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B.Sc. III, PAPER-5

Langmuir adsorption isotherm equation –

Freundlich adsorption isotherm is valid only on certain range of pressure only. To solve this difficulty Langmuir gave an adsorption isotherm which is called Langmuir adsorption isotherm. Following are main assumption for Langmuir adsorption isotherm.

(a) The ~~ads~~ adsorbed layer is unimolecular and not multilayer. This occurs at low pressure or at moderately high temperature.

(b) The adsorption is taking place on the fixed site of the surface and there is no any vander waal forces between adsorbate molecules to form multi layer. On site adsorbs only one ~~one~~ molecules when whole surface is covered by adsorbate molecule, a saturation state is establised and then there is no further adsorption.

c. In adsorption is dyanamic in nature i.e condensation process and evapouration of adsorbate molecule occurs ~~simul~~ simultaneously and at equilibrium.

Rate of condensation = Rate of evaporation.

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(e) Gas molecule behaves ideally.
(f) Surface of solid is uniform energetically.

Derivation of Langmuir adsorption isotherm:

Let

θ = the fraction of the surface of adsorbent covered by adsorbate at a time t.

$\therefore 1-\theta$ = will be fraction of bare and available for adsorption.

P = Pressure of gas.

Then according to Langmuir Theory of adsorption.

Rate of condensation $\propto (1-\theta)P$

or Rate of condensation $= K_1(1-\theta)P$ ←(i)

Here = K_1 = Proportionality constant

and Rate of evaporation $\propto \theta$

$= K_2\theta$ — (ii)

K_2 = proportionality Constant

At equilibrium

Rate of condensation = Rate of evaporation

From eqn (i) and (ii)

$\Rightarrow$ $K_1(1-\theta)P = K_2\theta$ — (iii)

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or $K_1 P - K_1 \theta P = K_2 \theta$

or. $K_1 P = \theta (K_2 + K_1 P)$

or $\theta = \frac{K_1 P}{K_2 + K_1 p}$

or $\theta = \frac{\frac{K_1}{K_2} P}{1 + \frac{K_1}{K_2} p} = \frac{bp}{1+bp}$ —— (IV)

Wher $b = \frac{K_1}{K_2}$

If x = amount of absorbate and m = amount of absorbent then considering unimolecular lay adsorption, the gas absorbed per unit area or per gram of adsorbent will be proportional to surface of area covered at any time.

$$\frac{x}{m} \propto \theta$$

or $\frac{x}{m} = K_3 \theta$ —— (V)

K_3 = proportionality constant

Putting value of θ from eq^n (IV) in eq^n (V)

$$\frac{x}{m} = K_3 \cdot \frac{bP}{1+bP}$$

or. $\frac{x}{m} = \frac{K_3 b P}{1+bp} = \frac{ap}{1+bP}$ —— (VI)

Where $a = K_3 b$.

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Equation (vi) is know as Langmuir adsorption isotherm

~~the reciprocal of eq^n (vi) is~~

eq^n (vi) is divided by p, then

$$\frac{x/m}{p} = \frac{a}{1+bp}$$

reciprocal of this equation

$$\frac{p}{x/m} = \frac{1+bp}{a}$$

or $$\frac{p}{x/m} = \frac{1}{a} + \frac{b}{a}p$$

Here, a, b are constant, hence plotting graph of $P/x/m$ verses p will be a straight line, the value of slope will be equal to b/a and intercept at y axis will give value of $\frac{1}{a}$