# Chapter 11

# Adsorption(1,2)

## INTRODUCTION

It is already well established that the molecular forces at the surface of a liquid are in a state of imbalance or unsaturation. The same is true of the surface of a solid, where the molecules or ions on the surface may not have all their forces satisfied by union with other particles. As a result of this unsaturation, solid and liquid surfaces tend to satisfy their residual forces by attracting and retaining onto their surfaces gases or dissolved substances with which they come in contact. This phenomenon of the concentration of a substance on the surface of a solid (or liquid) is called *adsorption*. Thus, the substance attracted to a surface is said to be the adsorbed phase or *adsorbate*, while the substance to which it is attached is the *adsorbent*. Adsorption should be carefully distinguished from absorption, the later process being characterized by a substance not only being retained on a surface, but also passing through the surface to become distributed throughout the phase. Where doubt exists as to whether a process is true adsorption or absorption, the noncommittal term "sorption" is sometimes employed.

The study of adsorption of various gases (or vapors) on solid surfaces has revealed that the forces operative in adsorption are not the same in all cases. Two types of adsorption are generally recognized: "physical" or *van der Waals adsorption* and "chemical" or *activated adsorption*.

Physical adsorption (physisorption) is the result of intermolecular forces of attraction between molecules of the solid and the substance adsorbed. When, for example, the intermolecular attractive forces between a solid and a gas (or vapor) are greater than those existing between molecules of the gas itself, the gas will condense upon the surface of the solid even though its pressure may be lower than the vapor pressure corresponding to the prevailing temperature. The adsorbed substance does not penetrate within the crystal lattice of the solid and does not dissolve in it but remains entirely upon the surface. Should the solid, however, be highly porous, containing many fine capillaries, the adsorbed substance will penetrate these interstices if it "wets" the solid. The partial pressure of the adsorbed substance at equilibrium equals that of the contacting gas phase, and by lowering the pressure of the gas phase, or by

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raising the temperature, the adsorbed gas is readily removed or *desorbed* in unchanged form. Physical adsorption is characterized by low heats of adsorption (approximately 40 Btu/lbmol of adsorbate) and by the fact that the adsorption equilibrium is both reversible and established rapidly. This latter point allows one to simplify calculations in most real-world adsorption applications.

*Chemisorption*, or activated adsorption, on the other hand, is the result of chemical interaction between the solid and the adsorbed substance. The strength of the chemical bond may vary considerably and identifiable chemical compounds in the usual sense may not form. Nevertheless, the adhesive forces are generally much greater than that found in physical adsorption. Chemisorption is also accompanied by much higher enthalpy changes (ranging from 80 to as high as 400 Btu/lbmol) with the heat liberated being on the order of the enthalpy of chemical reaction. The process is frequently irreversible, and, on desorption, the original substance will often have undergone a chemical change.

Although it is probable that all solids adsorb gases (or vapors) to some extent, adsorption, as a rule, is not very pronounced unless an adsorbent possesses a large surface area for a given mass. For this reason, such adsorbents as silica gel, charcoals, and molecular sieves are particularly effective as adsorbing agents. These substances have a very porous structure and, with their large exposed surface, can take up appreciable volumes of various gases. The extent of adsorption can be increased further by "activating" the adsorbents in various ways. For example, wood charcoal can be "activated" by heating between 350 and 1000°C in a vacuum or in air, steam, and certain other gases to a point where the adsorption of carbon tetrachloride, (e.g., at 24°C) can be increased from 0.011 g/g of charcoal to 1.48. The activation apparently involves a distilling out of hydrocarbon impurities and thereby leads to exposure of a larger free surface for possible adsorption.

The amount of gas adsorbed by a solid depends on a host of factors, including the surface area of the adsorbent, the nature of the adsorbent and gas being adsorbed, the temperature, and the pressure of the gas. Since the adsorbent surface area cannot always be readily determined, common practice is to employ the adsorbent mass as a measure of the surface available and to express the amount of adsorption per unit mass of adsorbing agent used.

