Adsorption at Fluid–Solid Interfaces

Dr. Pallab Ghosh

Associate Professor

Department of Chemical Engineering

IIT Guwahati, Guwahati–781039

India

Table of Contents

4.4.1 Physical and chemical adsorptions

- The solid surfaces are not smooth in the microscopic sense. There are irregular valleys and peaks distributed all over the area. The regions of irregularity are particularly susceptible to residual force fields. At these locations, the surface atoms of the solid may attract other atoms or molecules in the surrounding gas or liquid phase. The surfaces of pure crystals have non-uniform force fields because of the atomic structure in the crystal. Such surfaces also have sites or active centers where adsorption is favored.
- Adsorption on solid surfaces may be divided into two categories, viz. *physical* and *chemical* adsorption. Physical adsorption is non-specific and similar to condensation. The forces that attract the fluid molecules to the solid surface are weak van der Waals forces. The physical adsorption is also known as *van der Waals adsorption*.
- The heat evolved during physical adsorption is low, which usually lies between 2–25 kJ/mol. The energy of activation for physical adsorption is also low (<5 kJ/mol). Equilibrium between the solid surface and the gas molecules is usually attained rapidly and it is reversible because the energy requirements are small. Multiple layers of adsorbed molecules are possible, especially near the condensation temperature. The extent of physical adsorption decreases with increasing temperature. Physical adsorption is useful for determining the surface area and pore size of solid catalysts.
- Chemical adsorption or *chemisorption* is specific. It involves forces which are much stronger than physical adsorption. The amount of heat evolved in chemisorption is large (e.g., 50–500 kJ/mol), which is similar to chemical reactions.
- The name *chemisorption* was given by H. S. Taylor (1931). However, the concept of chemisorption was proposed by Langmuir much earlier (in 1916). According to him, in the interior of the solid material (i.e., the *adsorbent*), the atoms have their force field wholly satisfied by the atoms which surround them. The atoms on the surface however are not surrounded. These atoms have a residual force due to

unshared electrons towards exterior. This residual force-field leads to sharing of electrons with the striking gas molecules (i.e., the *adsorbate*).

- A sort of covalent linkage is formed between the gas molecules and the atoms of the solid at the surface. However, this linkage is not same as the covalent bond that exists in a chemical compound. In spite of the sharing of electron with the gas molecule, the surface atom remains bonded simultaneously with the other atoms in the crystal lattice.
- Langmuir observed that a stable film of oxide formed on tungsten wires in presence of oxygen, which was not same as the normal oxide, WO_3, in terms of its properties. This oxide gave off from the surface upon desorption. This adsorbed compound was designated as $W{\cdot}O_3$.
- Langmuir pointed out that because of the rapid falling-off of intermolecular forces with distance, it is probable that the adsorbed layers are no more than a single molecule in thickness. Langmuir (1918) proposed simple formulations for rates of adsorption and desorption of gases on solid surfaces. These are also applicable to liquids.
- Unlike physical adsorption, chemisorption does not take place on all solids. It occurs with some chemically reactive gases. Chemisorption usually occurs at high temperatures. The surface coverage is limited to a monolayer. The process is often irreversible. Chemisorption is used for finding the active centers of a catalyst.
- Chemisorption can be divided into two categories, viz. *activated chemisorption* and *non-activated chemisorption*. In activated chemisorption, the rate of chemisorption varies with temperature following Arrhenius law with finite activation energy. In some situations, chemisorption occurs very rapidly which suggests that the activation energy is nearly zero. This type of adsorption is called *non-activated chemisorption*. Both activated and non-activated chemisorption may take place at different stages of an adsorption process. A comparison between physical adsorption and chemisorption is presented in Table 4.4.1.

