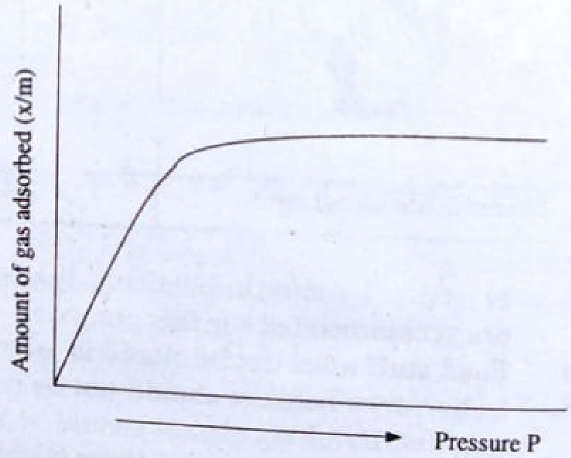
Adsorption and Langmuir Isotherms

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the *adsorbate* on the surface of the *adsorbent*. Some solids like charcoal, fuller's earth and cellulosic material have the tendency to hold molecules or ions on their surfaces. Adsorption takes place between boundaries of two surfaces. Solids having large surface area facilitate the adsorption. Amount of adsorbed substance depends on temperature and pressure. It means that

$$A = f(P,T)$$

Irving Langmuir proposed Adsorption Isotherm which explained the variation of Adsorption with pressure in 1916. He derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure in case of gases and concentration in case of liquids. Langmuir's theory is based on the following assumptions.



1. Fixed number of vacant or adsorption sites are available on the surface of solid.

2. All the vacant sites are of equal size and shape on the surface of adsorbent.

3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.

4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

$$A_{(g)} + B_{(s)} \underset{\text{Desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} AB$$

Where $A_{(g)}$ is unadsorbed gaseous molecule, $B_{(s)}$ is unoccupied metal surface and AB is Adsorbed gaseous molecule.

5. Adsorption is monolayer or monolayer. The general form of Adsorption isotherm is shown below.

Factor Affecting Adsorption

Adsorption of gases on solid surface depends upon:

1. **Nature of gas or adsorbent:**
2. **Adsorption $\propto$ Critical temperature of gas or van der Waal's force of attraction**
3. **Effect of Temperature: Since adsorption is exothermic. Hence**

$$\text{Adsorption (a)} \propto \frac{I}{\text{Temperatur}}$$

4. **Pressure: At constant temperature adsorption $\propto$ Pressure**
5. **Surface area of Adsorbent: Larger the surface area of adsorbent more will be active centers and faster will be the rate of adsorption.**
6. **Activation of Solid Adsorbent: When adsorbent is sub-divided or already adsorbed gases are removed, it becomes activated adsorbent and rate of adsorption increases.**

The simplified Langmuir adsorption equation is given below.

$$\frac{C_e}{x/m} = \frac{1}{k_1 k_2} + \frac{1}{k_2} C_e$$

where k_1 and k_2 are constants, C_e is equilibrium concentration of *adsorbate*, m is the amount of adsorbent and x is the amount of solute adsorbed.

A plot of $\frac{C_e}{x/m}$ vs $\frac{1}{k_1 k_2}$ is a straight line whose slope is equal to $\frac{1}{k_2}$ and intercept is $\frac{1}{k_1 k_2}$.

http://oscience.info/chemistry/factors-affecting-adsorption/ and http://en.wikipedia.org/wiki/Adsorption

EXPERIMENT 1

Verify Langmuir adsorption isotherm by considering the adsorption of acetic acid from aqueous media by using activated Charcoal.

Principle: **Some solids like charcoal, fuller's earth and cellulosic material have the tendency to hold molecules or ions on the surface. This is called adsorption. Adsorption takes place between boundaries of two surfaces. Solids having large surface area facilitate the adsorption. Amount of adsorbed substance depends on temperature and pressure. The simplified Langmuir adsorption equation is given below.**

$$\frac{C_e}{x/m} = \frac{1}{k_1 k_2} + \frac{1}{k_2} C_e$$

Where k_1 and k_2 are constants, C_e is equilibrium concentration of *adsorbate*, m is the amount of adsorbent and x is the amount of solute adsorbed.

A plot of $\frac{C_e}{x/m}$ vs $\frac{1}{k_1 k_2}$ is a straight line whose slope is equal to $\frac{1}{k_2}$ and intercept is $\frac{1}{k_1 k_2}$.

