Mass Transfer Operations II
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Lecture No. 26
Adsorption and Ion-exchange

Welcome back to mass transfer operations II course, we were discussing on adsorption and Ion-exchange.

Fluidized bed and Teeter bed, steady state moving bed and fmultiunsteady state fixed bed adsorbers:

A. Fluidized and teeter beds:

These are used to recover vapor from vapor-gas mixture, to fractionate light hydrocarbon vapors with carbon.

So in the beginning we need to learn about the different fluidized beds in should application of the adsorption processes and nowadays the use of this fluidized bed for the adsorption purpose is increasing gradually and these are used to recover vapor form this vapor gas mixture to fractionate the light hydrocarbon vapors with the carbon. And we need to consider bet of granular solids of thrho which a gas flows from the bottom and at low gas rates this gas suffers pressure drop which can be estimated by this Ergun equation like this.

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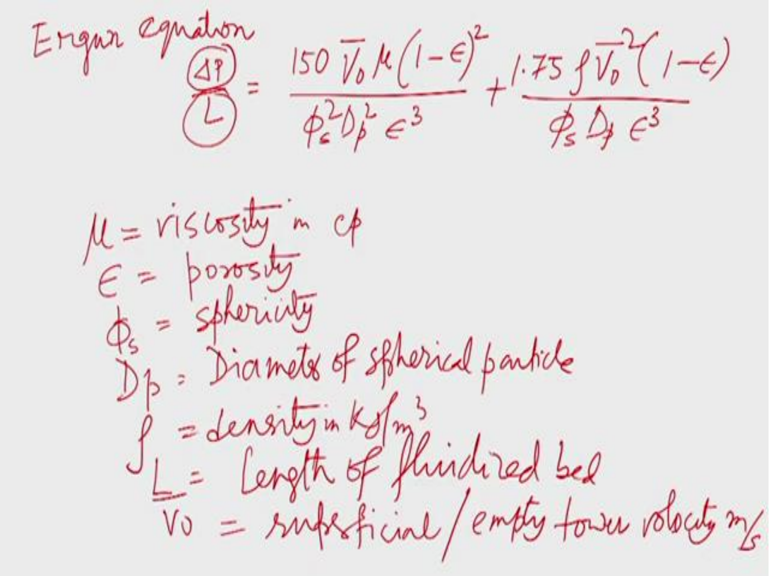
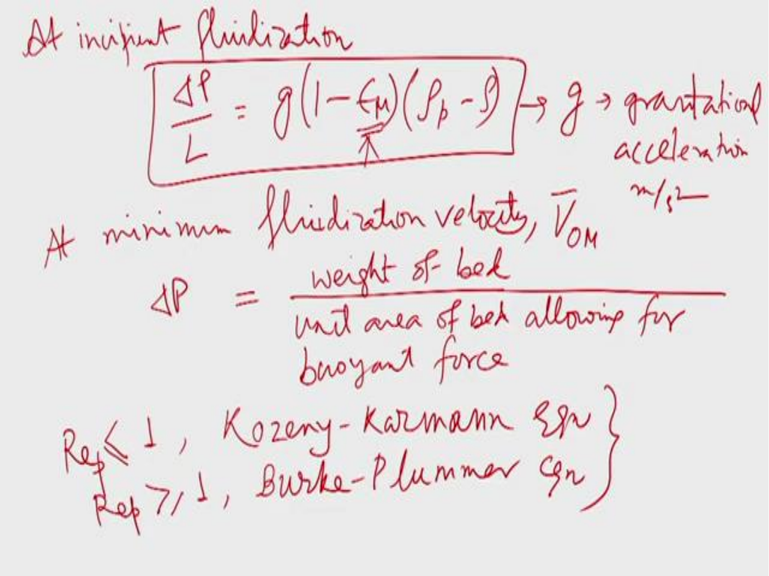


Ergun equation

$$\frac{\Delta P}{L} = \frac{150 \bar{V}_0 \mu (1-\epsilon)^2}{\phi_s^2 D_p^2 \epsilon^3} + \frac{1.75 \rho \bar{V}_0^2 (1-\epsilon)}{\phi_s D_p \epsilon^3}$$

μ = viscosity in cP
ϵ = porosity
ϕ_s = sphericity
D_p = Diameter of spherical particle
ρ = density in kg/m^3
L = Length of fluidized bed
V_0 = superficial/empty tower velocity m/s



At incipient fluidization

$$\boxed{\frac{\Delta P}{L} = g(1-\underset{\uparrow}{\epsilon_M})(\rho_p - \rho)} \rightarrow g \rightarrow \text{gravitational acceleration } m/s^2$$

At minimum fluidization velocity, $\bar{V}_{OM}$

$$\Delta P = \frac{\text{weight of bed}}{\text{unit area of bed allowing for buoyant force}}$$

$Re_p \leq 1$, Kozeny-Karmann eqn

$Re_p \gg 1$, Burke-Plummer eqn

These are used to recover vapor from vapor-gas mixture, to fractionate light hydrocarbon vapors with carbon.