Table 4.4.1 Comparison between physical adsorption and chemisorption

Physical adsorption	Chemisorption
All solids can be used as adsorbents	Some solids can be used as adsorbents
All gases below their critical temperatures can act as adsorbates	Some chemically reactive gases can act as adsorbates
Occurs at low temperatures	Generally occurs at the high temperatures
Low heat of adsorption	High heat of reaction, which is of the order of the heats of chemical reactions
High rate	Both low and high rates are observed
Low activation energy	Low activation energy for non-activated chemisorption, and high activation energy for activated chemisorption
Multilayer possible	Monolayer
Highly reversible	Often irreversible
Used for the determination of surface area and pore size	Used for the determination of active-center area and elucidation of surface reaction kinetics

4.4.2 Henry, Freundlich and Langmuir adsorption isotherms

- A simple adsorption isotherm which is sometimes used to describe the adsorption at a gas–solid interface is the Henry's law, given by,

$$\frac{y}{m} = k'_H p \tag{4.4.1}$$

where y kg of gas is adsorbed by m kg of adsorbent at pressure p.

- This equation qualitatively describes the experimental observation that the extent of adsorption of a gas on a surface generally increases with increasing pressure. At low temperatures, the adsorption of a gas increases very rapidly as the pressure rises. However, when the temperature is high, the increase in adsorption is relatively less.

- It has been found that the relationship between y/m and p is not linear, but varies according to the following equation for many adsorption systems (gases as well as liquids).

$$\frac{y}{m} = k_F \left(p\right)^{1/n_F}, \qquad n_F > 1 \tag{4.4.2}$$

  This equation is known as *Freundlich isotherm*.
- Equation (4.4.2) predicts that a plot of $\ln\left(y/m\right)$ versus $\ln\left(p\right)$ should be a straight line. From the slope and intercept of the plot, n_F and k_F can be determined.
- The Freundlich isotherm can be expressed in terms of concentration when p is replaced by equilibrium concentration of the adsorbate, c_a.

Example 4.4.1: The following data describe adsorption of a pesticide from aqueous solution on activated carbon at 298 K.

c_a (mmol/m^3)	y/m (mmol/kg)	c_a (mmol/m^3)	y/m (mmol/kg)
1.74×10^{-3}	0.83	38.80×10^{-3}	14.52
4.06×10^{-3}	1.94	78.30×10^{-3}	19.77
6.96×10^{-3}	3.87	104.93×10^{-3}	24.19
17.40×10^{-3}	7.47	158.80×10^{-3}	25.71

Fit Freundlich adsorption equation to these data and determine the constants, k_F and n_F.

Solution: From Eq. (4.4.2) we have,

$$\ln\left(\frac{y}{m}\right) = \ln k_F + \left(\frac{1}{n_F}\right)\ln c_a$$

The given data are plotted in Fig. 4.4.1.

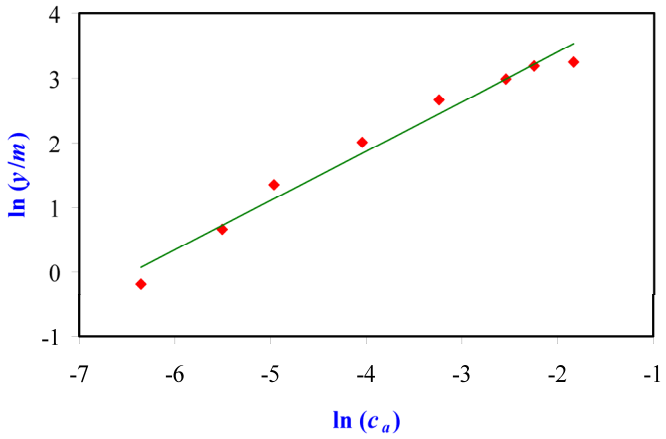

Fig. 4.4.1 Plot of $\ln(y/m)$ versus $\ln(c_a)$.

The slope and intercept of the fitted straight line are,

slope = $1/n_F = 0.77$

intercept = $\ln k_F = 4.94$

Therefore, $n_F = 1.3$ and $k_F = 139.8\ (\text{mmol})^{1-1/n_F}\ (\text{m})^{3/n_F}\ (\text{kg})^{-1}$

- The Langmuir isotherm for adsorption at solid–gas or solid–liquid interfaces can be expressed in a manner similar to that described in Lecture 2 of Module 4.

$$\frac{y}{m} = \frac{k_1 k_2 p}{1 + k_1 p} \tag{4.4.3}$$

  where p is the pressure of the gas, and k_1 and k_2 are constants.

