

From Langmuir to BET: The absorption theory of gas on solid surface

Zong Wei Huang
Qiushi science class (chemistry)
Chu Kochen Honor College

Rui Li
Qiushi science class (chemistry)
Chu Kochen Honor College

This review is intended to provide a rough summary of the absorption theory by tracing the original ideas from Langmuir and BET, as well as a brief introduction of a thermodynamical perspective towards the process of adsorption, in addition to descriptions of their applications.

Keywords: adsorption, Langmuir model, BET theory

CONTENTS

I. Introduction	1
II. Langmuir: unimolecular equilibrium	1
III. BET: multi-molecular equilibrium	1
IV. Adsorption in the thermodynamical equilibrium perspective	2
V. Methodology	3
VI. Pore size analysis	3
A. The classical approach	3
B. Density functional formulation	4
References	4

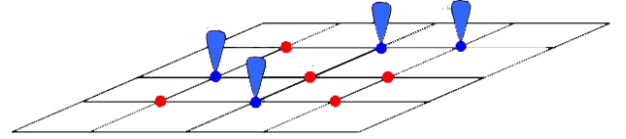


FIG. 1. A simple graphic representation of the Langmuir adsorption model, where the red dots signify the unoccupied area, the blue points the occupied area.

phase, while AS is the adduction product of the gas molecule and the molecule on the surface of the condensed substance.

Langmuir supposed that the adsorption rate is proportional to the pressure of gas A and the area on the surface which haven't been occupied, while the desorption rate is proportional to the area occupied, which is shown by

$$k_{ad}pS_0 = k_{de}S_1 \quad (1)$$

where k_{ad}, k_{de} represent the reaction rate constant of the adsorption and the desorption respectively, S_0, S_1 the unoccupied and the occupied area, and p the pressure of gas A in bulk phase.

Define the occupied percentage θ

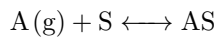
$$\theta = \frac{S_1}{[S]} = \frac{S_1}{S_0 + S_1} = \frac{k_{ad}p}{k_{ad}p + k_{de}} \quad (2)$$

and the adsorption equilibrium constant $K = \frac{k_{ad}}{k_{de}}$, then

$$\theta = \frac{Kp}{1 + Kp} \quad (3)$$

II. LANGMUIR: UNIMOLECULAR EQUILIBRIUM

The surface adsorption can be regarded as a equilibrium



which represents the process of adduction between the two substances, A(g) being the gas molecule in the gas

III. BET: MULTI-MOLECULAR EQUILIBRIUM

It is supposed that many layers of adsorbed molecules can be formed on the surface of condensed substance, and s_i is defined as the surface area that covered by i layers of adsorbed molecules. When considering monolayer system, it is derived from the Langmuir's equation that

$$a_1ps_0 = b_1s_1e^{-E_1/RT} \quad (4)$$

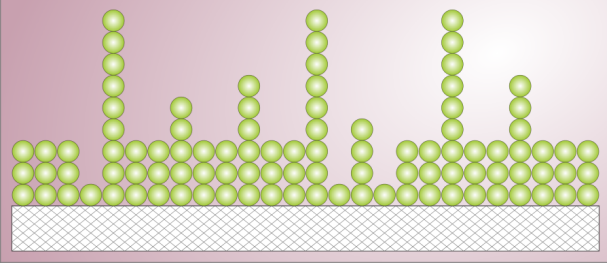


FIG. 2. Sketch of the multilayered adsorption

where the term $e^{-E_1/RT}$ is separated from K in the Langmuir's equation w.r.t. the Boltzmann distribution achieved between the adsorbed molecules and those in the bulk phase. For another system including only two layers of adsorbed molecules, the equilibrium is given by

$$a_2 p s_1 + b_1 s_1 e^{-E_1/RT} = b_2 s_2 e^{-E_2/RT} + a_1 p s_0 \quad (5)$$

with each term representing condensation on the first layer, evaporation from the first layer, evaporation from the second layer and condensation on the first layer, with a_2, b_2, E_2 similarly defined to a_1, b_1 and E_1 . Considering that (4) still holds in this system for the first layer, it is easily derived that

$$a_2 p s_1 = b_2 s_2 e^{-E_2/RT} \quad (6)$$

Similar mechanism can be applied for an arbitrary index i , namely

$$a_i p s_{i-1} = b_i s_i e^{-E_i/RT} \quad (7)$$

or

$$p s_{i-1} = g_i s_i e^{-E_i/RT} \quad (8)$$

The total surface area is given by

$$A = \sum_{i=0}^{\infty} s_i \quad (9)$$

and the total volume adsorbed is

$$v = v_0 \sum_{i=0}^{\infty} i \cdot s_i \quad (10)$$

where v_0 is the volume of gas adsorbed on unit area of the adsorbent surface when it is covered with a complete unimolecular layer of adsorbed gas. Then

$$\frac{v}{A v_0} = \frac{v}{v_0} = \frac{\sum_{i=0}^{\infty} i \cdot s_i}{\sum s_i} \quad (11)$$