Consider a bed of granular solids up through which a gas flows. At low gas rates, gas suffers a pressure drop which can be estimated by Ergun equation

$$\frac{\Delta P}{L} = \frac{150 * \bar{V_0} * \mu * (1-\epsilon)^2}{{\phi_S}^2 * {D_p}^2 * \epsilon^3} + \frac{1.75 * \rho * \overline{V_0^2} * (1-\epsilon)}{\phi_S * D_p * \epsilon^3}$$

Where μ= viscosity, cp

ϵ= porosity

ϕ_S= sphericity

D_p = diameter of the spherical particle

ρ = density

g= gravitational acceleration (m/s^2)

L= Length of the fluidized bed

$\bar{V_0}$ = superficial or empty tower velocity, m/sec.

At incipient fluidization,

$$\frac{\Delta P}{L} = g(1-\epsilon_M)(\rho_p - \rho)$$

At $\overline{V_{0M}}$, Pressure drop across the bed= weight of bed/unit area of bed allowing for buoyant force of the dispersed fluid

$$\frac{\text{Kozeny} - \text{carman equation}}{R_{ep} \leq 1} + \frac{\text{burke plummer equation}}{R_{ep} > 1000}$$

$$\frac{150*\overline{V_{0M}}*\mu*(1-\epsilon_M)^2}{\phi_S{}^2*D_P{}^2*\epsilon_M{}^3}+\frac{1.75*\rho*\overline{V_{0M}^2}*(1-\epsilon_M)}{\phi_S*D_P*\epsilon_M{}^3}=g(1-\epsilon_M)(\rho_P-\rho)$$

For small particle only laminar term is significant,

$R_{ep} \leq 1$ $$\overline{V_{0M}}=\frac{g*(\rho_P-\rho)*\epsilon_M{}^3*\phi_S{}^2*D_P{}^2}{150*\mu*(1-\epsilon_M)}$$

$R_{ep} > 1000$ $$\overline{V_{0M}}=\left(\frac{\phi_S*D_P*g*(\rho_P-\rho)*\epsilon_M{}^3}{1.75*\rho}\right)^{1/2}$$

- ✓ As gas velocity increases, pressure drop equals (wt. of solid/area)+friction of solids with wall.
- ✓ If gas velocity further increases, solid bed is enlarged, voidage increases…***quiescent fluidized bed***
- ✓ Further increase in velocity makes the bed like a boiling liquid
- ✓ This condition is used for adsorption.
- ✓ Solids are carried away with gas.
- ✓ A.M. Squires has distinguished between fluidized bed and teeter beds

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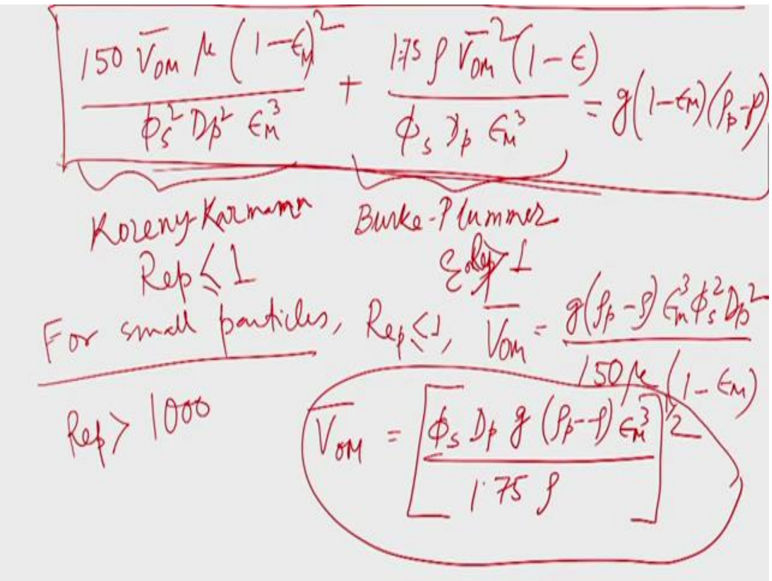

So whenever we have this particles Reynolds number ranging from very low Reynolds number to the higher Reynolds number so we have this combined form like whatever the first part is 150 V0m bar into mu into 1 minus epsilon m whole square divided by this phi s square into Dp square into epsilon m cube that is this part for Kozeny Karmann and 1.75 into rho into V0m bar square into 1 minus epsilon divided by phi s into Dp into epsilon m cube that will be equal to that is Del p by L that will be equal to g into 1 minus epsilon m into rho p minus rho.