- The limiting conditions of Eq. (4.4.3) (i.e., low and high pressure limits) can be analyzed as follows. At low pressure, y/m is proportional to p, whereas at high pressure, it is constant. At the intermediate pressures, the amount of adsorption may be described by the Freundlich isotherm, where $1/n_F$ lies between 0 and 1.
- The adsorption data are seldom fitted by any single isotherm over the entire range of pressure (or concentration) of the adsorbate.
- An important parameter associated with adsorption is the heat of adsorption (ΔH_a). It generally changes with the change in surface coverage. The heat of adsorption for chemisorption is generally much higher than that for physical

adsorption. It is assumed in the Langmuir theory that ΔH_a is independent of the fraction of surface covered by the adsorbed molecules. In the Freundlich isotherm, it is assumed that ΔH_a decreases logarithmically with the increasing fraction of surface covered.

4.4.3 Brunauer–Emmett–Teller (BET) theory

- The theory of chemical adsorption proposed by Langmuir is based on the formation of a monolayer. However, multilayers can form in physical adsorption. For example, several layers of nitrogen molecules can adsorb on top of each other on the surface of silica gel at 77 K below atmospheric pressure.
- The isotherm in the case of a monolayer assumes the shape shown in Fig. 4.4.2 (type I).

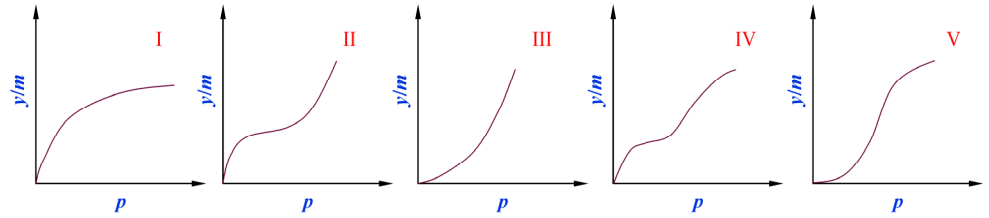

Fig. 4.4.2 Adsorption isotherms.

- The extent of adsorption increases with pressure and ultimately reaches a limiting value, as predicted by the Langmuir theory. However, for adsorption involving multilayer formation at low temperatures, at least four other types of adsorption isotherms can be observed (types II–V in the figure).
- To explain such varied adsorption isotherms, Brunauer, Emmett and Teller (1938) developed a theory of multilayer adsorption extending Langmuir's monolayer theory. They proposed that even after the formation of the monolayer, other layers of gas may condense on it. Langmuir's idea of fixed adsorption sites was however retained. They suggested that there is equilibrium between the first layer and the adsorbent. Similar dynamic equilibria exist for the successive molecular layers. The van der Waals forces provide the binding energy in these successive layers. The equation derived by them is,

$$\frac{p}{v\left(p^s - p\right)} = \frac{1}{v_m C} + \left(\frac{p}{p^s}\right)\left(\frac{C-1}{v_m C}\right) \tag{4.4.4}$$

where v is the volume of gas adsorbed under pressure p, p^s is the saturated vapor pressure, v_m is the volume of gas adsorbed when the surface is covered with a monolayer, and C is a constant which can be related to the heat of adsorption for the first layer (E_1) and the enthalpy of liquefaction of the gas (E_L).

