$$= 1.002 \times 10^6 \text{ cm}^2/\text{gm}$$

$$S_g = 100.2 \text{ m}^2/\text{gm}$$

Now will be getting this one just now we have solved this one that  $q_m$  is equal to 1 by slope plus intercept okay, so that is we can say this one 1 by slope is equal to 0.0249 plus intercept is equal to 0.0187 so it is coming out as 22.94 centimeter cube per gram of this adsorbent, okay and alpha that is we know this one that is 1.09 into M by M into rho to the power 2/3, okay so that is coming out as 1.09 into M is molecular weight is 28 for here and Avogadro number is 6.023 10 to the power 23 and density is given as 0.808 to the power two third.

Okay, so it is coming out as 1.625 into 10 to the power 15 centimeter square okay. So  $S_g$  will be equal to  $q_m$  into N by V into this alpha. So that will be coming out as 22.94 into 6.023 10 to the power 23 and into 1.625 into 10 to the power minus 15 divided by 22414. So that is the specific volume actually this we can say molar volume, so that is coming out as 1.002 into 10 to the power 6 centimeter square per gram or we can say 100.2 meter square per gram. Okay so this  $S_g$  we are getting as specific surface area, 100.2 meter square per gram.

So thank you very much and in the next class will be discussing about stage wise and continuous adsorption process.