So that this part Burke Plummer, this equation where RE particle that is greater than 1, where this part is RE particle less than equal to 1, so in that case so using this equation we will be able to get the we can say what is the minimum fluidization velocity for a particular material having this diameter with of the particle at Dp and the voidity as epsilon m so that we can get this one suppose for small particles only we have suppose small particles and where Reynolds number particle is less than equal to 1, then V0m bar that will be is equal to say from this equation we can say this one g into rho p minus rho into epsilon m cube into phi s square into Dp square so divided by 150 into mu into 1 minus epsilon m.

So that is if we do the manipulation or the second part of the left hand side of this equation that is will be vanished. So then for small particles like this whenever we can say if particles Reynolds number is very high, let us take for greater than 1000 like this. Then we have this in that case this minimum fluidization velocity will be equal to say this only second part will be their first part will be vanished, so by manipulation we will be getting that V0m is equal to phi s into Dp into g into rho p minus rho into epsilon m cube divided by 1.75 into rho this whole to the power 1 by 2. So in this case this minimum fluidization velocity will be this, so that way we will be getting the minimum fluidization velocity for different cases whenever we will be doing that adsorption process using the fluidized bed.

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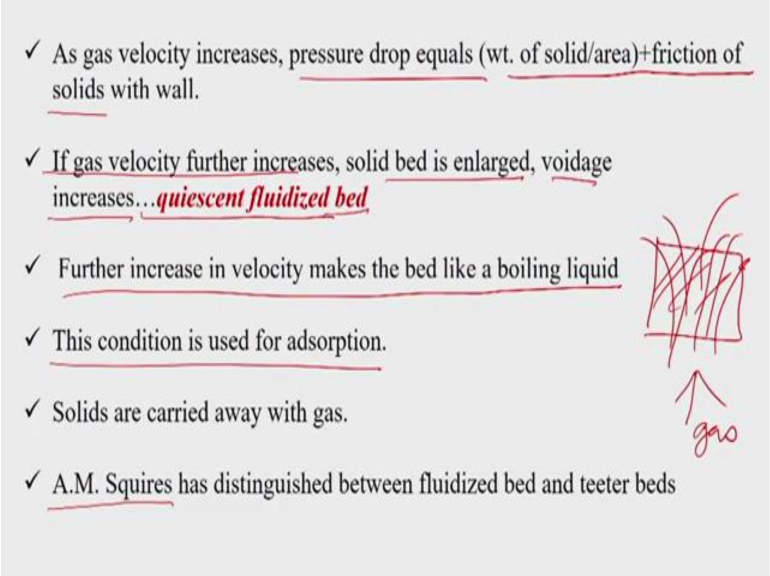


- ✓ As gas velocity increases, pressure drop equals (wt. of solid/area)+friction of solids with wall.
- ✓ If gas velocity further increases, solid bed is enlarged, voidage increases…*quiescent fluidized bed*
- ✓ Further increase in velocity makes the bed like a boiling liquid
- ✓ This condition is used for adsorption.
- ✓ Solids are carried away with gas.
- ✓ A.M. Squires has distinguished between fluidized bed and teeter beds

So then as we can say this velocity increases say then pressure drop actually equals this weight of solid plus friction of solids with the wall. So if gas velocity is further increased then solid bed will be enlarged and then voidage will be increased and then we say this one as quiescent fluidized bed, means the entire bed will be enlarged and then that is just before the fluidization like this of the entire solid material further increase in the velocity makes the bed like a boiling liquid so it will be like, so the entire thing will be boiled like the solids will be like your boiling.

Because we are applying this gas from the bottom and then suppose solids are placed here and then it will be like boiling like this. So this condition is used for the adsorption and in that this case the adsorption will be maximum. So solids are carried away with the gas so that then this one scientist A.M squires has distinguished between this fluidized bed and teeter bed. So these are almost the similar only the small small differences are them among these two beds.