$$C = \exp\left(\frac{E_1 - E_L}{RT}\right) \tag{4.4.5}$$

- According to Eq. (4.4.4), a plot of $\left[\frac{p}{v\left(p^s - p\right)}\right]$ with $\left(\frac{p}{p^s}\right)$ should give a straight line.
- The slope and intercept are given by,

$$\text{slope} = \frac{C-1}{v_m C} \tag{4.4.6}$$

$$\text{intercept} = \frac{1}{v_m C} \tag{4.4.7}$$

- From Eqs. (4.4.6) and (4.4.7), v_m is given by,

$$v_m = \frac{1}{\text{slope} + \text{intercept}} \tag{4.4.8}$$

- The adsorption isotherm of type II occurs when $E_1 > E_L$, and that of type III occurs when $E_1 < E_L$.
- Isotherms of types IV and V are observed when not only multilayer adsorption occurs, but the capillary pores of the adsorbent are filled by condensation at a pressure much lower than the saturation pressure, p^s: an isotherm of type IV is obtained if $E_1 > E_L$ and a type V isotherm is obtained when $E_1 < E_L$.

- The volume of gas adsorbed when the surface is covered by a monolayer (v_m) is recorded at standard temperature and pressure (STP) (i.e., at 273 K and 101.325 kPa). The volume occupied by one mole of gas at STP is 22.4×10^{-3} m^3. Therefore, the number of molecules of gas adsorbed is $(N_A v_m / 0.0224)$, where N_A is Avogadro's number. If the cross-section of each adsorbed gas molecule is A_c and if *m* kg of adsorbent is present, then the surface area (*S*) per kg of the adsorbent is,

$$S = \frac{N_A v_m A_c}{0.0224 m} \tag{4.4.9}$$

- In Eq. (4.4.9), v_m is expressed in m^3 and A_c is in m^2. The calculation of v_m and S is illustrated in Example 4.4.2.

Example 4.4.2: The following data were obtained for adsorption of nitrogen on 6.06×10^{-4} kg of silica gel at 77 K (Emmett, 1954).

p (kPa)	1.96	20.19	26.66	35.29	38.69	48.26
v at STP (m^3)	6.04×10^{-5}	9.46×10^{-5}	1.03×10^{-4}	1.15×10^{-4}	1.21×10^{-4}	1.44×10^{-4}

(i) Calculate the volume of nitrogen adsorbed over 1 kg of silica gel when a monolayer is formed

(ii) Calculate the surface area of silica gel.

Given: a nitrogen molecule occupies 16×10^{-20} m^2.

Solution: Since the normal boiling point of nitrogen is 77 K, $p^s = 101.325$ kPa. From the given data, $\left[\frac{p}{v\left(p^s - p\right)}\right]$ is plotted against p/p^s, as shown in Fig. 4.4.3.

p/p^s	0.019	0.199	0.263	0.348	0.382	0.476
$\left[\frac{p}{v\left(p^s - p\right)}\right]$, m^{-3}	326.550	2629.679	3484.321	4631.054	5126.221	6327.289

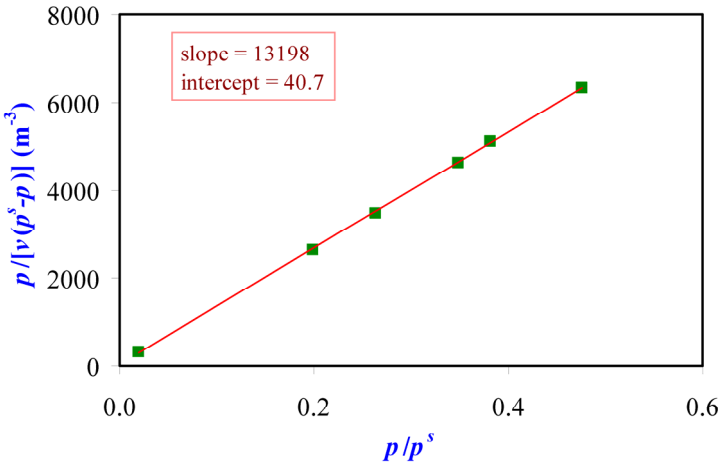

Fig. 4.4.3 Determination of v_m and surface area from BET plot.

