Lecture 4

Multilayer adsorption theory

Langmuir equation is valid for adsorption less than monolayer coverage and therefore more suited for chemisorption studies as it involves only monolayer coverage. Physical adsorption is not limited to monolayer formation and multilayer adsorption can occur on subsequent layers. Hence Langmuir isotherm is not applicable to multilayer adsorption. Brunauer , Emmette and Teller derived an relationship between the volume of gas physically adsorbed and the partial pressure of the adsorbate which is valid for multilayer adsorption. This relationship is utilized for measuring the total surface area of an adsorbent.

Multilayer adsorption: BET equation derivation

Let $s_0, s_1, s_2, s_3 \ldots\ldots s_i$ be the surface area covered by 0,1,2,3……….i layers of adsorbed molecules as shown in the Fig. 1. The total area of the adsorbent therefore, can be obtained by the summation of all the individual surface areas.
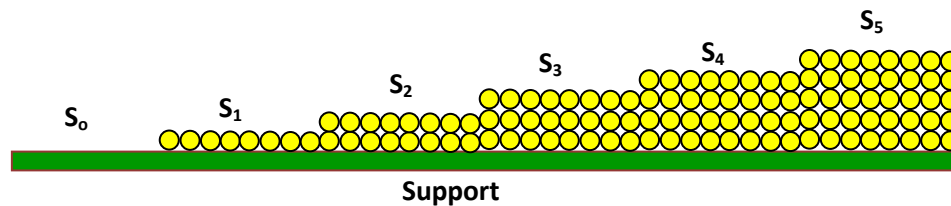

Fig.1. The representation of $s_0, s_1, s_2, s_3, s_4 \; and \; s_5$ surface areas covered by 0,1,2,3,4 and 5 layers of adsorbed molecules respectively.

Rate of adsorption on bare surface s_0 is $= a_1 p s_0 \exp\left[\dfrac{-E_a}{RT}\right]$

Rate of desorption from surface area s_1 having the first layer $= b_1 s_1 \exp\left[\dfrac{-E_d}{RT}\right]$

Since at equilibrium s_0 must remain constant, the rate of adsorption (or condensation) on bare surface is equal to the rate of desorption (evaporation) from first layer. Therefore,

$$a_1 p s_0 \exp \frac{-E_a}{RT} = b_1 s_1 \exp\left[\frac{-E_d}{RT}\right]$$

or $\quad a_1 p s_0 = b_1 s_1 \exp\left[\frac{-H_1}{RT}\right]$, where $E_d - E_a = -H_1$ heat of adsorption of first layer.

This is Langmuir equation for unimolecular adsorption. It is assumed that a, b and H are independent of the number of adsorbed molecules already present in the first layer.

Similarly, the rate of adsorption on s_1 = rate of desorption from s_2.

Therefore, $a_2 p s_1 = b_2 s_2 \exp\left[\frac{-H_2}{RT}\right]$

Extending to layer s_i with 'i' no of layers, $\quad a_1 p s_{i-1} = b_i s_i \exp\left[\frac{-H_i}{RT}\right]$

Total surface area $= A = \sum_{i=0}^{\infty} s_i$, $\quad s_i$ = surface area with 'i' no of layers

Total volume adsorbed $= v = v_0 \sum_{i=0}^{\infty} i s_i$

or , $\quad \dfrac{v}{A v_0} = \dfrac{\sum\limits_{i=0}^{\infty} i s_i}{A}$

$$\frac{v}{v_m} = \frac{\sum\limits_{i=0}^{\infty} i s_i}{\sum\limits_{i=0}^{\infty} s_i} \qquad \text{------------------ [1]}$$

v_0 is volume of gas adsorbed per unit area of adsorbent surface and $\quad v_m$ is the volume of gas adsorbed when the entire adsorbent surface is covered with a complete unimoleculer layer.

For simplification, it is assumed that the heat of adsorption of the 2nd, 3rd………upto i^{th} layer are equal to each other and equal to heat of liquefaction of the adsorbate.

Or $\quad H_2 = H_3 = ... = H_i = H_L$

and $\dfrac{b_2}{a_2} = \dfrac{b_3}{a_3} = ... = \dfrac{b_i}{a_i} = g$, g being an appropriate constant.

