

# Henry's Law Behavior of Multilayered Adsorption at Low Pressure

Cheol Ho KIM

*Faculty of Electrical and Electronic Engineering, Honam University, Kwangju 506-090*

## Abstract

One of the general properties of adsorption on multilayer is that the amount of adsorbing particles is not saturated. As another important property, in many cases, the amount of adsorbed particles is linearly proportional to the pressure of gases above the layers, at sufficiently low pressure, which is known to be Henry's experimental law. A purpose of this paper is to show qualitatively, in terms of a theory, that an adsorption on multilayer obeys Henry's law at the region of low pressure. For this, we introduce a simple multilayer adsorption model and establish an adsorption isotherm for the given model, which is analyzed in the limit of low pressure.

## §1. INTRODUCTION

Since Langmuir [1] has suggested an adsorption isotherm on monolayer to investigate the adsorption phenomena of hydrogen atoms on tungsten/filament surface, many isotherms have been reported on the basis of theoretical or experimental methods [2]. Isotherm contains the various physical informations for adsorption itself as well as for the dynamic behaviors of particles on surface, and for the surface structures. Increasingly growing importance of a role of the surface in recent high-technological material science spurred the advancement of adsorption isotherms and adsorption theory. The fields of the surface under very rigorous

study include the subject such as surface diffusions [3–5], inelastic collision and the trapping of gas atoms on crystal surface [6–8], energy dissipation process of the surface atom [9], crystallogrowth phenomena [10], surface phase transition [11–13], adsorption isotherm on the heterogenous surface [14–16], and the fractals. Especially, the fractal concept introduced by Mandelbrot [17,18] is known to be a very useful theoretical technique in studying the surface adsorption of particles [19–21].

Langmuir derived an isotherm of adsorption based on the following assumption [1,2]: there exists a monolayer in the interface between solid phase and gas phase in which monolayer there contain many active sites for gas molecules to be adsorbed, but each site can accommodate only one particle. This assumption implying that the particles can adsorb not to exceed the amount above one monolayer leads to the Langmuir adsorption isotherm [1] given by

$$\theta = \frac{KP}{1 + KP}, \quad (1)$$

where  $\theta$  is the occupied fraction of sites (the coverage),  $P$  the pressure, and  $K$  the adsorption equilibrium constant which is dependent on the temperature. The Langmuir theory, which admits only one monolayer of particles for adsorbing, is extended to the multilayered adsorption theory by Brunauer, Emmett and Teller (BET isotherm) [22], and independently by Cassie [23]. These isotherms, mainly BET isotherm, are very useful in determining the surface area of catalyst [24]. Up to date since Hill reformulated these topics, there have appeared many adsorption isotherms on multilayer as theories for predicting the phenomena and as experimental results for confirming or complementing the existing theories [25–29]. For example, Nakayama et al. [30] showed by introducing a model for adsorption on multilayer that as the pressure of gas phase increases to go to a saturation point, the amount of adsorbed particles rapidly increases. This adsorption was observed in the adsorption of bromine molecules on silica gel powder.

One of the general properties of adsorption on multilayer is that the amount of adsorbing particles is not saturated. As another important property, in many cases, the amount of

adsorbed particles is linearly proportional to the pressure of gases above the layers, at the sufficiently low pressure, which is known to be Henry's experimental law [31-33]. A purpose of this paper is to show qualitatively, in terms of a theory, that an adsorption on multilayer obeys Henry's law at the region of low pressure. For this, we introduce a multilayer model such that the molecules are allowed to adsorb just on the particles already adsorbed or on the substrate sites and establish an adsorption isotherm for the given model, which is analyzed in the limit of low pressure.

## §2. MODEL

Let us introduce a model and impose a restriction on the surface conformation for calculation. Many monolayer ( $n$  layers) are interspaced between a gas phase and a solid phase to form multilayers. A gas phase is assumed to comprise of the ideal gases of temperature  $T$  in equilibrium. Let us number the monolayers in sequence by 1, 2, 3,  $\dots$ ,  $n$  from the monolayer near the solid surface to the one far from the surface, and represent the number of particles adsorbed on the  $j$ th layer by  $X_j$ . The particles adsorbed on the  $j$ th layer forms the  $(j + 1)$ th layer and serves as the active sites for the  $(j + 1)$ th layer. Notice that  $X_0$  represents the number of sites for the first layer particles to be adsorbed. Since an active site can accommodate only one particle, the following inequalities hold

$$X_0 \geq X_1 \geq X_2 \geq \dots \geq X_n \geq 0. \quad (2)$$

We let the bonding energy of a particle adsorbed be  $-E$  ( $< 0$ ).

## §3. THEOREM AND DISCUSSIONS

In the absence of the interactions between adjacent layers the canonical partition functions of each layer become independent each other. And more, if the interactions between adsorbed particles within a layer are excluded, the particles are expected to be distributed at random. In this case, the canonical partition function  $Q(X_j, T)$  in the  $j$ th layer becomes

$$Q(X_j, T) = \frac{X_{j-1}!}{X_j!(X_{j-1} - X_j)!} \exp\left(\frac{EX_j}{kT}\right), \quad (3)$$

and the chemical potential becomes for  $j$ th layer by using the Stirling formula

$$\begin{aligned} \frac{u_j}{kT} &= -\frac{d}{dX_j} \ln Q(X_j, T) \\ &= \ln\left(\frac{X_j}{X_{j-1} - X_j}\right) - \frac{E}{kT}, \end{aligned} \quad (4)$$

where  $k$  is a Boltzmann constant.