A concept, which becomes especially important in determining adsorbent capacity, is that of "available" surface, i.e., surface area accessible to the adsorbate molecule. It is apparent from pore size distribution data that the major contribution to surface area is located in pores of molecular dimensions. It seems logical to assume that a molecule, because of steric effects, will not readily penetrate into a pore smaller than a certain minimum diameter—hence, the concept that molecules are screened out. This minimum diameter is the so-called *critical diameter* and is a characteristic of the adsorbate and related to molecular size. Thus, for any molecule, the effective surface area for adsorption can exist only in pores that the molecule can enter. Figure 11.1 attempts to illustrate this concept for the case in which two adsorbate molecules in a solvent (not shown) compete with each other for an adsorbent surface site.

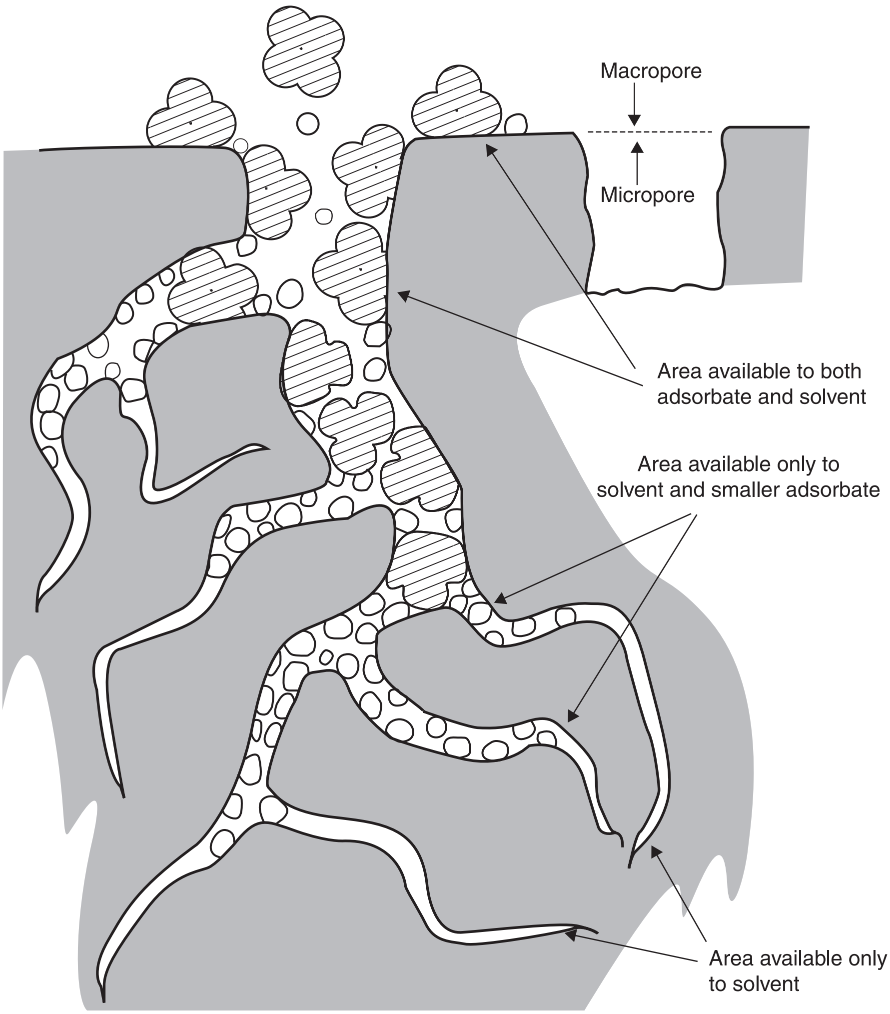

**Figure 11.1** Concept of molecular screening in micropores (diameter range = 10 to 1000 Å).

## ADSORPTION CLASSIFICATION

Four important adsorbents widely used industrially will be briefly considered, namely, activated carbon, activated alumina, silica gel, and molecular sieves. The first three of these are amorphous adsorbents with a nonuniform internal structure. Molecular sieves, however, are crystalline and therefore have an internal structure of regularly spaced cavities with interconnecting pores of definite size. Details of the properties peculiar to the various materials are best obtained directly from the manufacturer. The following is a brief description of these principal adsorbents.

