Estimating specific surface area in a given mixture of particles

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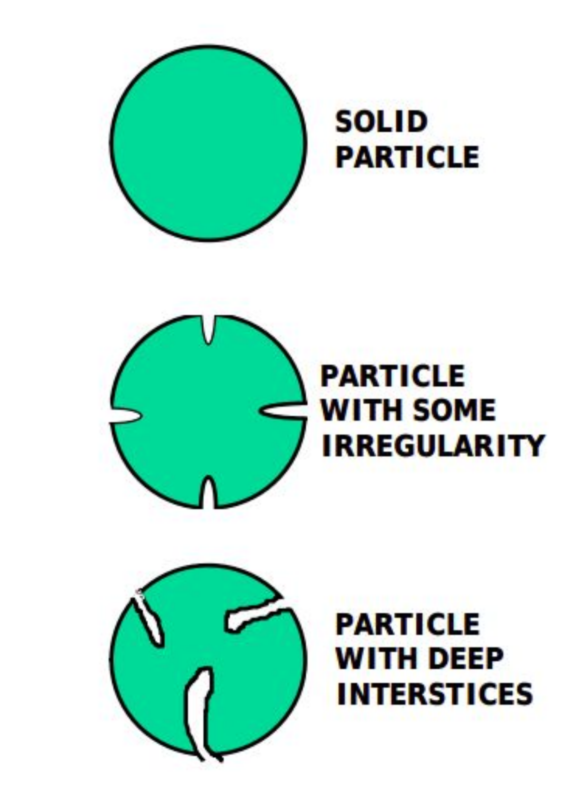
Motivation

Raw materials for different industrial processes are available in various shapes and sizes in nature. So the knowledge of their properties is very important from chemical engineering point of view.

When a solid is involved in a chemical reaction, either as a reagent or a catalyst, the surface area is the only accessible area for the reaction.



Applications

- Reactivity
- Dissolution
- Catalysis
- Seperation
- Pharmaceutical products
- Sintered materials

Dissolution of materials (e.g., API's) depends on surface area.

Noyes–Whitney Equation

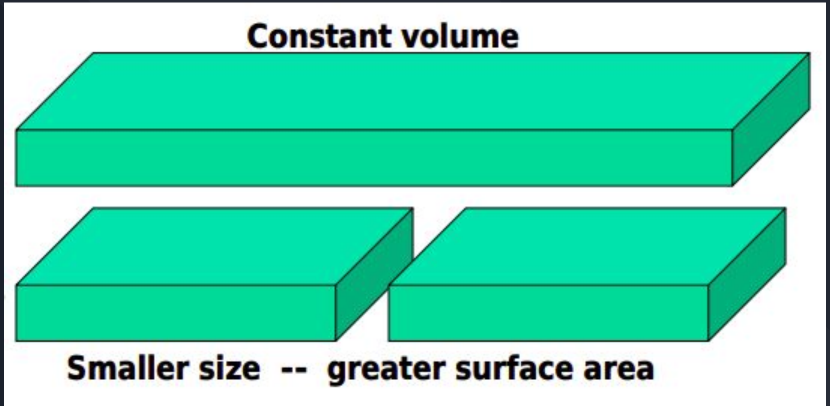
$$\frac{dm}{dt} = A\frac{D}{d}\left(C_s - C_b\right)$$

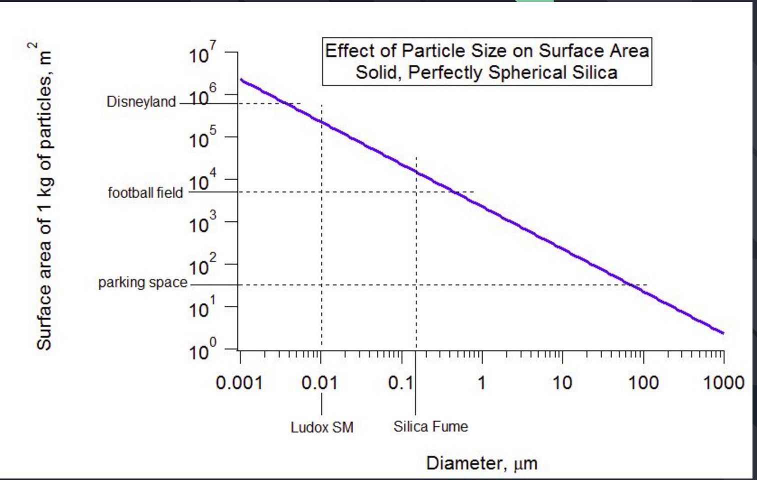
m = mass dissolved material
t = time
A = <u>Surface area of interface</u>
D = Diffusion coefficient
d = Boundary layer thickness
C_s = Concentration of substance on surface
C_b = Concentration of substance in solvent

Surface area vs particle size

When a particle of a given volume is broken into two parts as shown in the figure, total volume does not change.

