CHAPTER 15

Liquids and Gases in Equilibrium with Solids

15.1 Main Concepts 756

Your objectives in studying this chapter are to be able to

1. Predict adsorption of gases and liquids on solids at equilibrium
2. Determine the values of coefficients in adsorption equilibrium relations from physical measurements

In Chapter 8 you read about equilibria involving gas and liquids. Equilibria between fluids and solids are also important—they certainly cannot be ignored.

Looking Ahead

In this chapter we discuss the adsorption of gases and liquids on solids when the system is at *equilibrium.* You will learn what some of the relations are that are used to predict the amounts of absorption, and what kinds of data are collected to get the values of the coefficients in the relations.

15.1 Main Concepts

Many important processes involve the adsorption of gases or liquids on solids. Some examples for liquids are

- Decolorizing, drying, or "degumming" of petroleum fractions
- Odor, taste, and color removal from municipal water supplies
- Decolorizing of vegetable and animal oils, and of crude sugar syrups
- Clarification of beverages and pharmaceutical preparations
- Purification of process effluents and gases for pollution control

- Solvent recovery from air such as in removing evaporated dry-cleaning solvents
- Dehydration of gases
- Odor and toxic gas removal from air or vent gases
- Separation of rare gases at low temperatures
- Impurity removal from air prior to low-temperature fractionation
- Storage of hydrogen

What goes on in adsorption? **Adsorption** is a physical phenomenon that occurs when gas or liquid molecules are brought into contact with a solid surface, the **adsorbent.** Some of the molecules may condense (the **adsorbate**) on the exterior surface and in the cracks and pores of the solid. If interaction between the solid and condensed molecules is relatively weak, the process is called physical adsorption; if the interaction is strong (similar to a chemical reaction), it is called **chemisorption,** or activated adsorption. We focus on equilibria in physical adsorption in this chapter.

Equilibrium adsorption is analogous to the gas-liquid and liquid-liquid equilibria described in previous chapters. Picture a small section of adsorbent surface. As soon as molecules come near the surface, some condense on the surface. A typical molecule will reside on the adsorbent for some finite time before it acquires sufficient energy to leave. Given sufficient time, an equilibrium state will be reached: The number of molecules leaving the surface will just equal the number arriving.

The number of molecules on the surface at equilibrium is a function of the (1) nature of the solid adsorbent, (2) nature of the molecule being adsorbed (the adsorbate), (3) temperature of the system, and (4) concentration of the adsorbate over the adsorbent surface. Numerous theories have been proposed to relate the amount of fluid adsorbed to the amount of adsorbent. The various theories lead to equations that represent the equilibrium state of the adsorption system. Theoretical models hypothesize various physical conditions such as (1) a solid surface on which there is a monomolecular layer of molecules, or (2) a multimolecular layer, or (3) capillary condensation.

Figure 15.1 illustrates typical simple equilibrium adsorption isotherms for the adsorption of water vapor on Type 5A molecular sieves at various temperatures. Note how the amount of gas adsorbed decreases as the temperature increases.

No single relation can represent all of the myriad types of equilibrium data found in practice, as indicated by the variety of curves for isothermal adsorption called **adsorption isotherms,** shown in Figure 15.2.