**Table 11.1** Properties of Activated Carbon

| | |
|---|---|
| Bulk density | 22–34 lb/ft$^3$ |
| Heat capacity | 0.27–0.36°F Btu · lb |
| Pore volume | 0.56–1.20 cm$^3$/g |
| Surface area | 600–1600 m$^2$/g |
| Average pore diameter | 15–25 Å |
| Regeneration temperature (steaming) | 100–140°C |
| Maximum allowable temperature | 150°C |

## Activated Carbon

Charcoal, an inefficient form of activated carbon, is obtained by the carbonization of wood. Various raw materials have been used in the preparation of adsorbent chars, resulting in the development of active carbon, a much more adsorbent form of charcoal. Industrial manufacture of activated carbon is obtained from shells or coal that is subjected to heat treatment in the absence of air, in the case of coal, followed by steam activation at high temperature. Other substances of a carbonaceous nature also used in the manufacture of active carbons include wood, coconut shells, peat, and fruit pits. Zinc chloride, magnesium chloride, calcium chloride, and phosphoric acid have also been used in place of steam as activating agents. Some approximate properties of typical granular gas adsorbent carbons are given in Table 11.1. Gas adsorbent carbons find primary application in gas purification, solvent recovery (hydrocarbon vapor emissions), and pollution control.

## Activated Alumina

Activated alumina (hydrated aluminum oxide) is produced by special heat treatment of the precipitate of native alumina or bauxite. It is available in either granular or pellet form with typical properties given in Table 11.2. Activated alumina is primarily used for the drying of gases and is particularly useful for the drying of gases under pressure.

**Table 11.2** Properties of Activated Alumina

| | |
|---|---|
| Density in bulk granules | 38–42 lb/ft$^3$ |
| Density in pellets | 54–58 lb/ft$^3$ |
| Heat capacity | 0.21–0.25 Btu/lb · °F |
| Pore volume | 0.29–0.37 cm$^3$/g |
| Surface area | 210–360 m$^2$/g |
| Average pore diameter | 18–48 Å |
| Regeneration temperature | 200–250°C |
| Stable up to | 500°C |

**Table 11.3** Properties of Silica Gel

| | |
|---|---|
| Bulk density | 44–46 $lb/ft^3$ |
| Heat capacity | 0.22–0.26 Btu/lb · °F |
| Pore volume | 0.37 $cm^3/g$ |
| Surface area | 750 $m^2/g$ |
| Average pore diameter | 22 Å |
| Regeneration temperature | 120–250°C |
| Stable up to | 400°C |

## Silica Gel

The manufacture of silica gel consists of the neutralization of sodium silicate by mixing with dilute mineral acid, washing the gel formed free from salts produced during the neutralization reaction, followed by drying, roasting, and grading processes. It is generally used in granular form, although bead forms are available (see Table 11.3). Silica gel also finds primary use in gas drying and also finds application in gas desulfurization and purification.

## Molecular Sieves

Unlike the amorphous adsorbents (i.e., activated carbon, activated alumina, and silica gel), molecular sieves are crystalline, being essentially dehydrated zeolites (i.e., alumino-silicates in which atoms are arranged in a definite pattern). The complex structural units of molecular sieves have cavities at their centers to which access is by pores or "windows". For certain types of crystalline zeolites, these pores are precisely uniform in diameter. Due to the crystalline porous structure and the near precise uniformity of the small pores, the adsorption phenomena only takes place with molecules that are of small enough size and of suitable shape to enter the cavities through the pores. The fundamental building block is a tetrahedron of four oxygen

**Table 11.4** Properties of Molecular Sieves

| | Anhydrous sodium aluminosilicate | Anhydrous calcium aluminosilicate | Anhydrous aluminosilicate |
|---|---|---|---|
| Type | 4A | 5A | 13X |
| Density in bulk ($lb/ft^3$) | 44 | 44 | 38 |
| Heat capacity (Btu/lb · °F) | 0.19 | 0.19 | – |
| Effective diameter of pores (Å) | 4 | 5 | 13 |
| Regeneration temperature | 200–300°C | 200–300°C | 200–300°C |
| Stable up to (short period) | 600°C | 600°C | 600°C |

anions surrounding a smaller silicon or aluminum cation. The sodium ions or other cations serve to make up the positive charge deficit in the alumina tetrahedra. Each of the four oxygen anions is shared, in turn, with another silica or alumina tetrahedron to extend the crystal lattice in three dimensions. The resulting crystal is unusual in that it is honeycombed with relatively large cavities, each cavity connected with six adjacent ones through apertures or pores. The sieves are manufactured by hydrothermal crystal growth from aluminosilicate gels followed by heat treatment to effect dehydration. Typical properties are given in Table 11.4.