The total surface area, however, **INCREASES** by the amount of the two newly-exposed edges.





Possible Scenarios while estimating specific surface area

For large particles - Sieving analysis

- Particles of same material
- Particles of different material

For very small particles

- BET Theory
- Gas Permeability

Specific surface area ratio (n)

Ratio of the specific surface area (surface per unit mass, s_p) of the particle to the specific surface area of a spherical particle of the same diameter (s_{ps}).

- $n = s_p/s_{ps}$
- $s_{ps} = \pi d^2_{avg}/((\pi d^3_{avg}/6)*\rho_s)$
- $s_{ps} = 6/\rho_s d_{avg}$
- On simplifying we have,

ρ_s=density of the particle

d_{avg}=average size of the particle

$$n = s_p \rho_s d_{avg}/6$$

$$\mathbf{s_p = 6n/\rho_s d_{avg}}$$

a)Specific Surface area if the mixture is made of particles of same materials :

Here in this case we have variable size,shape of the mixture and density of particles is same as of the bulk material (i.e. density remains constant for a mixture).

Specific surface area of the i^{th} fraction separated ,

$$s_{pi}=6n_i/\rho_s d_{avgi}$$

Total surface area of the ith fraction,

$$\mathbf{S_i = s_{pi}.m_i}$$ where m_i=mass of the i^{th} fraction.

$$S_i = 6n_i.m_i/\rho_s d_{avgi}$$

The specific surface area of the mixture,

S_m =Total surface area of all fractions/Total mass of the mixture

$$= (6n_1m_1/\rho_s d_{avg1.}+6n_2m_2/\rho_s d_{avg2}+6n_3m_3/\rho_s d_{avg3}.................)/(m_1+m_2+m_3+.................)$$

$$= (6n_1m_1/\rho_s d_{avg1.}+6n_2m_2/\rho_s d_{avg2}+6n_3m_3/\rho_s d_{avg3}.................)/M$$

$M=(m_1+m_2+m_3+.................)$=Total mass of the mixture

$$S_m = (6n_1m_1/\rho_s d_{avg1.}+6n_2m_2/\rho_s d_{avg2}+6n_3m_3/\rho_s d_{avg3}.................)/M$$

$$= (6n_1x_1/\rho_s d_{avg1.}+6n_2x_2/\rho_s d_{avg2}+6n_3x_3/\rho_s d_{avg3}.................)$$

x_i=mass fraction of i^{th} component in the mixture=(m_i/M)

$S_m = \sum 6n_i.x_i/\rho_s d_{avgi} = (6/\rho_s)\sum n_i x_i/d_{avgi}$

Specific surface area of the mixture:

$$\boxed{S_m = (6/\rho_s) \sum n_i x_i/d_{avgi}}$$

- Since sieving method is dependent on size of particles,it cannot be used to separate a mixture which contains particles of the same size say flour and chalk powder.

b)Specific surface area analysis if the mixture is made of different materials:

- If we have a mixture of different particles having variable density and sizes, since sieving method cannot be used to separate particles of same size and different density we will undergo density separation of the particles before analysing the specific surface area.
- Hydrocyclones or liquid separation can be used to separate particles having different density .
- Also , if we mix the mixture in a container ,agitating the container(either shaking or rolling type action) will allow the solid particles to move around in relation to one another.The denser particles will find their way to the bottom of the container while the less dense particles are sitting on the top

- After separating the mixture based on their density, the separated mixture will undergo sieve analysis for further separation based on their sizes.
- For example: If we get a mixture of density ρ_1, ρ_2, ρ_3 ,the first separated mixture having density ρ_1 will undergo sieve separation and will result in specific surface area ,
  - $S_{m1} = (6/\rho_{s1})\sum n_i x_i / d_{avgi}$

Similarly for ρ_2 and ρ_3 specific surface area derived will be:

$S_{m2} = (6/\rho_{s2})\sum n_i x_i / d_{avgi}$

$S_{m3} = (6/\rho_{s3})\sum n_i x_i / d_{avgi}$

- Total specific surface area of any one of the sample of mixture will be:

$$S_m = (M_1S_1 + M_2S_2 + M_3S_3)/ M$$

$$M = M_1 + M_2 + M_3$$

S_i = Specific surface area of i^{th} fraction

M_i = Mass of i^{th} fraction

BET Theory

Introduction

- Extension of Langmuir Adsorption Model.
- **Assumptions:**
  - Gas molecules physically adsorb on solid in layers infinitely.
  - The Langmuir theory can be applied to each layer.
  - The enthalpy of adsorption for the first layer is constant and greater than the second (and higher).
  - The enthalpy of adsorption for the second (and higher) layers is the same as the enthalpy of liquefaction.