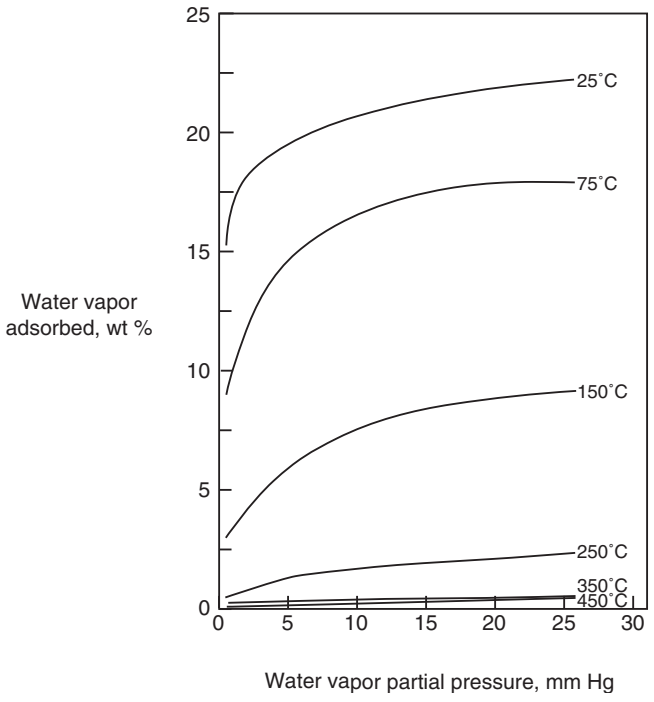


Figure 15.1 Equilibrium adsorption of water on Type 5A molecular sieves

Two of the simpler equilibrium relations for physical adsorption of Type I in Figure 15.2 relate the amount adsorbed for a single component (the adsorbate) on the adsorbent as a function of the adsorbate partial pressure in the gas phase, or the concentration in the liquid phase, at some temperature. These equations apply for low concentrations at equilibrium.

Freundlich Isotherm

For a gas:	*For a liquid:*
$y = k_1 p^{n_1}$	$y = k_2 x^{n_2}$

where p is the partial pressure of the adsorbate in the gas phase

y is the cumulative mass of solute or gas adsorbed (adsorbate) per mass of adsorbent in the solid phase

x is the mass of solute per mass of solution in the liquid phase

n_i and k_i are coefficients

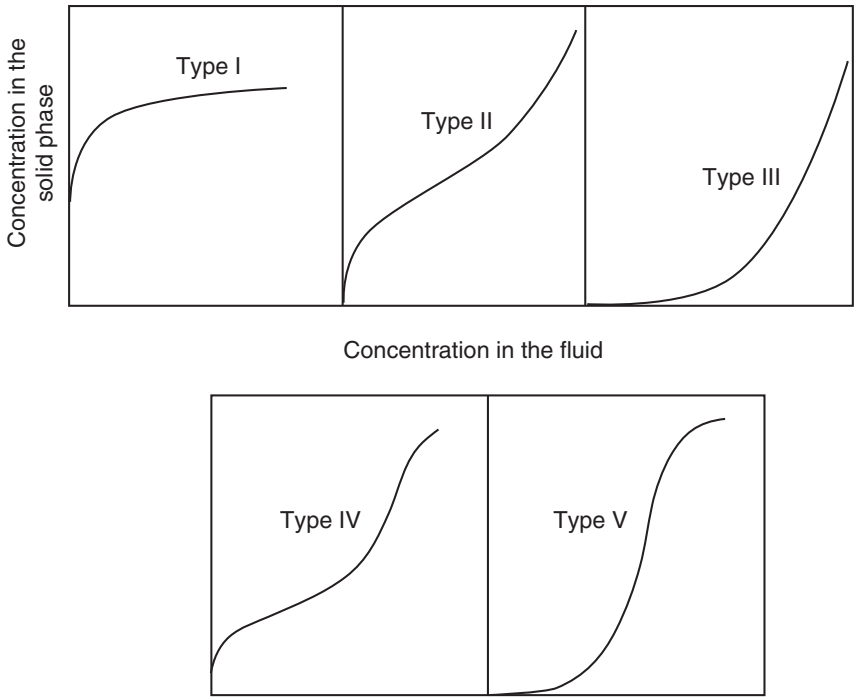


Figure 15.2 Some typical adsorption isotherms [S. Brunauer, *J. Am. Chem. Soc.*, **62**, 1723 (1940.)]

Langmuir Isotherm

For a gas:

$$y = \frac{(1 + ak_3)p}{1 + k_3 p}$$

For a liquid:

$$y = \frac{(1 + bk_4)x}{1 + k_4 x}$$

The respective equations correspond to monolayer adsorption. Numerous other relations have been developed to match the particular shapes of the adsorption equilibrium data shown in Figure 15.2. Refer to the references at the end of this chapter.

You can obtain values for the coefficients in the equilibrium isotherms by fitting them to experimental data, as shown in Example 15.1. The expressions $(1 + ak_3)$ and $(1 + bk_4)$ can be treated as single coefficients in the fitting.