## ADSORPTION EQUILIBRIA

The adsorption process involves three necessary steps. The fluid carrying the adsorbate must first come in contact with the adsorbent, at which time the adsorbate is preferentially, or selectively, adsorbed on the adsorbent. Next, the unadsorbed fluid must

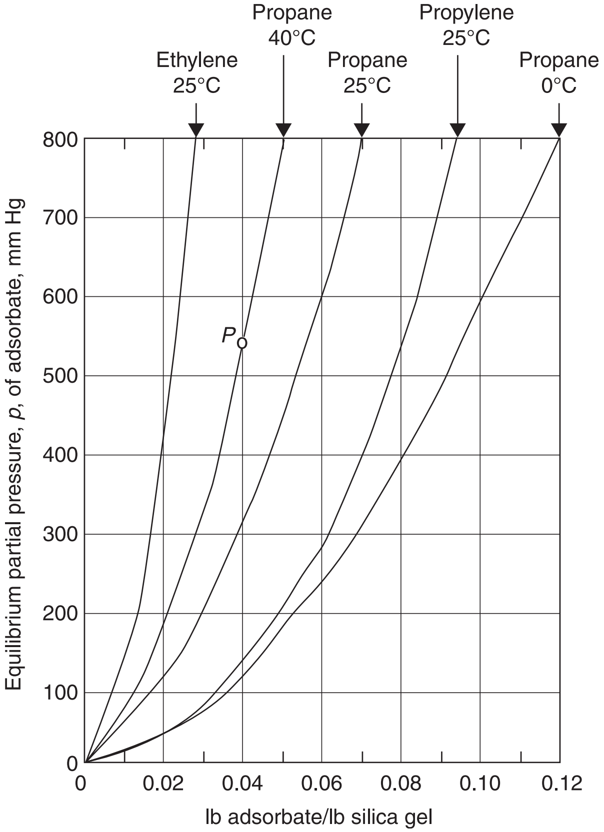

**Figure 11.2** Vapor–solid adsorption equilibrium isotherms of some hydrocarbons on silica gel.

be separated from the adsorbent-adsorbate, and, finally, the adsorbent must be regenerated by removing the adsorbate or discarding the used adsorbent and replacing it with fresh material. Regeneration is performed in a variety of ways, depending on the nature of the adsorbate complex. Gases or vapors are usually desorbed by either varying the temperature (thermal cycle) or reducing the pressure (pressure cycle) of the adsorbent-adsorbate. The more popular thermal cycle is accomplished by passing hot gas through the adsorption bed in the opposite direction to the flow during the adsorption cycle. This ensures that the gas passing through the unit during the adsorption cycle always meets the most active adsorbent last and that the adsorbate concentration in the adsorbent at the outlet end of the unit is always maintained at a minimum.

In the first step mentioned above where the molecules of the fluid come in contact with the adsorbent, an equilibrium is established between the adsorbed fluid and that remaining in the fluid phase. Although adsorption equilibrium and equilibrium relationships were reviewed in Chapter 6, material associated specifically with the adsorption process was not included. Because of the unique nature of adsorption equilibrium and the method of representation, this topic is included in the next section. Figures 11.2–11.4 show experimental equilibrium adsorption isotherms.

