Chapter 3

GAS ADSORPTION THEORY

Adsorption is a phenomenon, in which certain types of molecules in fluid, called adsorbates, adhere to the surface of a solid, called an adsorbent. When adsorption occurs, the adsorbed molecules loose their molecular motion and release energy that is often called "heat of adsorption". In general, adsorption can be divided into two types, i.e. chemical and physical adsorption. The former, known as chemisorption, is characterized mainly by large interaction potential, which leads to release large amount of energy frequently approaching chemical bonds. Results of spectroscopic, electron spin resonance, and magnetic susceptibility measurements demonstrates that chemisorption involves true chemical bonding between the adsorbate molecules and certain portions of the surface [10]. Since chemisorption occurs in the same manner as a chemical reaction, it is often found to occur at temperatures above the critical temperature of the adsorbate [11, 12]. However, chemisorption is restricted to a single layer of adsorbates on the surface. In other words, the adsorbate molecules can be adsorbed on certain surface of the adsorbent leading to saturation of adsorption at a given temperature.

The latter is physical adsorption which exhibits physical characteristics for adsorbing some adsorbates on the surface. Such characteristics consist of van der Waals forces, polarization and/or electrostatic forces [13]. Such forces may act as attraction forces or repulsion one depending upon relative characteristics between the adsorbent surface and the adsorbate molecules. Furthermore, each adsorbed molecule may produce attraction forces in order to adsorb another molecule upon the adsorbed one. Under the circumstances, adsorbate molecules can be adsorbed upon the layer of adsorbed molecules, which has been known as multilayer adsorption. Although it seems to be analogy between physical adsorption of adsorbates from gas phase and condensation of such components, the adsorption still occurs even at temperatures above the critical temperatures of the corresponding adsorbates.

3.1 Adsorption Equilibrium in Gas Phase

For a system of a single adsorbate in gas phase, the adsorption equilibrium can be achieved after a sufficiently long period of existence of a selected adsorbent. In the circumstances, the adsorbed amount of the adsorbate (q) depends on the state of the system, i.e. the partial pressure of the adsorbate (p) and temperature (T), as described phenomenologically by

$$q = f(p, T) \tag{3.1}$$

The adsorbed amount (q) can be expressed in terms of volumes adsorbed per unit mass of adsorbent, moles adsorbed per unit mass of adsorbent, or mass adsorbed per unit mass of adsorbent. An expression of relationship between the adsorbed amount and the partial pressure of the adsorbate at a given temperature has been known as "an adsorption isotherm".

3.1.1 Linear Isotherms

When the adsorbed amount (q) is far small compared with the adsorption capacity of the adsorbent; at equilibrium, the adsorbed amount becomes proportion to the partial pressure of the adsorbate. The equilibrium relationship has been known as a linear isotherm, which is analogous to Henry's law of dilute solution as written below:

$$q_i = K_i p_i \tag{3.2}$$

where K_i is adsorption equilibrium constant for component i. The equilibrium constant varies with the temperature of the system, which corresponds with the exothermic phenomenon. The temperature dependence obeys the van't Hoff equation [13, 14], written as

$$\frac{\partial lnK}{\partial T} = \frac{+\Delta H}{RT^2} \tag{3.3}$$

Where ΔH is heat of adsorption. If the heat of adsorption is independent of temperature, the logarithmic adsorption equilibrium constant (lnK) will be proportional to the reciprocal temperature ($1/T$). In the circumstances, the heat of

adsorption can be determined from the slope of the linear plot of the temperature dependence on the adsorption equilibrium constant, as expressed in equation 3.3.

3.1.2 Nonlinear Isotherms

For a system of concentrated adsorbate, the relationship between the adsorbed amount (q) and the partial pressure usually becomes nonlinear. One of most well-known adsorption equilibrium models is Langmuir isotherm which was analogous reversible reaction. At equilibrium, the rate of adsorption, which is proportional to the partial pressure and a fraction of unoccupied adsorption sites, is equal to the rate of desorption, which is proportional to the other fraction of adsorption sites, or a fraction of the occupied adsorption sites. The resulted isotherm can be expressed as equation 3.4.

$$\frac{q}{q_{s,i}} = \frac{K_L P_i}{1 + K_L P_i} \qquad (3.4)$$

As an increase in the partial pressure of the adsorbate, the adsorbed amount approaches to the saturation limit of the adsorbed amount. The result corresponds to monolayer adsorption. While the Langmuir isotherm (equation 3.4) is reduced to linear isotherm (equation 3.2) as decreasing the partial pressure. In the circumstances, the product of the saturation limit of the adsorbed amount ($q_{s,i}$) and the Langmuir constant (K_L) becomes equal to the adsorption Henry's constant (K_H). Another common adsorption equilibrium models is Freundlich isotherm, which was developed from experimental results. The isotherm can be expressed

as

$$q = K_F p^{1/n} \tag{3.5}$$

In spite of the difference between Langmuir isotherm and Freundlich one in the equilibrium models and the background of developement, both models provides similar adsorption equilibrium curves. However, there is no saturation limit for the Freundlich isotherm. Under the circumstances, the Freundlich isotherm can be employed for multilayer adsorption.