Example 15.1 Fitting Adsorption Isotherms to Experimental Data

The following data for the adsorption of CO_2 on 5A molecular sieves at 298 K have been taken from the PhD dissertation *Periodic Countercurrent Operation of Pressure-Swing Adsorption Processes Applied to Gas Separations* by Carol L. Blaney [University of Delaware (1985), p. 131].

p_{CO_2} (mm Hg)	y (g adsorbed/g sieves)
0	0
25	6.69×10^{-2}
50	9.24×10^{-2}
100	0.108
200	0.114
400	0.127
760	0.137

The estimated coefficients in the respective isotherms obtained by using the regression function in Polymath 5 were:

Freundlich Isotherm			**Langmuir Isotherm**		
Model: $y + ap^n$	$R^2 = 0.993$		**Model:** $ap/(1 + bp)$		$R^2 = 0.981$
Variable	Initial guess	Final value	Variable	Initial guess	Final value
a	1	0.0448	a	100	0.0052
n	0.5	0.1729	b	1	0.0386

The parameter R^2 is a measure of the degree of fit; $R^2 = 1$ is a perfect fit. Figure E15.1 shows the data and the adsorption isotherms.

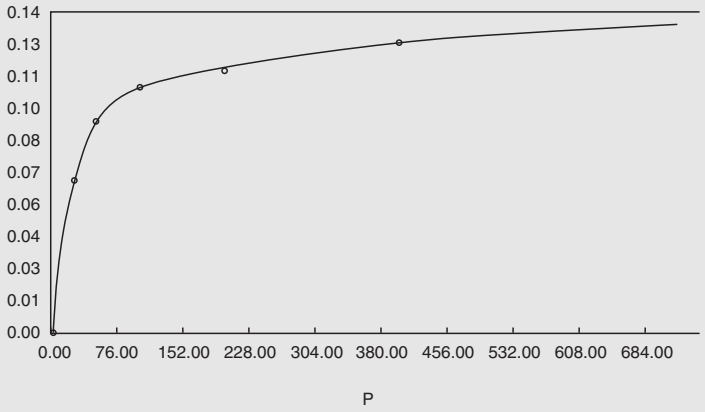


Figure E15.1 The Freundlich and Langmuir isotherms coincide for the adsorption of CO_2 on 5A molecular sieves; ○ are the experimental points.

A type of constant that is used in environmental studies is the soil sorption partition coefficient, K_{oc}. It characterizes the partitioning of a compound between the solid and liquid phases in soil, and is used to determine the mobility of a compound in soil:

$$K_{oc} = \frac{\dfrac{\mu g \text{ of compound adsorbed}}{\text{g of organic carbon in the soil}}}{\dfrac{\mu g \text{ of compound in the liquid phase}}{\text{mL liquid in the liquid phase}}}$$

How do you use the information about adsorption in practice? One way is to combine it with material balances to help design adsorption equipment. Examine Figure 15.3 in which a carrier G (gas or liquid) is contacted with an adsorbent A (solid). Assume that the vessel is well mixed and that the exit streams are in equilibrium with each other.

The mass of G is the mass of the carrier excluding the solute, and the mass of A is also solute free. Often we assume the solution entering is dilute enough so that G is equivalent to the total flow. The material balance corresponding to the process in Figure 15.3 is (note that x and y are *not* mass fractions in what follows)

$$\begin{matrix} \text{In} & & \text{Out} \\ G(x_0 - x_1) & = & A(y_1 - y_0) \end{matrix} \tag{15.1}$$

Usually the A entering is free of solute so that $y_0 = 0$, and thus the material balance becomes

$$G(x_0 - x_1) = Ay_1 \tag{15.2}$$

Example 15.2 shows how the Freundlich isotherm can be combined with a material balance to solve a design problem.