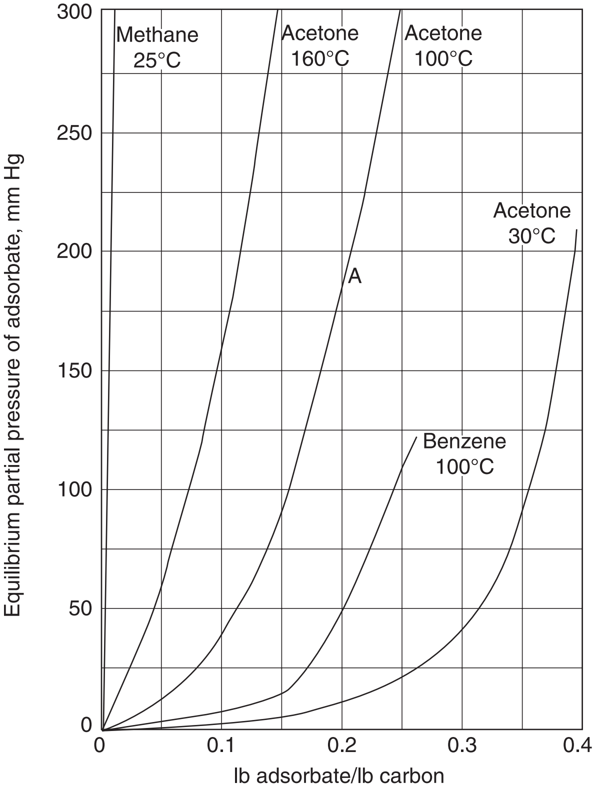

**Figure 11.3** Vapor–solid equilibrium isotherms of some hydrocarbons on activated carbon.

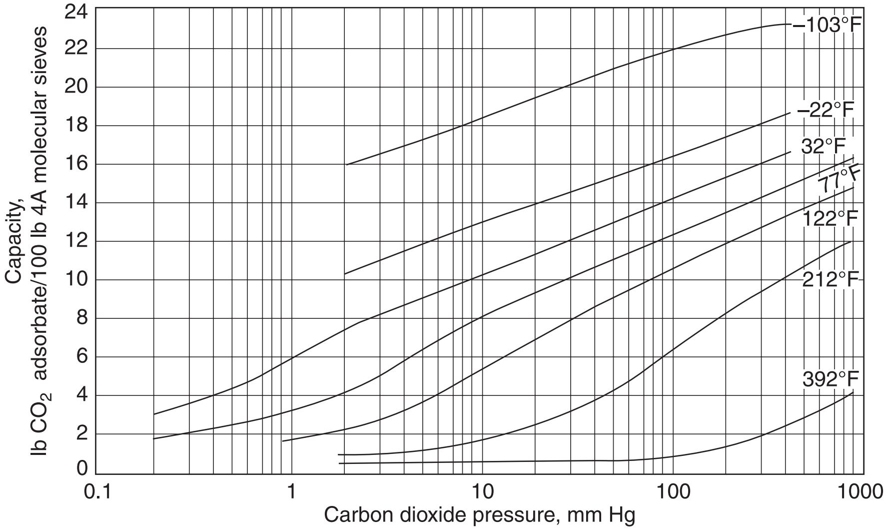

**Figure 11.4** Vapor–solid equilibrium isotherms on molecular sieves.

Consider Figure 11.2, where the concentration of adsorbed gas on the solid is plotted against the (equilibrium) partial pressure, $p$, of the adsorbate vapor or gas at constant temperature. At 40°C, for example, pure propane vapor at a pressure of 550 mm Hg is in equilibrium with an adsorbate concentration at point $P$ of 0.04 lb adsorbed propane/lb silica gel. Increasing the pressure of the propane will cause more propane to be adsorbed, while decreasing the pressure of the system at $P$ will cause propane to be desorbed from the carbon.

As described earlier, adsorption is an exothermic process; hence, the concentration of adsorbed gas decreases with increased temperature at a given equilibrium pressure. This is evident from the behavior of the isotherm curves. The process of a gas being brought into contact with an evacuated porous solid, and part of it being taken up by the solid, is always accompanied by the liberation of heat. The extent to which the process is exothermic depends on the type of sorption and the particular system. For physical adsorption, the amount of heat liberated is usually equal to the latent enthalpy of condensation of the adsorbate plus the heat of wetting of the solid by the adsorbate. The heat of wetting is usually only a small fraction of the heat of adsorption. On the other hand, in chemisorption, the heat evolved approximates the enthalpy of chemical reaction.