It is assumed that $E_i = E_j = E_L, g_i = g_j = g$ for $i, j \geq 2$, in the consideration of the similarity among these layers, and s_i is given by

$$s_0 = c x^i s_0 \quad (12)$$

where $x = (p/g)e^{E/RT}, c = g g_1 e^{(E_1 - E_L)/RT}$. Thus

$$\frac{v}{v_m} = \frac{c \sum_{i=1}^{\infty} i x^i}{1 + c \sum_{i=1}^{\infty} x^i} \quad (13)$$

Then

$$\frac{v}{v_m} = \frac{c x}{(1 - x)(1 - x + c x)} \quad (14)$$

w.r.t. the fact that

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1 - x} \quad (15)$$

(14) indicates that endless adsorption will occur if $x \rightarrow 1$, which is evidently the result of $p \geq p_0$, p_0 representing the saturated vapor pressure of the adsorbed substance. Considering that $x \propto p$, it is assumed that

$$x = \frac{p}{p_0} \quad (16)$$

Then (14) is reduced to

$$\frac{v}{v_m} = \frac{c p}{(p_0 - p) \left[1 + (c - 1) \frac{p}{p_0} \right]} \quad (17)$$

or its linear form

$$\frac{c p}{V(p_0 - p)} = \frac{1}{V_m} \left[1 + (c - 1) \frac{p}{p_0} \right] \quad (18)$$

IV. ADSORPTION IN THE THERMODYNAMIC EQUILIBRIUM PERSPECTIVE

BET theory is based on dynamical equilibrium achieved between the adsorption and the desorption of the adsorbed species along with the assumption of indifference among the addition energy and reaction rate constant g_i between layers, which lacks theoretical evidence. Based on his collaborated work with Kai Gu[3], Kaihang Shi along with Shicheng Li established a statistical mechanical model combined with Monte Carlo method to provide computational analysis of the adsorption process.

If the adsorption between monolayer and gas phase (bulk phase) reaches an equilibrium, the chemical potentials of two phases must be equal:

$$\mu_{\text{bulk}} = \mu_{\text{ads}} \quad (19)$$

and the chemical potential of adsorbed phase is contributed by two parts:

$$\mu_{\text{ads}} = \mu_{2D} + \mu_w \quad (20)$$

where μ_w represents the contribution of chemical potential from the adsorbed wall, and μ_{2D} the chemical potential of the 2D monolayer. Regarding the adsorbed molecules packed hexagonally and interact with each

other according to two-dimensional Lennard-Jones equation, the total specific configurational energy is given by

$$U_0^* = \lim_{L,M \rightarrow \infty} \frac{2}{(L+1)(M+1)} \sum_{i,j}^{L,M} \sum_{l,m}^{L,M} \left[\left(\frac{1}{\|\mathbf{r}_{i,j}^* - \mathbf{r}_{l,m}^*\|} \right)^{12} - \left(\frac{1}{\|\mathbf{r}_{i,j}^* - \mathbf{r}_{l,m}^*\|} \right)^6 \right] \quad (21)$$

where $\|*\|$ is defined as the norm, and $\mathbf{r}_{i,j}^*$ is defined as

$$\mathbf{r}_{i,j}^* = r_0^* \left[\left(i + \frac{1}{2}j \right) \mathbf{e}_x + \frac{\sqrt{3}}{2}j \mathbf{e}_y \right] \quad (22)$$

which matches the hexagonal alignment of the molecules, with $r_0^* = r_0/\sigma$ to simplify the form. The pressure at is further defined,

$$P_{2D,T=0}^* = (\rho_{2D}^*)^2 \left(\frac{\partial U_0^*}{\partial \rho_{2D}^*} \right) \quad (23)$$

where ρ_{2D}^* is the density of the molecules in two dimensional form. With these the chemical potential can be deduced. Using similar method the chemical potential of the wall can be given as a function of $\sigma_{\text{ad-solid}}$, $\varepsilon_{\text{ad-solid}}$, $\lambda\sigma_{\text{ad-ad}}$ and T , representing the collision diameter between the adsorbed molecules and the wall, the adsorbate-surface energy depth, the depth of the monolayer and temperature respectively. Computational analysis reveals that the cross-sectional area of each molecule, as well as the density of the layer, is highly dependent on the interaction between the wall and the adsorbed molecules, which is neglected in the BET theory.