Equation

$$\frac{\frac{P}{P_0}}{V\left(1-\frac{P}{P_0}\right)} = \frac{C-1}{V_m \cdot C}\left(\frac{P}{P_0}\right) + \frac{1}{V_m \cdot C}$$

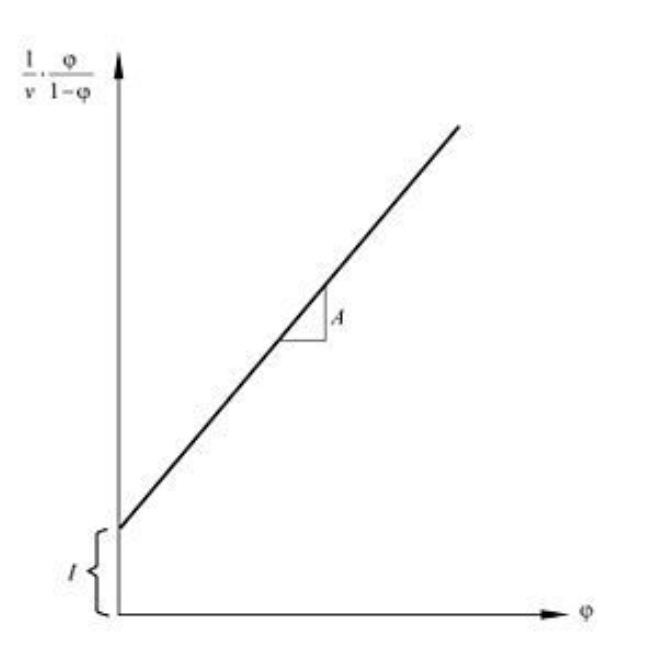
- P = Partial pressure of adsorbate
- P0 = Saturation partial pressure of adsorbate
- V =Vol. of adsorbed particles.
- Vm= Vol. of adsorbed particles in monolayer.

- C = BET constant
- E1 = Heat of Adsorption (H_{oA}) for the 1st layer.
- EL = H_{oA} for the 2nd layer onwards.

$$C = exp\left(\frac{E_1 - E_L}{RT}\right)$$

Finding C & Vm (Multipoint)

- Suitable for unknown materials.
- We plot the LHS of the equation along with the ratio of the actual & saturation partial pressure in the Y & x-axis respectively.
- For this we obtain C & Vm. Now the total & Specific Surface Areas can be calculated from the equations below.



Surface Area (multipoint)

- From the slope & y-intercept of the graph, we get C & Vm.
- Next we can find the total & the specific surface area of the the solid using the following formulas

$$S_{total} = \frac{V_m N s}{V}$$

$$S_{BET} = \frac{S_{total}}{a}$$

- N = Avogadro Number
- s = Adsorption cross-section of the adsorbing species
- V_m = Vol. of adsorbed particles in monolayer
- V= Molar Vol. of Adsorbate
- a = Mass of the Adsorbent.

Surface Area (singlepoint)

- Applicable for most materials.

Calculation of Vm

$$\frac{\frac{P}{P_0}}{V\left(1-\frac{P}{P_0}\right)} = \frac{C-1}{V_m \cdot C}\left(\frac{P}{P_0}\right)+\frac{1}{V_m \cdot C}$$

$$c \to \infty \quad \frac{1}{V_m C} \to 0 \quad (C-1) \to C$$

$$V\left(1-\frac{P}{P_0}\right) = V_m$$

Calculation of Surface Area

$$S_t = \frac{W_m \cdot N_A \cdot A_X}{M_W}$$

- St =Total surface area
- Wm = Mass of N_2 monolayer
- M w = Molecular weight of N_2 = 28 g/mol
- Na = Avagadro's Number
- Ax = Area of cross section of adsorbent (m^2)/molecule

Gas Permeability Method

Introduction

- This method depends on the relationship between the specific surface area of particles and the resistance to gas flow of a porous bed of powder.