As discussed in Chapter 6, the relation between the amount of substance adsorbed by an adsorbent and the equilibrium pressure or concentration at constant temperature is called the adsorption isotherm. The adsorption isotherm is the most important and by far the most often used of the various equilibria data that can be measured. Five general types of isotherms have been observed in the adsorption of gases on solids. These are shown in Figure 11.5. In cases of chemisorption, only isotherms of Type I are encountered, while in physical adsorption, all five types occur.

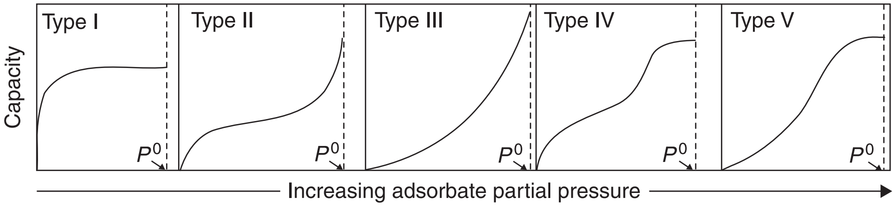

**Figure 11.5** Types of adsorption isotherms. $P^0$ represents the saturation pressure.

## Freundlich Equation

In isotherms of Type I, the amount of gas adsorbed per given quantity of adsorbent increases relatively rapidly with pressure and then much more slowly as the surface becomes covered with gas molecules. To represent the variation of the amount of adsorption per unit area or unit mass with pressure, Freundlich proposed the following equation:

$$Y = kp^{1/n} \tag{11.1}$$

where $Y$ is the weight or volume of gas adsorbed per unit area or unit mass of adsorbent, $p$ is the equilibrium partial pressure and $k$ and $n$ are empirical constants dependent on the nature of solid and adsorbate, and on the temperature. Equation 11.1 may be rewritten as follows. Taking logarithms of both sides,

$$\log(Y) = \log(k) + \frac{1}{n}\log(p) \tag{11.2}$$

If the $\log(Y)$ is now plotted against $\log(p)$, a straight line should result with the slope equal to $(1/n)$ and an ordinate intercept equal to $\log(k)$. Although the requirements of the equation are met satisfactorily at lower pressures, the experimental points curve away from the straight line at higher pressures, indicating that this equation does not have general applicability in reproducing adsorption of gases by solids.

## Langmuir Isotherms

A much better equation for Type I isotherms was deduced by Langmuir from theoretical considerations. Langmuir postulated that gases, on being adsorbed by a solid surface, cannot form a layer more than a single molecule in depth. Further, he visualized the adsorption process as consisting of two opposing actions, a condensation of molecules from the gas phase onto the surface and an evaporation of molecules from the surface back into the body of the gas. When adsorption first begins, every molecule colliding with the surface may condense on it. However, as adsorption proceeds, only those molecules that occupy a part of the surface not already covered by adsorbed molecules may be expected to be adsorbed. The result is that the initial rate of condensation of molecules on a surface is high and then falls off as the surface area available for adsorption is decreased. On the other hand, a molecule adsorbed on a surface may, by thermal agitation, become detached from the surface and escape into the gas. The rate at which desorption will occur will depend, in turn, on the amount of surface covered by molecules and will increase as the surface becomes more fully saturated. These two rates, condensation (adsorption) and evaporation (desorption), will eventually become equal and when this happens, an adsorption equilibrium will be established.

If $\theta$ is the fraction of the total surface covered by adsorbed molecules at any instant, then the fraction of bare surface available for adsorption is $(1-\theta)$. According to kinetic theory, since the rate at which molecules strike a unit area of a surface is proportional to the pressure of the gas, the rate of condensation of molecules should be determined both by the pressure and the fraction of bare surface, or $k_1(1-\theta)p$, where $k_1$ is a proportionality constant. If $k_2$ is the rate at which molecules evaporate from a unit surface when the surface is fully covered, then for a fraction $\theta$ of a fully covered surface, the rate of evaporation will be $k_2\theta$. For adsorption equilibrium, these rates must be equal. Therefore,

$$k_1(1-\theta)p = k_2\theta$$

or

$$\theta = \frac{k_1 p}{k_2 + k_1 p} = \frac{bp}{1+bp} \tag{11.3}$$

where $b = k_1/k_2$. Now, the amount of gas adsorbed per unit area or per unit mass of adsorbent, $Y$, must obviously be proportional to the fraction of surface covered; hence,