V. METHODOLOGY

The use of nitrogen adsorption becomes one of the most widely-used method for the characterization of porous materials. The earliest reported studies of the adsorption nitrogen and other gases at liquid air temperature (~ 88 K) appear to have been made by Dewar and Ramsay in the course of their investigations of the composition of the atmosphere and the separation of the noble gases.[4]

Gas adsorption manometry is the method generally used for the determination of adsorption isotherms of nitrogen at the temperature of liquid nitrogen (~ 77 K). This type of approach was known as a ‘volumetric determination’ (or alternatively as the ‘BET volumetric method’) since it originally involved the measurement of gas volumes, before and after adsorption. However, it has been pointed out that it is no longer appropriate to use the term ‘volumetric’ since the amount adsorbed is now generally evaluated by measuring the change of gas pressure, rather than a change in gas volume.

Two different operational procedures can be used for the determination of the adsorption isotherm. The conventional technique makes use of a discontinuous, point-by-point procedure. Successive amounts of the adsorptive are introduced and at each stage the system is allowed sufficient time to attain equilibrium, which of course corresponds to a series of single points on the adsorption isotherm. The continuous approach is more recent and is dependent on the principle of ‘quasi-equilibrium’. In this case, the introduction of the adsorptive must be slow enough to provide a continuous ‘equilibrium’ isotherm (i.e. with an infinite number of points). If properly used, the continuous manometric procedure has the great advantage that it is possible to reveal inconspicuous features (e.g. sub-steps), which may not be detectable by the discontinuous method.

The aims of outgassing are two-fold —(a) to reach a well-defined intermediate state by the removal of physisorbed molecules; (b) to avoid any drastic change as a result of ageing or surface modification. Conventional vacuum outgassing is the generally preferred technique, but with fine powders, there is always a risk of spurting. Spurting can be avoided and changes in the adsorbent minimised by controlling the rate of outgassing by the application of a form of controlled rate thermal analysis, CRTA, which is also termed ‘sample controlled thermal analysis’.

VI. PORE SIZE ANALYSIS

A. The classical approach

Capillary condensation is generally responsible for the filling of mesopores and macropores (i.e. pores of width, $w \geq 2$ nm). However, capillary condensation is a secondary process since it is always preceded by multilayer adsorption on the pore walls. Thus, the onset of capillary condensation is indicated by an upward deviation from the corresponding multilayer (Type II) isotherm and the process is complete if a plateau is attained at higher p/p_0 . Since macropore ($w \geq 50$ nm) filling occurs only at very high p/p_0 , the characteristic Type IV isotherm shape is generally associated with mesoporous adsorbents. The mesopore capacity is the amount adsorbed at the plateau and the mesopore volume is then obtained by assuming the condensate density to be that of liquid nitrogen (i.e. 0.808 g/cm^3).

According to the classical approach, a corrected form of the Kelvin equation can be used to evaluate the pore width from the pore filling pressure:

$$\ln \frac{p}{p_0} = \frac{2\gamma V_m}{rRT} \quad (24)$$

where r is the radius of the droplet. It is necessarily assumed that the pores are rigid and all of the same simple shape (cylinders or parallel-sided slits) and that the meniscus curvature is dependent on the dimensions of

the pores. In the computation of the mesopore size distribution, allowance must be made for the effect of the multilayer thickness in reducing the dimensions of the free pore space available for capillary condensation.

B. Density functional formulation

Over the past few years density functional theory (DFT), which in the refined form of nonlocal density functional theory (NLDF), has become an important tool for the characterisation of porous materials. The approach is based on the established principles of statistical mechanics and necessarily assumes a model solid structure and pore topology. The pores of different size are assumed to be all of the same regular shape (e.g. cylinders or slits) and generally each pore is assumed to behave independently. The adsorbate is pictured as an inhomogeneous

fluid, which is characterised by its density profile across the pore. According to the DFT theory, the solid–fluid and fluid–fluid interactions control the pore filling, which may take the form of micropore filling or capillary condensation. If the adsorbent surface is assumed to be homogeneous, the derived energetic heterogeneity can be attributed to the pore size distribution. The interpretation is evidently more complicated when the energetic heterogeneity is associated with both the surface chemistry and the pore structure.

With the availability of commercial software, DFT has become user friendly. However, it must be kept in mind that it is of limited value unless the solid and surface structures are known and the pores are all of a similar, well-defined, shape. Much attention has been given so far to assemblies of slits between graphitic slabs, which are taken to represent porous carbons. Another favoured structure is an assemblage of non-intersecting tubular pores as in MCM-41.

-
- [1] I. Langmuir, Journal of the American Chemical society **40**, 1361 (1918).
 - [2] S. Brunauer, P. H. Emmett, and E. Teller, Journal of the American chemical society **60**, 309 (1938).
 - [3] K. Shi, K. Gu, Y. Shen, D. Srivastava, E. E. Santiso, and K. E. Gubbins, The Journal of chemical physics **148**, 174505 (2018).
 - [4] K. Sing, Colloids and Surfaces A: Physicochemical and Engineering Aspects **187-188**, 3 (2001).