Now $s_{1,} s_2 ....s_i$ can be expressed in term of s_0

$$a_1 p s_0 = b_1 s_1 \exp \dfrac{-H_1}{RT}$$

$$s_1 = \left(\dfrac{a_1}{b_1}\right) p \exp\left(\dfrac{H_1}{RT}\right) s_0 = y s_0 \qquad\qquad \because y = \left(\dfrac{a_1}{b_1}\right) p \exp\left(\dfrac{H_1}{RT}\right)$$

$$a_2 p s_1 = b_2 s_2 \exp\left(\dfrac{-H_2}{RT}\right)$$

$$s_2 = \left(\dfrac{a_2}{b_2}\right) p \exp\left(\dfrac{H_2}{RT}\right) s_1 = x s_1 \qquad \because x = \left(\dfrac{a_2}{b_2}\right) p \exp\left(\dfrac{H_2}{RT}\right) = \left(\dfrac{p}{g}\right) \exp\left(\dfrac{H_L}{RT}\right)$$

$$s_3 = x s_2 = x^2 s_1$$

$$s_i = x^{i-1} s_1 = x^{i-1} y s_0 = \dfrac{y}{x} x^i s_0 = c x^i s_0 \qquad\qquad \because c = \dfrac{y}{x}$$

$$c = \dfrac{y}{x} = \dfrac{\left(\dfrac{a_1}{b_1}\right) p \exp\left(\dfrac{H_1}{RT}\right)}{\left(\dfrac{p}{g}\right) \exp\left(\dfrac{H_L}{RT}\right)} = \left(\dfrac{a_1}{b_1}\right) g \exp\left(\dfrac{H_1 - H_L}{RT}\right)$$

Substituting $s_i = cx^i s_0$ in $\dfrac{v}{v_m} = \dfrac{\sum\limits_{i-0}^{\infty} is_i}{\sum\limits_{i-0}^{\infty} s_i}$ we get

$$\frac{v}{v_m} = \frac{cs_0 \sum\limits_{i=1}^{\infty} ix^i}{s_0 + cs_0 \sum\limits_{i=1}^{\infty} x^i} = \frac{cs_0 \sum\limits_{i=1}^{\infty} ix^i}{s_0 \left[1 + c\sum\limits_{i=1}^{\infty} x^i\right]}$$

Sum of the infinite geometric progression

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x}$$

$$\sum_{i=1}^{\infty} ix^i = \frac{x}{(1-x)^2}$$

Substituting ,

$$\frac{v}{v_m} = \frac{c\dfrac{x}{(1-x)^2}}{1 + \dfrac{cx}{1-x}} = \frac{cx}{\left[(1-x) + cx\right](1-x)} \quad \text{-----------------[2]}$$

For adsorption on free surface, at saturation pressure of gas p_0 , infinite no of layers can build up on the surface. Further to make $v \to \infty$ at $p = p_0$, x must be equal to unity in equation [2].

Now,

$$x = \frac{p}{g}\exp\frac{H_L}{RT}$$

$$\therefore \quad 1 = \frac{p_0}{g}\exp\frac{H_L}{RT}$$

$$x = \frac{p}{g}\frac{p_0}{p_0}\exp\frac{H_L}{RT}$$

$$x = \frac{p}{p_0}$$

Substituting this in equation [2]

$$\frac{v}{v_m} = \frac{c\left(\dfrac{p}{p_0}\right)}{\left(1 - \dfrac{p}{p_0} + \dfrac{cp}{p_0}\right)\left(1 - \dfrac{p}{p_0}\right)}$$

Or $\quad \dfrac{v}{v_m} = \dfrac{cp}{\left(1 + (c-1)\dfrac{p}{p_0}\right)(p_0 - p)}$

Or $\quad \dfrac{p}{v(p_0 - p)} = \dfrac{1}{v_m c} + \dfrac{c-1}{v_m c}\dfrac{p}{p_0}$ ---------------------- [3]

The Eq. 3 is known as the BET equation for multilayer adsorption. This equation can explain type II isotherm.