- The specific surface area is derived from the resistance to flow of air through a porous bed of powder.

- Measurement consists of packing the powder into a cylindrical bed having a known porosity. A pressure drop is set up along the length of the bed cylinder. Hence the resulting flow rate of air through the bed yields the specific surface area.

Equation

$$S = \frac{7d}{\rho(1-\epsilon)}\sqrt{\frac{\epsilon^3 \pi \delta P}{l \eta Q}}$$

S is specific surface, $m^2 \cdot kg^{-1}$

d is the cylinder diameter, m

ρ is the sample particle density, $kg \cdot m^{-3}$

ε is the volume porosity of the bed (dimensionless)

δP is the pressure drop across the bed, Pa

l is the cylinder length, m

η is the air dynamic viscosity, Pa·s

Q is the flowrate, $m^3 \cdot s^{-1}$

Advantages

1. Method is simple and quick
2. Method can be used for particles which may be unstable under vacuum
3. Cost effective method

Limitations

1. Fails to measure much of the deep surface texture

Applications

The major fields where gas permeability has been used to determine specific surface area includes

1. Paint and Pigment Industry
2. Cement Industry
3. Preparation of Metallurgical Powders

VOLUME SHAPE FACTOR(λ_v)

- Volume of a particle is proportional to the cube of its diameter and the proportionality constant is called Volume Shape Factor.
- It depends on the size of the Particle but the variation is not very large and an average value can be considered.

$$V_p \propto d^3_{avg}$$

$$V_p = \lambda_V d^3_{avg}$$

NUMBER OF PARTICLES IN A MIXTURE

PARTICLE OF SAME SIZE

For a sample of particles having same size(d_{avg}) and density(ρ_s), Number of particles(N) can be calculated as:

$$N = \frac{MassOfTheSample}{MassOfASingleParticleInSample} = \frac{m}{\rho_s * V_p} = \frac{m}{\rho_s [\lambda_v * {d_{avg}}^3]}$$

m = mass of the sample, Vp = Volume of a particle

PARTICLE OF DIFFERENT SIZE

For a mixture of particles having different size, We have to sort the mixture in fractions having same size using techniques like sieving.

Number of particle in i^{th} Sample(N_i):

$$N_i = \frac{m_i}{\rho_s V_{pi}} = \frac{m_i}{\rho_s \lambda_{vi} {d_{avgi}}^3}$$

Number of particles per unit mass in the mixture(N):

$$N_m = \frac{\sum N_i}{M} = \frac{\frac{m_1}{\rho_s \lambda_{v1} {d_{avg1}}^3} + \frac{m_2}{\rho_s \lambda_{v2} {d_{avg2}}^3} + \frac{m_3}{\rho_s \lambda_{v3} {d_{avg3}}^3} + \ldots\ldots}{m_1 + m_2 + m_3 + \ldots\ldots} = \frac{1}{\rho_s} \sum \frac{x_i}{\lambda_{vi} {d_{avgi}}^3}$$

PARTICLE OF DIFFERENT MATERIALS

For a mixture of particles having both different size and density, We have to first separate them into fraction having same density and then separate each sample into fraction of different size using sieving.

Number of particle in ith Sample(N_i):

$$N_i = \frac{m_{i1}}{\rho_{si}\lambda_{vi1} d_{avgi1}^3} + \frac{m_{i12}}{\rho_{si}\lambda_{vi2} d_{avgi2}^3} + \frac{m_{i3}}{\rho_{s3}\lambda_{vi3} d_{avgi3}^3} + \dots\dots = \frac{1}{\rho_{si}} \sum \frac{m_{ij}}{\lambda_{vij} d_{avgij}^3}$$

Number of particles per unit mass in the mixture(N):

$$N_m = \frac{\sum N_i}{M} = \frac{\frac{1}{\rho_{s1}}\sum \frac{m_{1j}}{\lambda_{v1j} d_{avg1j}^3} + \frac{1}{\rho_{s2}}\sum \frac{m_{2j}}{\sum_{m1j}\lambda_{v2j} d_{avg2j}^3} + \frac{1}{\rho_{s3}}\sum\frac{x_{3j}}{\lambda_{v3j} d_{avg3j}^3} + \dots}{\sum_{m1j} + \sum_{m2j} + \sum_{m3j} + \dots} = \sum \frac{x_{ij}}{\rho_{si}\lambda_{vij} d_{avgij}^3}$$

Thank You