Comparison between Fluidized bed and Teeter bed

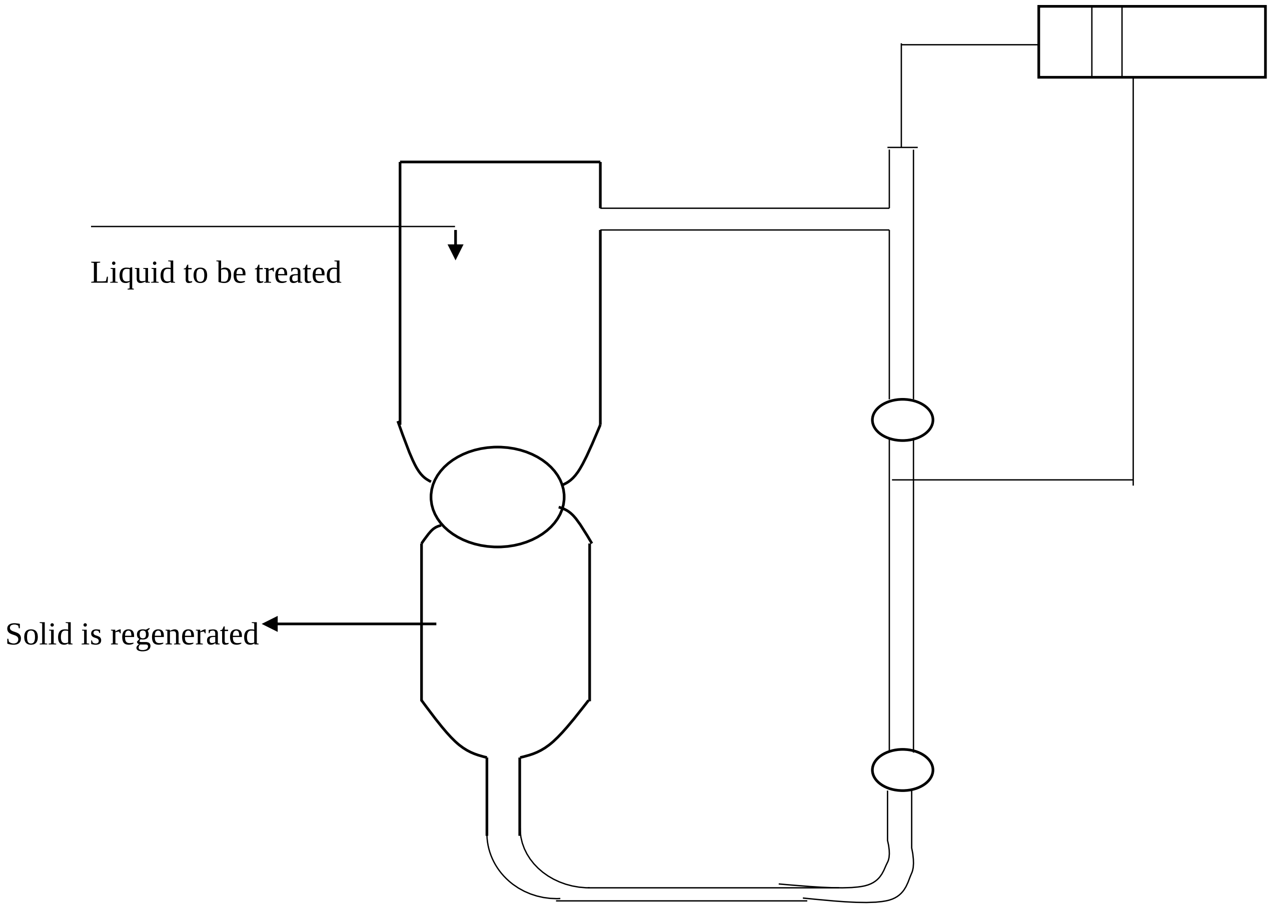
Fluidized beds	***Teeter beds***
Particle size: 20 mesh – 350 mesh	≤ 10 mesh , coarser particle
Superficial velocity: 0.6m/sec (10 times $\overline{V_{0M}}$)	1.5 – 3.0 m/sec (2 times $\overline{V_{0M}}$)
Lesser fluid solid contacting	Better fluid solid contacting
Solids are fluidized by gas only	Solids are fluidized by both gas and solid

B. Steady State Moving Bed Adsorber:

Contact operations between fluid and adsorbent are continuous steady state mode throughout the entire apparatus. This is characterized by movement of solid as well as fluid.

Requirement: movement of both adsorbent as well as fluid through adsorber and fluid through adsorber.

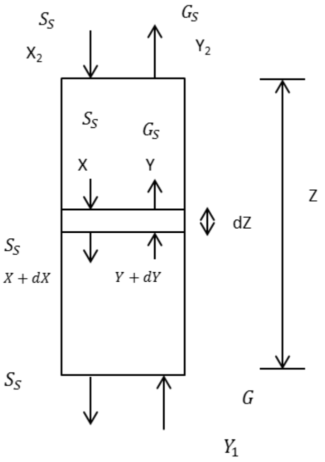
Higgins contractor



Solute balance: $G_s(Y_1 - Y_2) = S_s(X_1 - X_2)$

Rate of solute transfer over different height dz

$$S_S dX = G_S = K_Y a(Y - Y^*)dZ$$



$K_Y a \rightarrow$ Overall mass transfer coefficient based on a outside surface area of solid

$$N_{toG} = \int_{Y_2}^{Y_1} \frac{dY}{Y - Y^*} = \frac{K_Y}{G_S} \int_0^Z dZ = \frac{Z}{H_{toG}}$$