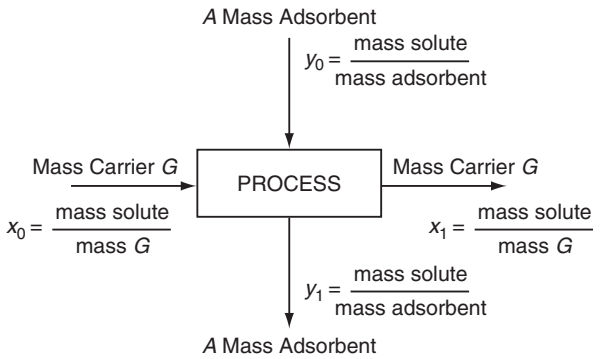


Figure 15.3 The process of adsorption with the notation

Example 15.2 Combination of an Adsorption Isotherm with a Material Balance

You are asked to calculate the minimum mass of activated carbon required to reduce a contaminating solute in a fermentation system from $x_0 = 19.2$ g solute/L solution (for simplicity the value can be treated as grams of solute per 1000 g solution) to $x_1 = 1.4$ g solute/L solution for a 1 L batch of solution by adsorption on activated charcoal in a well-mixed vessel so that the output products are in equilibrium. To solve this problem you collect the following liquid-solid equilibria data. Note that the third column contains calculated, not measured, values.

Measured at equilibrium		
Cumulative g Carbon Added per 1000 g Solution	**x g Solute / 1000 g Solution**	**y (Calculated) g Solute Adsorbed / g Carbon**
0	19.2	—
0.01	17.2	(19.2–17.2)/0.01 =200
0.04	12.6	(19.2–12.6)/0.04 =165
0.08	8.6	(19.2–8.6)/0.08 = 133
0.20	3.4	(19.2–3.4)/0.20 = 79
0.40	1.4	(19.2–1.4)/0.40 = 45

Solution

Steps 1–4

If you fit the data using Polymath, the Freundlich isotherm proves to be

$$y = 37.919\, x^{0.583} \qquad R^2 = 0.999 \tag{a}$$

and the Langmuir isotherm is

$$y = (29.698x) \,/\, (1 + 0.0955x) \qquad R^2 = 0.987 \tag{b}$$

Figure E15.2, the process diagram, shows the flows in and out of the system. From a different viewpoint, the process is equivalent to a batch process in which the materials are put into an empty vessel at the start and removed at the end of the process. Let G be the grams of solution. Because the solution is so dilute, G is essentially equivalent to the grams of solute-free solvent. If you wanted to, you could calculate the ratios of the solute to the solute-free solvent coming in and out of the process, but we will not do so.

Step 5

Let the basis be 1000 g solution (1 L).

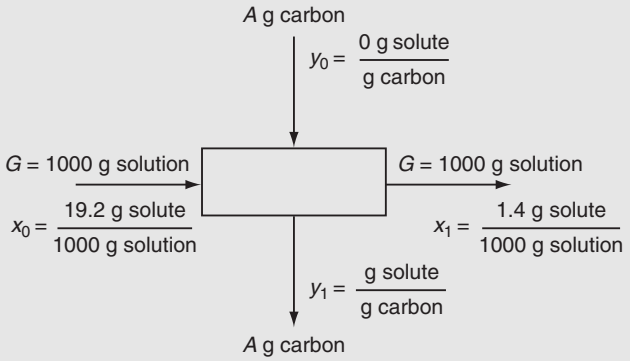


Figure E15.2

Steps 6–9

Two independent equations are involved in the solution, an equilibrium relation and the material balance. Two unknowns exist, y_1 and the ratio A/G.

Combine Equation (a) with Equation (15.2) to get

$$\frac{A}{G} = \frac{x_0 - x_1}{y_1} = \frac{(19.2 - 1.4)\dfrac{\text{g solute}}{1000 \text{ g solution}}}{37.919(1.4)^{0.583}\dfrac{\text{g solute}}{\text{g carbon}}} = \frac{17.8}{46.1} = 0.39\frac{\text{g carbon}}{1000 \text{ g solution}}$$

Hence, 0.39 g carbon is required.