$$Y = k\theta = \frac{kbp}{1+bp} = \frac{ap}{1+bp} \tag{11.4}$$

where the constant $a$ has been written for the product $kb$. Equation (11.4) is the Langmuir adsorption isotherm. The constants $a$ and $b$ are characteristic of the system under consideration and are evaluated from experimental data. Their magnitude also depends on the temperature. The validity of the Langmuir adsorption equation at any one temperature can be verified most conveniently by first dividing both sides of Equation (11.4) by $p$ and then taking reciprocals. The result is

$$\frac{p}{Y} = \frac{1}{a} + \frac{b}{a}p \tag{11.5}$$

Since $a$ and $b$ are constants, a plot of $(p/Y)$ vs $p$ should yield a straight line with slope equal to $(b/a)$ and an ordinate intercept equal to $(1/a)$.

## ILLUSTRATIVE EXAMPLE 11.1

Of the following vapors, which one would be most readily adsorbed using activated carbon?

**1** $H_2O$ at 140°F

**2** $CH_4$ at 70°F

**3** $C_4H_{10}$ at 140°F

**4** $C_4H_{10}$ at 70°F

***SOLUTION*:** The general rule of thumb is that organics are more easily adsorbed on activated carbon. Furthermore, the higher the molecular weight, the more easily it can be captured (because of the larger molecular diameter). Finally, increasing the temperature decreases the adsorption capability. The correct answer is therefore (4). ■

## ILLUSTRATIVE EXAMPLE 11.2

The carbon dioxide adsorption isotherms for Columbia ("Columbia" is a registered trademark of Union Carbide Corporation) activated carbon are presented in Figure 11.6 for temperatures of 30, 50, and 95°C. Determine the constants of the Freundlich equation at a temperature of 50°C.

***SOLUTION*:** For the Freundlich equation

$$Y = kp^{1/n} \tag{11.1}$$

The data/calculations presented in Table 11.5 are obtained/generated from Figure 11.6.

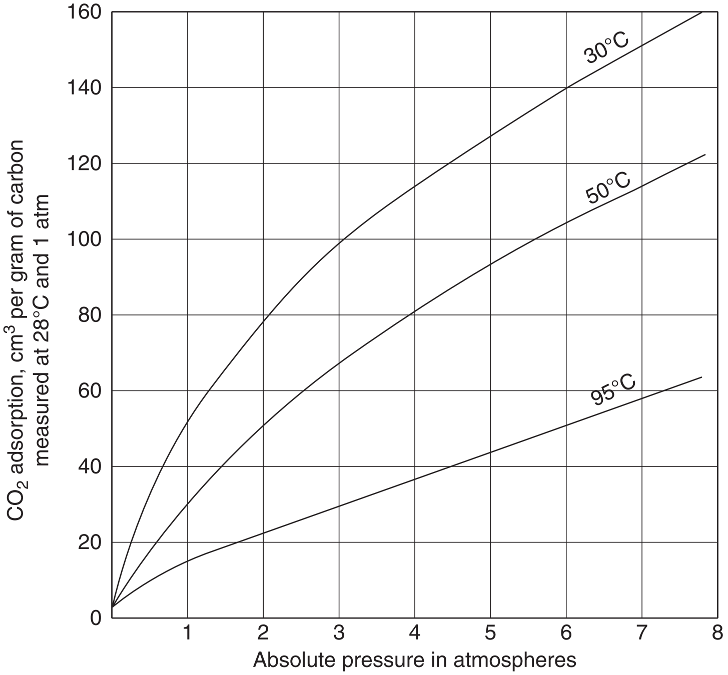

**Figure 11.6** $CO_2$ adsorption isotherms on activated carbon.

**Table 11.5** Calculations for the Freundlich Equation at 50°C

| $Y$ (cm$^3$/g) | $p$ (atm) | log $Y$ | log $p$ |
|---|---|---|---|
| 30 | 1 | 1.477 | 0.000 |
| 51 | 2 | 1.708 | 0.301 |
| 67 | 3 | 1.826 | 0.477 |
| 81 | 4 | 1.909 | 0.602 |
| 93 | 5 | 1.969 | 0.699 |
| 104 | 6 | 2.017 | 0.778 |