$$H_{toG} = \frac{G_S}{K_Y a}$$

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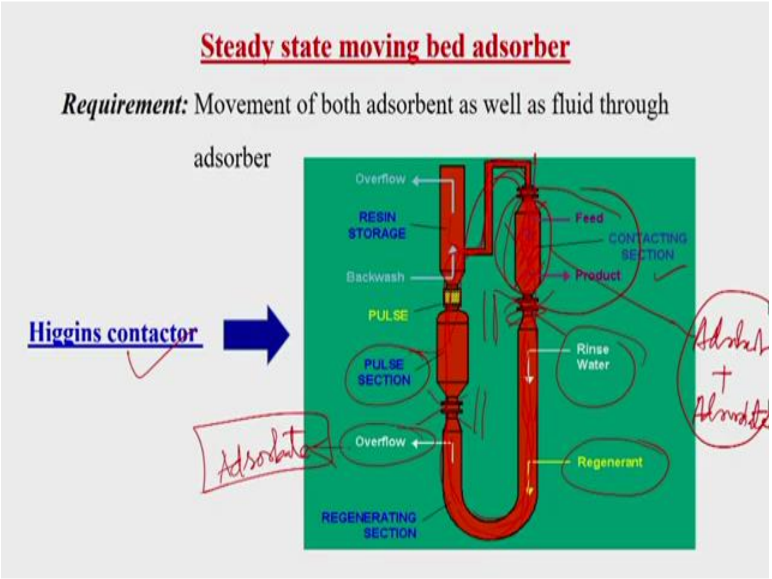

Steady state moving bed adsorber

Requirement: Movement of both adsorbent as well as fluid through adsorber

Higgins contactor

Now, we will be discussing about the solid state moving bed absorber, this is we can say the like this Higgins contactor this is very good in adsorbing this target components very efficiently using the solid materials and followed by regeneration and it is done steadily or as till now whatever we have discussed as we have the adsorbent and adsorbeds are sticked on the top of the adsorbent sides and once the adsorption process is over then all the adsorbents will be regenerated to use in the next adsorption process.

But in this case, we will be able to use the same adsorbents very efficiently for a continuous operation using the same adsorbent, so somewhere it will be adsorbed and at the same time other part will be regenerated. So like this if we say this is the contacting part so we can say suppose the adsorbents are placed here and we are feeding this feed from this top like this, then in this zone say suppose adsorption is taking place then this valve will remain closed and the bottom part actually we can say this one this is regeneration zone.

So here say suppose this valve actually we can say here also will remain closed so this one pulse section will be there, that will be used to we can say regenerated, we can say this to the adsorption process to have to be held here. So what is happening say in the beginning suppose in the first stage this adsorption process is going on, and at the same time whatever the adsorbed this one what is called solutes or adsorbents where there or exhausted adsorbents where there, these are now placed in this section just by say if we just pressurize the system then whatever the adsorbed material will be coming, what is it came actually from the previous operation.

Whenever it will be entering then say some reagents are added there along with some rinse water and this over flow is actually used to separate the target components or adsorbed so through over flow we can say adsorbed actually is separated during this regeneration process. So this regeneration process is like this temperatures showing or concentration showing that will be discussing in the next class and but you see, in the beginning using this pulse, suppose this adsorbed actually is entering here, and adsorbent is clouded here, this phase adsorbent.

So whenever we have this adsorption process then regeneration process will be going on parallel, so once the we can say it is entirely exhausted, then we need to open this valve and we need to open these 2 valves. Then what will be happening say the whatever the adsorbed solids or we can say this here so this adsorbent and adsorbed are adsorbed so these, both these will be taken to here, just by opening this valve and the total adsorbed and adsorbent will be coming here, and that time this is fresh adsorbent actually whatever was generated in the previous section, previous operation will be coming and filling this we can say the contacting chamber, so that way using this Higgins contactor the adsorption process is made continuous.

Though, these are of we can say batch type or semi batch type but the process will be going on in this way. So firstly in this contacting chamber with the fresh adsorbent, adsorbed will be added and at the same time in the regeneration chamber whatever the adsorbed and adsorbent were there, this will be regenerated means this through the over flow adsorbed will be separated so fresh adsorbent will be coming. So, in the next operation this fresh adsorbent actually will be dosing to this contacting chamber and at the same time whatever exhausted adsorbent and adsorbed will be there that will be come to regeneration chamber. So this is cyclic process at the same time we can say the fresh adsorbents will be coming and it will be attached, it will be adsorbing the adsorbed.

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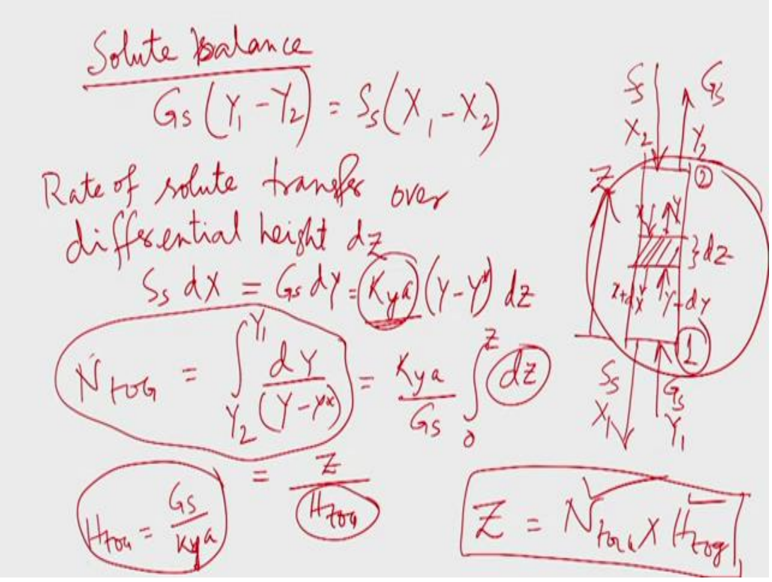