Step 10

You can check the answer by using the Langmuir isotherm together with the material balance:

$$\frac{A}{G} = \frac{19.2 - 1.4}{y_1}$$

$$y_1 = \frac{29.698(1.4)}{1 + 0.0955(1.4)} \quad \text{or } y_1 = 36.67$$

hence

$$\frac{A}{G} = \frac{17.8}{36.67} = 0.48 \text{ g carbon}/1000 \text{ g solution}$$

Because $y_1 = 46.1$ from the Freundlich isotherm is closer to the experimental value of 45 than is 36.7 from the Langmuir isotherm, the value of 0.39 g as the answer would be preferred. Of course, more carbon will have to be used in practice because to reach equilibrium takes a very long time.

Can you now calculate how much carbon would be required to remove all of the polluting solute?

Self-Assessment Test

Questions

1. Would condensation of water below its dew point on charcoal be considered adsorption?
2. Would the conversion of solid NaOH by HCl gas to NaCl be considered adsorption?
3. Would the drying of moist air by charcoal be considered adsorption?
4. Can more than one component be removed simultaneously from a gas or liquid by a solid adsorbent?

Problems

1. One hundred pounds per minute of moist air at 70°F that has a humidity of 0.01 lb H_2O/lb dry air is dehumidified to 0.002 lb H_2O/lb dry air in a dryer. If 7 lb/min of dry silica gel enter the dryer at 70°F, how many pounds of H_2O leave the dryer per pound of silica gel entering?
2. The dissertation of Blaney (see Example 15.1) contains the following data for the adsorption of N_2 on activated coconut charcoal at 298 K:

P (mm Hg)	y (g mol N_2/g Charcoal) $\times 10^4$
0	0
26.8	0.1562
45.93	0.2945
67.72	0.4149
88.21	0.5354
108.05	0.6360
127.91	0.7406
147.42	0.8477
166.77	0.9458
246.86	1.3786
369.93	1.9808
428.79	2.2396
492.32	2.5430
587.86	2.9713
688.05	3.3996
761.10	3.6851

   Determine the coefficients in the Langmuir relation $y = k_0\, k_1\, p/1 + k_1\, p$.
3. Water contains organic color, which is to be extracted with alum and lime. Five parts of alum and lime per million parts of water will reduce the color to 25% of the original color, and 10 parts will reduce the color to 3.5%.

   Estimate how much alum and lime as parts per million are required to reduce the color to 0.5% of the original color.

Thought Problems

1. Why might a solid adsorbent be used rather than distillation to separate a liquid mixture?
2. How might you regenerate an adsorbent used for the separation of a mixture of (a) gases and (b) liquids?

Glossary

Adsorbent A solid surface on which gas or liquid molecules condense to form a film.

Adsorption The physical process that occurs when gas or liquid molecules are brought into contact with a solid surface and condense on the surface.

Adsorption isotherm The mathematical or experimental relation between the amount a single component adsorbed (the adsorbate) on the adsorbent, and the bulk amount of the adsorbate in a different phase expressed in terms of the partial pressure in the gas phase, or the concentration in the liquid phase, at some temperature.

Chemisorption Adsorption when interaction between the solid and the condensed molecules is relatively strong as contrasted with physical adsorption.

Freundlich isotherm Mathematical relation for adsorption that takes place at equilibrium.

Langmuir isotherm Mathematical relation for adsorption that takes place at equilibrium.

Supplementary References

Basmadjian, D. *The Little Adsorption Book: A Practical Guide for Engineers and Scientists,* CRC Press, Boca Raton, FL (1996).

De Nevers, N. *Physical and Chemical Equilibrium for Chemical Engineers,* Wiley-Interscience, New York (2002).

Masel, R. I. *Principles of Adsorption and Reaction on Solid Surfaces,* Wiley-Interscience, New York (1996).

Thomas, W. J. *Adsorption Technology and Design,* Butterworth-Heinemann, Oxford, UK (1998).

Toth, J. *Adsorption,* Marcel Dekker, New York (2002).

Web Site

http://ias.vub.ac.be/

Problems

*15.1 The adsorption of sulfur dioxide by polymer pellets at 0°C is listed below. Using these data, determine the Langmuir constants and the Freundlich constants.

p_{SO_2} (mm Hg)	Uptake (mg mol/g)
5	1.75
10	2.20
15	2.40
20	2.62
30	2.75
40	2.85
50	3.00
60	3.05
70	3.12

Do these two isotherms fit the data well?