Table 1. Isotherms most commonly used in catalysis

Type	Isotherm equations	Type of adsorption
Langmuir	$\dfrac{v}{v_m} = \theta = \dfrac{bp}{1+bp}$	Chemisorption Physisorption
Freundlich	$v = c\, p^{1/n} \qquad (n > 1)$	Chemisorption and physisorption at low coverage
Temkin	$\dfrac{v}{v_m} = \theta = k_1 \ln k_2 p$	Chemisorption
Brunauer-Emmet-Teller	$\dfrac{p}{v(p_o - p)} = \dfrac{1}{v_m c} + \dfrac{c-1}{v_m c}\dfrac{p}{p_o}$	Multilayer physical adsorption

Capillary (pore) condensation and evaporation: Kelvin equation

As discussed in the previous section for porous solids, the desorption curve lies above the adsorption curve from $\frac{p}{p_0} = 1$ to some intermediate value resulting in a hysteresis loop. This phenomenon occurs due to capillary condensation – evaporation process. It was recognized by Kelvin that the vapor pressure of a liquid contained in a small diameter capillary is less than the normal value for a free surface.

Consider a capillary filled with a liquid of surface tension σ. The change in free energy due to evaporation of a differential volume of liquid 'dv' is n ΔG, where $n = \frac{dv}{\upsilon_{mol}}$. Here υ_{mol} is the molar volume. Now ,

$n\Delta G = change\ in\ surface \times\ surface\ tension$

$n\Delta G = \left(2\pi rdl\right)\sigma\cos\theta$ -------[4]

Again , $n\Delta G = -nRT\left(\ln\frac{p}{p_0}\right)$ --------[5]

Equating [4] and [5]

$$\left(2\pi rdl\right)\sigma\cos\theta = -nRT\left(\ln\frac{p}{p_0}\right) = -\frac{\pi r^2 dl}{\upsilon_{mol}}RT\left(\ln\frac{p}{p_0}\right) \qquad \because n = \frac{dv}{\upsilon_{mol}} = \frac{\pi r^2 dl}{\upsilon_{mol}}$$

Or , $\ln\frac{p}{p_0} = -\frac{2\upsilon_{mol}\sigma}{rRT}$ cos θ = 1

$$\frac{p}{p_0} = \exp\left[-\frac{2\upsilon_{mol}\sigma}{rRT}\right]$$

This is the general form of the Kelvin equation assuming wetting angle to be zero. This equation states that the pressure at which condensation or evaporation will occur is always less than the free surface vapor pressure if the capillary radius is small enough for the given liquid. When a nonporous solid or solid containing large pores is subjected to physical adsorption – desorption

equilibrium experiments, actual condensation of adsorbate will occur when the gas pressure equals the vapor pressure at the prevailing temperature; that is at $\dfrac{p}{p_0} = 1$. On other hand, if pores of appropriate radius exists, condensation will occur before $\dfrac{p}{p_0} = 1$. Thus, liquid N_2 will form within the pores at $\dfrac{p}{p_0} < 1$. On adsorption, this would account for the rapid increase in the volume of gas adsorbed with $\dfrac{p}{p_0}$, typical of adsorption isotherms of porous solids.

However, this mechanism does not account for the occurrence of hysteresis loop, if filling of pores on adsorption and their emptying on desorption follow the same mechanism. In this physisorption mechanism, pores are assumed to undergo vertical filling and emptying. Therefore, occurrence of hysteresis suggests that filling mechanism of pores is different than the desorption mechanism. Later a different mechanism was forwarded for pore filling by Cohan. It was suggested that during adsorption, the pores may be filling radially instead of vertically. As gas molecules are condensing radially on the surface of pores, the effective radius 'r' is decreased on condensation of first layers. This causes further condensation at a fixed p/p_o. In other words, pores of a radius 'r' corresponding to a given p/p_o, fill instantaneously. In this condition, the change in volume $dv = 2\pi r l dr$ and that of surface is $2\pi l dr$. Kelvin equation can be modified as $\dfrac{p}{p_o} = \exp\dfrac{-\sigma \upsilon_{mol}}{rRT}$

For a given pore radius r , adsorption with radial capillary condensation occurs at

$$p_{ads} = p_o \exp\dfrac{-\sigma \upsilon_{mol}}{rRT}$$

While vertical emptying of the pores occurs during desorption at about

$$p_{des} = p_o \exp\dfrac{-2\sigma \upsilon_{mol}}{rRT}$$

Wetting angle is taken as zero. The adsorption pressure is related to the desorption pressure by $p_{ads}^2 = p_o\, p_{des}$. This implies that the pressure required to empty the capillary is proportional to the square of that necessary to fill it and hence hysteresis.