Solute Balance

$$G_s(Y_1 - Y_2) = S_s(X_1 - X_2)$$

Rate of solute transfer over differential height dz

$$S_s\,dX = G_s\,dY = K_ya\,(Y - Y^*)\,dz$$

$$N_{toG} = \int_{Y_2}^{Y_1} \frac{dY}{(Y - Y^*)} = \frac{K_ya}{G_s}\int_0^Z dz = \frac{Z}{H_{toG}}$$

$$H_{toG} = \frac{G_s}{K_ya}$$

$$\boxed{Z = N_{toG} \times H_{toG}}$$

So this if we do the mass balance actually in this bed like this suppose this is the adsorbent bed like this we can be say like whatever we have done in case of this humidification operation let us take suppose this gas is entering with this flow rate of g with this concentration of the target component of Y1 and say we can say it will be leaving this chamber like this with G or Gs whatever we can say this one if we say this one Gs then it is, then I can say Gs with Y2 this is station 1 this is station 2.

And whatever the adsorbed actually that is entering this one SS with we can say the concentration of x2 whenever it will be leaving the chamber then dry weight flow rate is SS with this solid concentration of x1, let us take one differential thickness of say dz because we assumed that this z direction will be say from point 1 to point 2 like this so dz will be there so through this we can say the both this liquid flow rate and gas flow rate will be or adsorbed flow rate and the whatever the adsorbent flow rate will be there suppose this is taking place here and we will be doing the simple mass balance.

And there we can say this if is we can say Y plus dY then it will be like Y and if it is X then it will be X plus say dX or the concentration of the target component in both the streams like then we can say if we do the solute balance so across this tower then it will be solute balance then will be Gs into say Y1 minus Y2, that will be equal to SS into x1 minus x2 and this rate of solute transfer over this differential height dZ will be like this, SS into dX is equal to Gs into dY will be is equal to Kya into y minus y star into dZ.

So where this Kya, we know this one over mass transfer coefficient actually based on this outside surface area we have already discussed this one previously and then we can say this

NTOG and STOG that also we have derived that is Y2 to Y1 will be having this dY by from here actually this one from this equation Y minus Y star that will be equal to Kya say that is we can say this constant parameter by Gs also that is as this is we can say this solute flue gases, so that will be also constant so we can say 0 to Z means from bottom to top that will be we can say this one dZ.

So it will be nothing but this NTOG will be nothing but that will be is equal to Z by HTOG where this that will be dZ and where HTOG will be we can say this HTOG that will be is equal to Gs by Kya so, this is STOG and NTOG will be like this NTOG will be coming from this expression so from there if we just multiply this NTOG and STOG then we will be getting Z because Z is equal to the multiplication of NTOG and STOG. So from these two we can say we will be getting if we know NTOG and STOG then we will be getting what is the height of this adsorber column.

Problem 4:

Adsorption of a pure gas A on activated carbon follows the Langmuir isotherm; $= \frac{6.4p}{1+1.53p}$; where *p* is in kPa and q in m mole/gm. If molecular weight of A is 65, what is maximum quantity of gas that can be adsorbed in kg adsorbate/kg carbon?

Solution:

Maximum adsorption occurs at large *p* i.e.,

$$q = q_m = \frac{6.4p}{1.53p} = 4.183 m\ mole/gm$$

$$= 4.183 \times 65 \times \frac{10^{-3} gm}{gm}$$

$$= 0.272\ {}^{kg}\!/_{kg\ adsorbent}$$

Problem 5:

Equilibrium adsorption data for propane on activated carbon at two different temperatures are given below. Fit the data using Langmuir isotherm and get the correlation coefficients (q_m; K). Determine the isosteric heat of adsorption.