Because the layers and gas phase are in equilibrium, the chemical potentials satisfy the following relations:

$$u_1 = u_2 = \dots = u_n, \quad (5)$$

and

$$u_n = u_g, \quad (6)$$

where  $u_g$  is the chemical potential of gas phase. Substituting Eq. (4) into Eq. (5), we get

$$\begin{aligned} \frac{X_1}{X_0 - X_1} &= \frac{X_2}{X_1 - X_2} \\ &\vdots \\ &= \frac{X_n}{X_{n-1} - X_n}, \end{aligned} \quad (7)$$

and Eq. (6) gives

$$\ln \frac{X_n}{(X_{n-1} - X_n)} - \frac{E}{kT} = \ln f(T) + \ln P, \quad (8)$$

where  $P$  is the pressure of gas phase, and  $f(T)$  is given by [34]

$$f(T) = \frac{1}{kT} \left( \frac{h^2}{2\pi mkT} \right)^{3/2}. \quad (9)$$

Here  $h$  is the Planck constant, and  $m$  the mass of a gas particle (or an adsorbed particle).

Let the pressure satisfying  $X_n = X_{n-1}/2$  be  $P_0$  and let  $b$  be a ratio of pressures with a reference pressure  $P_0$ ,

$$\frac{P}{P_0} = b, \quad (10)$$

which contains  $T$ . Then Eq. (8) reduces to

$$X_n = b(X_{n-1} - X_n), \quad (11)$$

and Eq. (7) is rearranged as the following sequence of equations

$$\begin{aligned} (X_0 - X_1) X_n &= X_1 (X_{n-1} - X_n) \\ (X_1 - X_2) X_n &= X_2 (X_{n-1} - X_n) \\ &\vdots \\ (X_{n-2} - X_{n-1}) X_n &= X_{n-1} (X_{n-1} - X_n). \end{aligned} \quad (12)$$

From Eq. (11) and Eq. (12), we get relations

$$X_j = (X_{j-1} - X_j) b. \quad (13)$$

The total number of adsorbed particles  $N$  is obtained through Eq. (13) as

$$\begin{aligned} \frac{N}{X_0} &= (X_1 + X_2 + \dots + X_n) / X_0 \\ &= \frac{1}{X_0} \left( \frac{bX_0}{1+b} + \frac{bX_1}{1+b} + \dots + \frac{bX_{n-1}}{1+b} \right) \\ &= \sum_{j=1}^n \left( \frac{b}{1+b} \right)^j \\ &= b \left[ 1 - \left( \frac{b}{1+b} \right)^n \right]. \end{aligned} \quad (14)$$

An adsorption isotherm on multilayer Eq. (14) reduces to a Langmuir adsorption isotherm Eq. (1) for  $n = 1$ :

$$\frac{N}{X_0} = \frac{b}{1+b}. \quad (15)$$

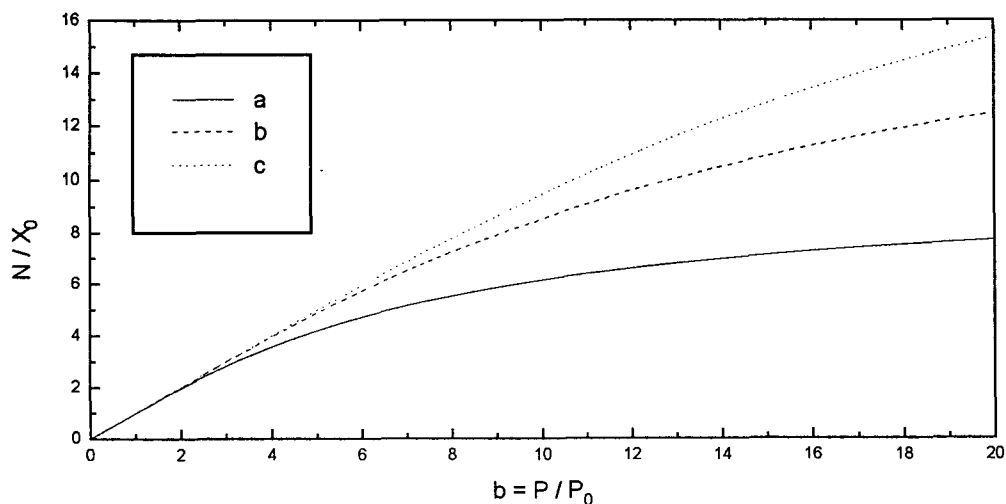
Eq. (14) becomes approximately

$$\frac{N}{X_0} \sim b \quad (16)$$

for large  $n$  and low pressure, which satisfies Henry's law such that the adsorbed particles are linearly proportional to the pressure. Fig. 1, plot of a schematic diagram of Eq. (14) for a reduced amount of adsorbed particles,  $N/X_0$ , versus the reduced pressure,  $b = P/P_0$  for some values of finite  $n$ , represents qualitatively well this fact. This plot shows that the amount of adsorbed particles monotonically increases as the pressure increases and the curves through the origin go to a straight line as the number of layers  $n$  increases or as the pressure decreases. Henry's law behavior is universal at sufficiently low pressure, and is more satisfactory in the dissolution of gases into liquid phase [31–33] and in the adsorption of gases on graphitized carbon black and on zeolites [35–37]. From Eq. (15), we see that Henry's law is also true of an adsorption on monolayer with a very small amount of adsorbed particles .

In this paper, we have not considered the interactions between adjacent layers or between adsorbed particles within a layer. Our adsorption model excluded those interactions is useful for the limit of low particle density, that is, for the range of low pressure in which we are interested. It is required to study of the adsorption isotherm considered of those interactions to explain the various adsorption behavior for the wide range of pressure.

**Fig. 1 :** The reduced amount of adsorbed particles ,  $N/X_0$ , versus the reduced pressure,  $b = P/P_0$  for  $n = 10$  (a), 20 (b), and 30 (c).



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