(i) From the values of slope and intercept we get,

$$v_m = \left(\frac{1}{6.06\times10^{-4}}\right)\left(\frac{1}{13198+40.7}\right) = 0.125 \text{ m}^3 \text{ for } m = 1 \text{ kg}$$

(ii) From Eq. (4.4.9) we get,

$$S = \frac{N_A v_m A}{0.0224m} = \frac{6.023\times10^{23}\times0.125\times16\times10^{-20}}{0.0224\times1} = 5.4\times10^5 \text{ m}^2/\text{kg}$$

- The surface area analyzer developed by Beckman–Coulter is shown in Fig. 4.4.4.

Fig. 4.4.4 Beckman–Coulter surface area analyzer SA 3100 (reproduced by permission from Beckman–Coulter India, © 2010).

4.4.4 Adsorption hysteresis

- The adsorption and desorption curves often do not coincide. This phenomenon is called *hysteresis*. The first experimental report on hysteresis (for the adsorption of water on silica gel) dates back to 1897. Since that time, the adsorption hysteresis phenomenon has been a subject of continuous scientific research.
- Two hysteresis patterns are shown in Fig. 4.4.5.

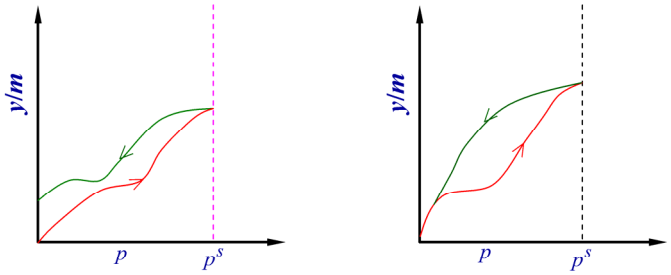

Fig. 4.4.5 Hysteresis in the adsorption on porous solid materials: (a) open loop, and (b) closed loop.

- Hysteresis is mainly associated with porous solids in which the pore size distribution is broad. Below the critical temperature of the adsorbate, multilayer adsorption is generally observed. Capillary condensation takes place inside the pores.

- The open loop hysteresis pattern shown in the Fig. 4.4.5 (a) can be explained by two ways, viz. (i) if the solid has pores which are wider in the interior than at the exit (ink-bottle pores), they can trap the adsorbate, and (ii) irreversible changes may occur in the structure of the pores on adsorption, and the situation when desorption takes place differs from the situation that existed during adsorption.
- The porous adsorbent is often modeled as a bundle of capillaries having different diameters. The filling and emptying processes depend on the geometry of the pores. The adsorption branch in the closed loop hysteresis pattern depicted in Fig. 4.4.5 (b) represents the formation of an increasingly thick film whose radius of curvature would be equal to that of the capillary. Therefore, the radius of capillaries, which are just filling in by condensation, is given by Kelvin equation (see Lecture 3 of Module 2).

$$\frac{p}{p^s} = \exp\left(-\frac{\gamma \bar{v}}{rRT}\right), \quad \bar{v} = \text{ molar volume of liquid} \tag{4.4.10}$$

- In that part of the adsorption curve where $p \to p^s$, the pores fill and empty without hysteresis. This happens when the pores are large and cone-shaped. After all capillaries are filled, they empty on desorption by the retreat of a meniscus of curvature $2/r$. At each stage of desorption, the radius of the capillaries becoming empty is given by,

$$\frac{p}{p^s} = \exp\left(-\frac{2\gamma \bar{v}}{rRT}\right) \tag{4.4.11}$$

- The bundle-of-capillaries model can be wrong at times. This is mainly caused by the ink-bottle pores, which empty at the capillary vapor pressure of the access channel, but discharge the contents of a larger cavity (Adamson and Gast, 1997).

4.4.5 Direct experimental techniques for measurement of adsorption at fluid–solid interfaces

- For studying adsorption on the solid surface, characterization of the surface is a very important task. There are several vacuum and non-vacuum characterization methods.