T=310.9 K		***T=366.5 K***	
p (kPa)	***q (m mol/g)***	***p (kPa)***	***q (m mol/g)***
2.27	1.044	21.07	1.677
15.6	2.819	45.33	2.386
31.74	3.48	93.34	2.954
89.74	4.207	279.2	3.584
293	4.94	461.9	3.922
479.2	5.294	634.3	4.244

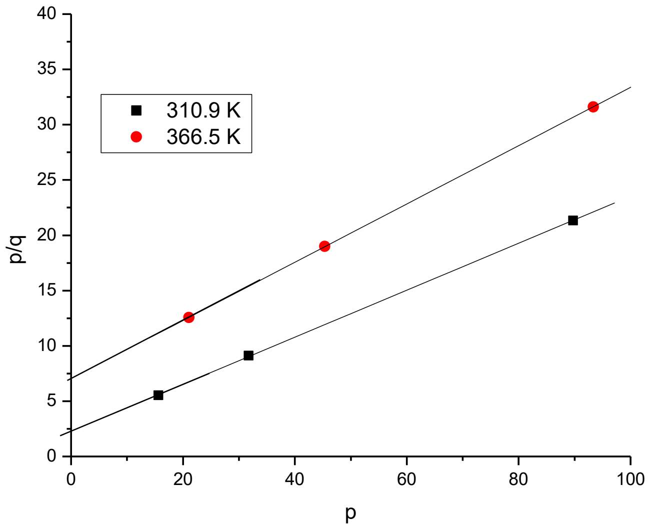
Solution:

At T=310.9 K,

q_m=4.695 m mole/gm; K=0.096 kPa^{-1}

At T=366.5 K,

q_m=3.802 m mole/gm; K=0.0374 kPa^{-1}



Say, q = 4 m mole/gm

Slope = -4745.46

$$(\Delta H)_{iso\ steric} = -RT^2 \frac{d\ln P}{dT}$$

$$= -4745.46 \times 1.987\ {}^{Kcal}\!\big/_{gm\ mole}$$

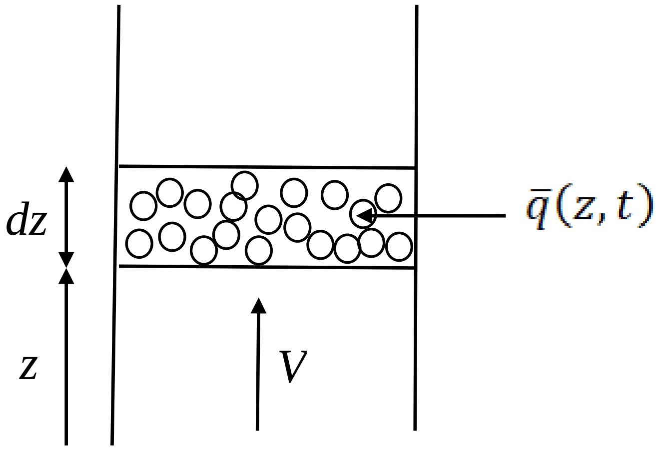
$$= -9.429\ {}^{Kcal}\!\big/_{gm\ mole}$$

Dynamics of Adsorption Columns:

Single transition systems

The differential mass balance equations for an element of the adsorption column and for an adsorbent particle within such an element provide the starting point for development of a mathematical model to describe the dynamic behaviour of the system.

- ✓ Fluid stream containing concentration $c(z,t)$.
- ✓ Axially dispersed plug flow.



The differential fluid phase mass balance is,

$$-D_L \frac{\partial^2 c}{\partial z^2} + \frac{\partial}{\partial z}(vc) + \frac{\partial c}{\partial t} + \left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \bar{q}}{\partial t} = 0$$

Mass balance for an adsorbent particle yields the adsorption rate expression

$$\frac{\partial \bar{q}}{\partial t} = f(q,c)$$

If the system contains two adsorbable components, rather than one adsorbable component in an inert carrier, mass balance equations may be written for both species.

Equilibrium Considerations:

- Three general cases can be distinguished depending on whether the equilibrium relationship is *linear*, *favourable*, or *unfavourable* over the concentration range corresponding to the transition considered.
- The *X*-*Y* diagram is simply a non dimensional representation of the equilibrium relationship, expressed in terms of the reduced variables $(q^* - q_o')/(q_o - q_o')$ and $(c - c_o')/(c_o - c_o')$

  where $(q_o - q_o')$ = respective changes in adsorbed phase

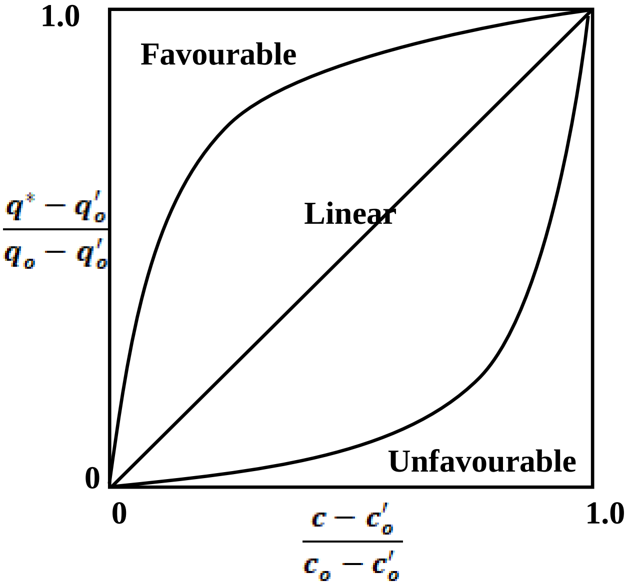
$(c_o - c_o')$ = respective changes in fluid phase concentrations over the mass transfer zone.