3.2 Adsorption Equilibrium Measurement

Two direct methods for the determination of adsorption equilibrium are volumetric and gravimetric methods.

3.2.1 Volumetric Method

The commonest is the volumetric method which a certain amount of adsorbents has to be placed under vacuum and let adsorbate gas into the system of which the volume and temperature are controlled. The adsorbed amounts of adsorbate is a difference of the amounts of adsorbate between the feed amounts into system and the amounts remained in the system. The remaining amounts of the adsorbate can be determined from an incremental pressure of the system. The concept is similar to BET adsorption measurement.

3.2.2 Gravimetric Method

In this method, a change of grained weight of the adsorbent is measured. Thus, the unadsorbed amount is a different amounts of the adsorbed amounts from the fed amounts.

In order to obtained the equilibrium rapidly, the measurement has to be carried under the vacuum condition.

3.2.3 Chromatographic Method

Although both volumetric and gravimetric methods can be employed to measure equilibrium adsorption properly, both methods are restricted to moderate adsorbed amounts upwards. Because of the limitation of accuracy of measurement devices, both methods may provide improper adsorbed amounts, leading to erroneous isotherm. Under the circumstances, the adsorbed amounts may be measured indirectly by measuring the equilibrium constant instead, where the isotherm usually becomes linear. The indirect measurement is chromatographic method, under which a relatively small pulse of adsorbate is injected into a packed column containing a selected adsorbent. The chromatogram obtained provides information of the equilibrium constant, which has to be estimated from the first absolute moment of the chromatogram given as equation 3.6 and equation 3.7 [15].

$$t_R = \frac{\int_0^\infty ct\,dt}{\int_0^\infty c\,dt} \tag{3.6}$$

$$t_R = \left(1 + \left\{\frac{1-\epsilon}{\epsilon}\right\}K\right)\frac{L}{v} \tag{3.7}$$

In order to obtain reliable equilibrium constant, several small pulses of adsorbate have to be injected into the column at various flow of carrier gas

The equilibrium constant can then be estimated from the slope of the linear plot of the first absolute moment with the reciprocal velocity.

3.3 Gas Adsorption Kinetics

Since adsorption occurs mostly on the internal surface, the adsorption mechanism consists of diffusion across the external film around adsorbent particles and diffusion in the pore volume. As diffusing in the pore volume, adsorbate molecules can be adsorbed instantly at the interface between gas phase and adsorbed phase. Therefore, the rate of adsorption is contrrolled by either the external film diffusion or the pore diffusion, as illustrated in Figure 3.1. For a single adsorbate system, the adsorbed phase contains adsorbate molecules only so that the adsorbed molecules do not diffuse further in the adsorbed phase.

3.3.1 External Film Diffusion

If the rate of adsorption is controlled by the external film diffusion, it can be expressed conveniently in term of the external film mass transfer coefficient, as follow:

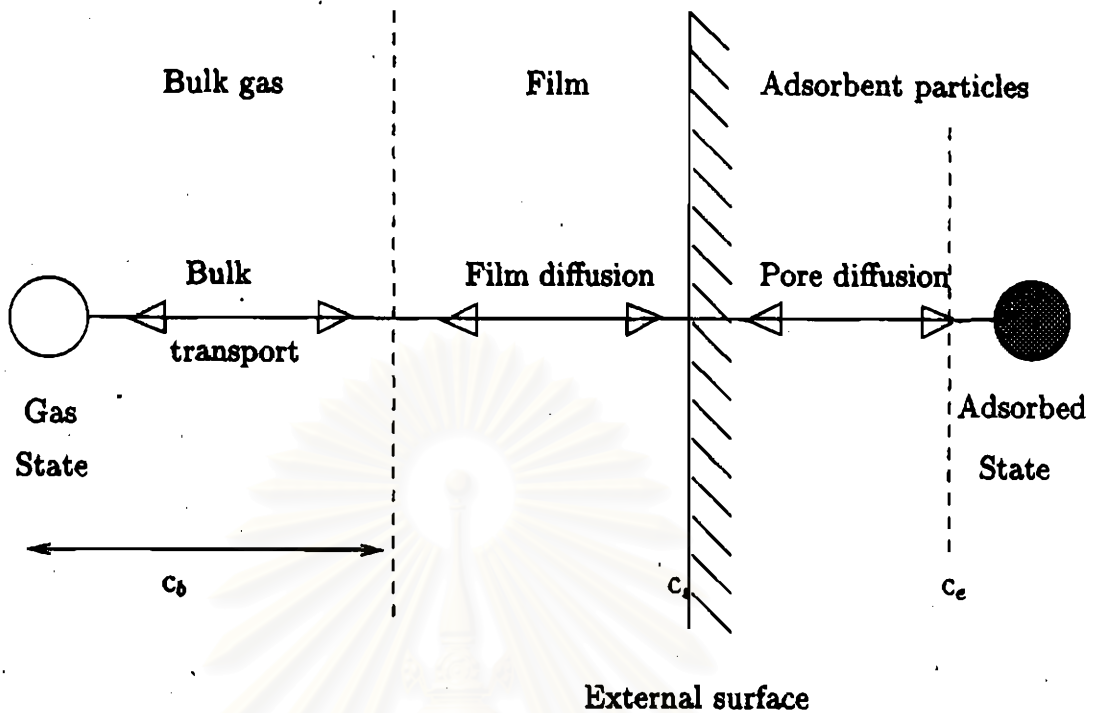$$R_{ads} = (k_f a) \frac{\epsilon(c_b - c_s)}{\rho_s(1 - \epsilon)} \tag{3.8}$$