- Some of the vacuum characterization methods are field emission microscopy, low energy electron diffraction technique, Auger electron spectroscopy, X-ray photoelectron spectroscopy and scanning tunneling microscopy.
- Some of the non-vacuum techniques are atomic force microscopy, total internal reflectance microscopy, attenuated total reflectance spectroscopy, and total internal reflectance fluoroscopy. The details of these methods have been presented by Adamson and Gast (1997).
- For studying the kinetics of adsorption and desorption of gases on the solid surfaces, temperature-programmed desorption is used. In this method, a clean surface is exposed to a flowing gas at a very low pressure (e.g., one millionth of atmospheric pressure). After some time elapses, the monolayer is formed. The surface is then heated by laser or electrical methods. The rate of heating is slow so that the pressure of the gas can be monitored. Therefore, a programmed desorption curve can be obtained.
- The pattern of desorption can show the nature of the site where the adsorption has taken place, i.e., whether the gas is adsorbed on flat surfaces, at steep dislocations or at kink sites. The temperature-programmed desorption can also provide the desorption energy (Adamson and Gast, 1997).
- The rate of desorption may be expressed as,

$$-\frac{d\xi}{dt} = A\xi \exp\left(-\frac{E}{RT}\right) \tag{4.4.12}$$

where ξ is the coverage (i.e., number of surface sites occupied/total number of surface sites), E is the desorption energy and A is the frequency factor. If it is assumed that the temperature rises linearly with time: $T = T_0 + \beta t$ (where β is the rate of temperature rise), the following equation (known as *Redhead equation*) may be used to compute the activation energy (Hunter, 2005).

$$\frac{E}{RT_m^2} = \frac{A}{\beta}\exp\left(-\frac{E}{RT_m}\right) \tag{4.4.13}$$

where T_m is the temperature of the maximum desorption rate. The value of the frequency factor, A, is usually taken as 10^{13} s^{-1}.

- For chemisorption, usually a rapid heating process (flash desorption) is used and the products are analyzed with a mass spectrometer.

Exercise

Exercise 4.4.1: The following data were obtained for adsorption of oxygen on 6.06×10^{-4} kg of silica gel at its normal boiling point of 90 K.

p (kPa)	6.2	17.7	25.4	37.5	46.2	57.0
$v \times 10^5$ at STP (m^3)	5.6	8.0	9.3	11.0	13.0	15.0

Calculate the volume of oxygen adsorbed over 1 kg of silica gel when a monolayer is formed.

Exercise 4.4.2: The following data are available on the adsorption of ethylene on charcoal at 318 K.

$p \times 10^{-5}$ (Pa)	3.161	12.108	15.280	20.984	30.337	31.836	40.074
y/m	0.1219	0.1494	0.1502	0.1608	0.1705	0.1678	0.1687

Obtain the parameters of Langmuir adsorption isotherm from these data.

Exercise 4.4.3: Answer the following questions clearly.

1. Explain the terms physical adsorption and chemical adsorption. Explain the difference between them.
2. Explain the significance of Freundlich isotherm.
3. Describe the BET theory of adsorption. Using this theory, how can you explain the various adsorption curves?
4. What is *adsorption hysteresis*? Why does it occur?
5. What are ink-bottle pores?
6. Mention two techniques by which adsorption at solid surfaces can be characterized.

Suggested reading

Textbooks

- P. Ghosh, *Colloid and Interface Science*, PHI Learning, New Delhi, 2009, Chapter 6.

Reference books

- A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces*, John Wiley, New York, 1997, Chapters 8, 16 & 17.
- G. J. M. Koper, *An Introduction to Interfacial Engineering*, VSSD, Delft, 2009, Chapter 7.
- R. J. Hunter, *Foundations of Colloid Science*, Oxford University Press, New York, 2005, Chapter 6.

Journal articles

- H. S. Taylor, *J. Am. Chem. Soc*., **53**, 578 (1931).
- I. Langmuir, *J. Am. Chem. Soc*., **38**, 2221 (1916).
- I. Langmuir, *J. Am. Chem. Soc*., **40**, 1361 (1918).
- S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc*., **60**, 309 (1938).