Apparatus and Chemicals: **Standard Oxalic acid solution (0.1 N), NaOH solution, CH3COOH solution, Activated charcoal, Phenolphthalein indicator, Reagent Bottles (5 each), Burette (50 mL), Pipette (10 mL), Conical flask (250 mL, 100 mL), filter papers.**

Procedure:

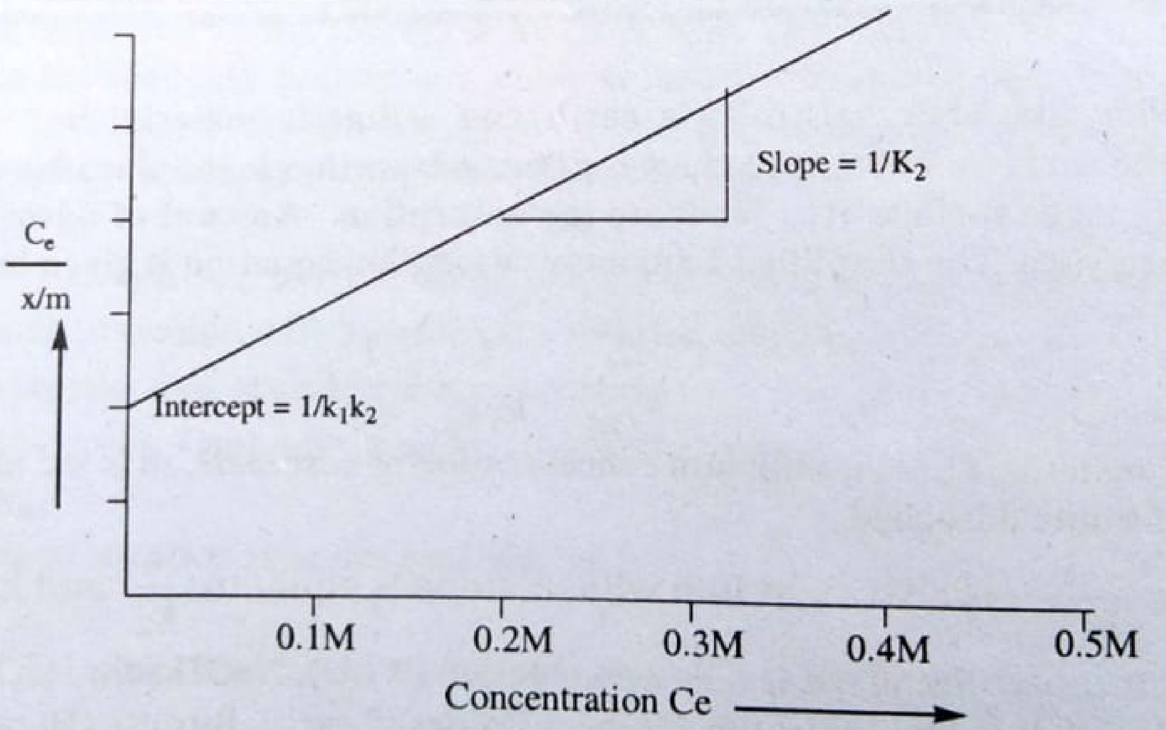
1. **Prepare 250cm^3 solution of 0.5M acetic acid and 250cm^3 solution of 0.1M sodium hydroxide and standardize both solutions.**
2. **Take five clean and dry stoppered reagent bottles and numbered them as 1, 2, 3, 4, and 5**
3. **Take 0.5M acetic acid and distilled water in these bottles as given below.**
4.

Bottles	Bottle 1	Bottle 2	Bottle 3	Bottle 4	Bottle 5
0.5M acetic acid in cm^3	50	40	30	20	10
Water	0	10	20	30	40
Initial conc. of acetic acid	0.5M	0.4M	0.3M	0.2M	0.1M

4. **Add 1g activated charcoal to each bottle and shake each flask vigorously and place all bottles on shaker for 1 hour.**
5. **Filter solution from each bottle and keep the filtrate in numbered beaker. First 5-6cm^3 filtrate should be discarded during filtration in each case.**
6. **Take 10cm^3 of each filtrate in titration flask and titrate with standard 0.1M NaOH solution using phenolphthalein as indicator. Take three concordant reading in each case.**
7. **Plot a graph between $\frac{C_e}{x/m}$ and C_e and find out the slope $1/k_2$ and intercept $1/k_1 k_2$ as shown in figure.**

Observations and Calculations

Bottle No	Initial conc. of acetic acid C_i	Equilibrium conc. of acetic acid C_e	Amount of acetic adsorbed $(C_i - C_e) = x$	x/m	$\frac{C_e}{x/m}$
1					
2					
3					
4					
5					



Result: **The plot between $\frac{C_e}{x/m}$ and C_e is a straight line, therefore, 0.5M solution of acetic acid validate the Langmuir adsorption isotherm.**