Figure 3.1: Mass transport steps in adsorption by porous adsorbents

While the mass transfer coefficient can be estimated from an appropriate correlation of Sherwood number, Sh, with Reynolds number, Re, and Schmidt number, Sc. For a single spherical adsorbent with radius ,R_p, for instance, the rate of mass transfer can be determined from the correlation of Ranz and Marshall [13], wriiten as

$$k_f \frac{2R_p}{D_m} = 2.0 + 0.6 Sc^{1/3} Re^{1/2} \qquad (3.9)$$

For a packed bed of uniform size of adsorbent particles with radius, R_p, an appropriate correlation for determination of the external mass transfer coefficient was developed by Wakao and Funazki [13], written as

$$k_f \frac{2R_p}{D_m} = 2.0 + 1.1 Re^{0.6} Sc^{1/2} \qquad (3.10)$$

The estimated mass transfer coefficient is satisfied as the Reynolds number is in the range of 3-10,000.

3.3.2   Pore Diffusion

Diffusion in the pore volume of the selected adsorbent depends on the collision frequency among adsorbate molecules and that between adsorbate molecules and the pore area. If the collision frequency among adsorbate molecules is higher than the other, the pore diffusion can be represented by the molecular diffusion in open space. On the contrary, the pore diffusion has been known as Knudsen diffusion [13]. A common criteria for identification of diffusion in pore volume is the ratio of the average pore diameter of the selected adsorbent to the mean free path of the adsorbate. If the ratio is greater than unity, the pore diffusion is equivalent to the molecular difusion. Otherwise, it becomes Knudsen diffusion. In order to increase the specific surface area, the average pore diameter tends to be relatively small so that the diffusion in the pore volume should be Knudsen type. In the circumstances, the rate of adsorption relates to Knudsen diffusivity. Which can be determined from the following expression:

$$D_k = \frac{2\sqrt{8RT}R_p}{3\sqrt{\pi M}} = 9700 R_p (T/M)^{1/2} \qquad (3.11)$$

Alternatively, the rate of adsorption, which is controlled by the pore diffusion, may be expressed in term of pore mass transfer coefficient (k_{pore}), defined as

$$R_{ads} = k_{pore}(c_s - c_e) \qquad (3.12)$$

However, the mass transfer coefficient must be obtained from experimental results only. Instead of determination of the rate of pore diffusion, the effective rate of adsorption is determined practically in term of overall mass transfer coefficient, (k_o), which is defined as

$$R_{ads} = k_o(c_b - c_\epsilon) \tag{3.13}$$

The overall mass transfer coefficient is a combined mass transfer coefficient of the external film and the pore mass transfer coefficient. Equation 3.13 has been known as "linear driving force rate of adsorption"

The overall mass transfer coefficient has to be determined from experimental results. One of simple methods is the chromatographic method as mentioned previously. According to moment analysis of pulse chromatograms. The second central moment of the chromatogram, which is defined as equation 3.14

$$\sigma^2 = \frac{\int_0^\infty (t - t_R)^2 dt}{\int_0^\infty c\, dt} \tag{3.14}$$

provides information of the overall mass transfer coefficient as the following relationship [16]

$$\frac{\sigma^2}{2t_R^2} \frac{L}{v} = D_L \left(\frac{1}{v^2}\right) + \left(\frac{\epsilon}{1-\epsilon}\right) \left(\frac{1}{kK}\right) \left(1 + \frac{\epsilon}{(1-\epsilon)K}\right)^{-2} \tag{3.15}$$

However, the determination of the overall mass transfer coefficient requires the equilibrium constant, which can be determined from the first absolute moment of such chromatograms, as described previously. The overall mass transfer coefficient is determined from the intercept of the linear plot, as expressed in equation 3.15

This equation was related to the second central moment of the chromato-graphic peak at the column outlet to the width of the injected pulse, the parameters which characterize the column and the adsorbent, the constants which describe the adsorption, and the overall mass transfer coefficient. The axial dispersion coefficient can be evaluated by the slope of the second moment versus $1/v^2$.