Three general cases,

Favourable → $\frac{q^* - q_o'}{q_o - q_o'} > \frac{c - c_o'}{c_o - c_o'}$

Linear → $\frac{q^* - q_o'}{q_o - q_o'} = \frac{c - c_o'}{c_o - c_o'}$

Unfavourable → $\frac{q^* - q_o'}{q_o - q_o'} < \frac{c - c_o'}{c_o - c_o'}$



Multiple transition systems:

Consider an element of the bed through which a stream containing concentration $c_i(z,t)$ of adsorbable species *i* is flowing.

The differential fluid phase mass balance equation for each component,

$$-D_L \frac{\partial^2 c_i}{\partial z^2} + \frac{\partial}{\partial z}(v c_i) + \frac{\partial c_i}{\partial t} + \left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \bar{q}_i}{\partial t} = 0$$

Particle mass balance yields the adsorption rate equation for each component,

$$\frac{\partial \bar{q}_i}{\partial t} = f(q_i, q_j, \ldots, c_i, c_j, \ldots)$$

Classification of Adsorption Systems:

1. Single-Transition Systems

(a) One adsorbable component plus inert carrier, isothermal or near isothermal operation.

(b) Two adsorbable components (no carrier), isothermal or near isothermal operation.

2. Two-Transition Systems

(a) Two adsorbable components plus inert carrier, isothermal operation.

(b) Three adsorbable components (no carrier), isothermal operation.

(c) One adsorbable component plus inert carrier, adiabatic operation.

(d) Two adsorbable components (no carrier), adiabatic operation.

3. Multiple-Transition Systems

(a) Four or more components, isothermal operation.

(b) Three or more components, adiabatic operation.

(c) Three components, isothermal operation with selectively reversal.

(d) Two components, adiabatic operation, with selectively reversal.

Consider an element of the bed through which a stream containing concentration $c_i(z,t)$ of adsorbable species *i* is flowing.

The differential fluid phase mass balance equation for each component,

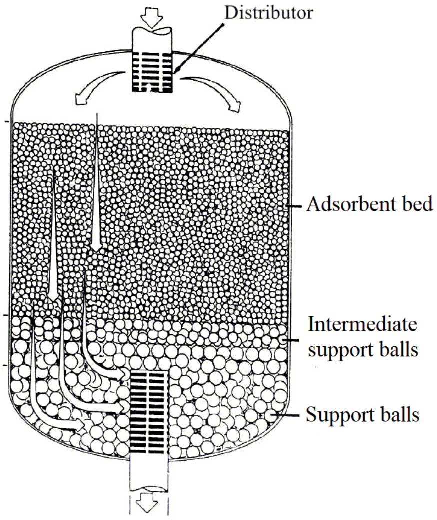
$$-D_L \frac{\partial^2 c_i}{\partial z^2} + \frac{\partial}{\partial z}(v c_i) + \frac{\partial c_i}{\partial t} + \left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \bar{q}_i}{\partial t} = 0$$

Particle mass balance yields the adsorption rate equation for each component,

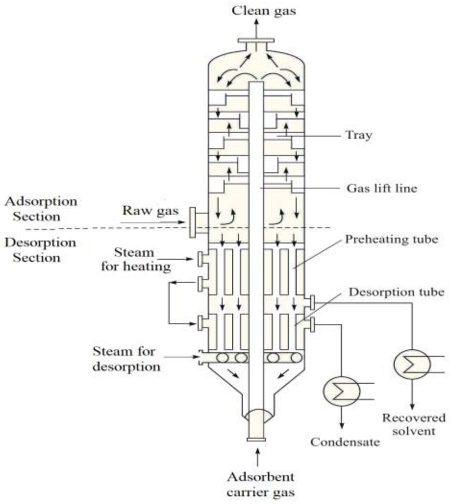
$$\frac{\partial \bar{q}_i}{\partial t} = f(q_i, q_j, \ldots, c_i, c_j, \ldots)$$

Now, we will be discussing about the multiple transition systems whatever the transition systems are adopted for single transition systems for multiple transition systems only we will be writing all the expression in terms of i$^{\text{th}}$ term. Like this if we consider an element of the bed through which a system containing concentration of ci so of adsorbable species i is flowing so we can say other species also are there, so then we can say these differential fluid phase balance equations for each component will be, so whatever we have written actually for the single transition systems like this, only the difference is like this in the concentration terms or we can say this one in the this loading term or capacity terms.

Adsorption Equipment



Packed adsorption bed



Continuous moving bed

Thank you.

So in the next class we will be discussing on the steady state fixed bed adsorbers and the last topic as ion-exchange.