*15.2 Emmett studied the adsorption of argon on 0.606 g of silica gel at −183°C. From the following data, calculate the Freundlich and Langmuir constants:

p (mm Hg)	Uptake (cm^3 at S.C.)
78.46	55.03
176.92	72.73
224.62	80.00
378.46	106.67
432.31	117.58
515.38	138.18
584.62	166.06

Do these two isotherms fit the data well?

*15.3 The adsorption of ethane on 5A molecular sieves was studied by Glessner and Myers (1969) at 35°C. Using the data given below, determine (a) if the Langmuir equation can be used to model the data and (b) if the Freundlich equation can be used to model the data.

p (mm Hg)	Uptake (cm^3 at S.C./g)
0.17	0.059
0.95	0.318
5.57	1.638
12.09	3.613
111.32	24.236
220.87	34.278
300.05	38.340
401.25	41.779
500.18	44.037
602.74	45.693

*15.4 In the isothermal adsorption of a mixture of butanol-2 (component 1) and t-amyl alcohol (component 2) on porous activated carbon, the following relation represented the data within an accuracy of ±2%:

$$c_{s1} = \frac{1.06{c_{f1}}^{1.217}}{{c_{f1}}^{0.812} + 0.626{c_{f2}}^{0.764}}$$

where c_s = concentration of solute in the solid phase, g/cm^3
c_f = concentration of the solute in the fluid phase, g/cm^3

What would the Freundlich equation be for butanol-2 as a pure liquid?

*15.5 A solution containing a trace amount of chloroform (12 mg/L) is to be reduced to 1 μg/L of CCl_4 using activated charcoal as the adsorbent. The Freundlich equation that applies to this system is $y = k\,C^n$ where C is in milligrams adsorbate per liter of solution after processing, and y is the cumulative milligrams of adsorbate per gram of adsorbent. $k = 100$ and $n = 0.30$ at the temperature of the process. How much activated charcoal is required per liter of solution?

**15.6 One hundred pounds per minute of moist air that includes 1 lb of water vapor flow through a dehumidifier. Dry silica is fed to the process and flows counter-current to the air. The water content of the exit air is reduced to 10^{-3} lb of water per pound of dry air. The water in the exit silica gel is in equilibrium with the water in the entering air. What is the required flow rate of the silica gel per minute? The equilibrium relation that applies to this process is $y = 0.0375\text{p}^{0.65}$ where y is the grams of water per gram of silica gel and p is the partial pressure of the water in the entering air in millimeters of Hg.

**15.7 The compound 1, 1-dichloroethane (DE) in air at 40°C and with a dew point of 12°C is to be removed with 2 kg/min of activated carbon. The entering activated carbon contains 50 g DE per kilogram of DE-free activated carbon and leaves the process with a DE content of 300 g of DE per kilogram of DE-free activated carbon. Calculate the concentration of DE in the exit air, assuming that the DE in the exit air is in equilibrium with the exit activated carbon. The barometer is 770 mm of Hg. The equilibrium relation for the DE is $y = 0.089p^{0.51}$ where y is the grams of DE adsorbed per gram of activated charcoal, and p is the partial pressure in the gas phase of the DE in millimeters of Hg. How many gram moles of bone-dry air pass through the process per minute?

*15.8 The partition of a compound between soil and water can be estimated by using a soil adsorption coefficient K_{OC}

$$\text{K}_{\text{OC}} = \frac{\dfrac{\text{Mass of compound adsorbed in } \mu\text{g}}{\text{Mass of organic carbon in the soil in g}}}{\dfrac{\text{Mass of compound in the liquid in } \mu\text{g}}{\text{Volume of the liquid in mL}}}$$

Values of K_{OC} for low adsorption are in the range $2.5 > \log_{10}(\text{K}_{\text{OC}}) > 1.5$.

How much nitrobenzene will be adsorbed at equilibrium from 1 L of a saturated solution in water at 20°C by 1 kg of soil that has a carbon content of 11%? Data: The solubility of nitrobenzene in water is 0.19 g/100 g water at 20°C, and $\log_{10}(\text{K}_{\text{OC}}) = 2.27$.