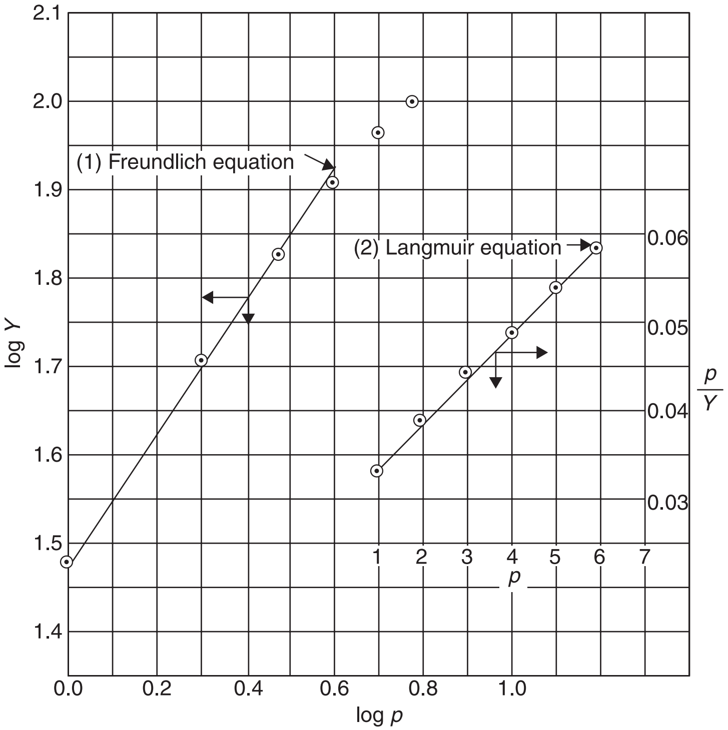

**Figure 11.7** Adsorption isotherms from Illustrative Example 11.2.

For the Freundlich equation (1), the plot of (log $Y$) vs (log $p$) in Figure 11.7 leads to the equation:

$$Y = 30p^{0.7}$$ ■

## ILLUSTRATIVE EXAMPLE 11.3

Refer to Illustrative Example 11.1. Determine the constants of the Langmuir equation.

**Table 11.6** Calculations for the Langmuir Equation at 50°C

| $p/Y$ | $p$ |
|---|---|
| 0.033 | 1 |
| 0.039 | 2 |
| 0.045 | 3 |
| 0.049 | 4 |
| 0.054 | 5 |
| 0.058 | 6 |

***SOLUTION*:** For the Langmuir equation, employ

$$\frac{p}{Y} = \frac{1}{a} + \frac{b}{a}p \tag{11.5}$$

and the information generated in Table 11.6 from Figure 11.6.

From Figure 11.7 (see insert), a plot of $(p/Y)$ vs $p$ leads to the equation

$$Y = \frac{35.7p}{1 + 0.186p}$$

■

## ILLUSTRATIVE EXAMPLE 11.4

Which equation provides a better fit to the experimental data discussed in the two previous illustrative examples.

***SOLUTION*:** As is evident from the lines drawn in Figure 11.7, the Langmuir equation provides the better fit. Strictly speaking, a regression coefficient should be calculated for both results to provide a better basis for comparison. ■

## DESCRIPTION OF EQUIPMENT

Because of the high cost of maintenance of air recovery and purification systems for applications with high concentrations of organic vapors, scientists and engineers have been forced into researching and designing systems for solvent recovery. The result has been the development of three types of systems, differentiated by the manner in which the adsorbent bed is maintained or handled during both phases of the adsorption-regeneration cycle: (1) fixed or stationary bed, (2) moving bed, and (3) fluidized bed.(3)

Figure 11.8 presents a flow diagram of a dual stationary-bed solvent recovery system with auxiliaries for collecting the vapor–air mixture from various point sources, then transporting through the particulate filter and into the on-stream carbon adsorber—in this case, bed 1. The effluent air, which is virtually free of vapors, is usually vented outdoors. The lower carbon adsorber (number 2) is regenerated during the service time of bed 1. A steam generator or other source of steam is

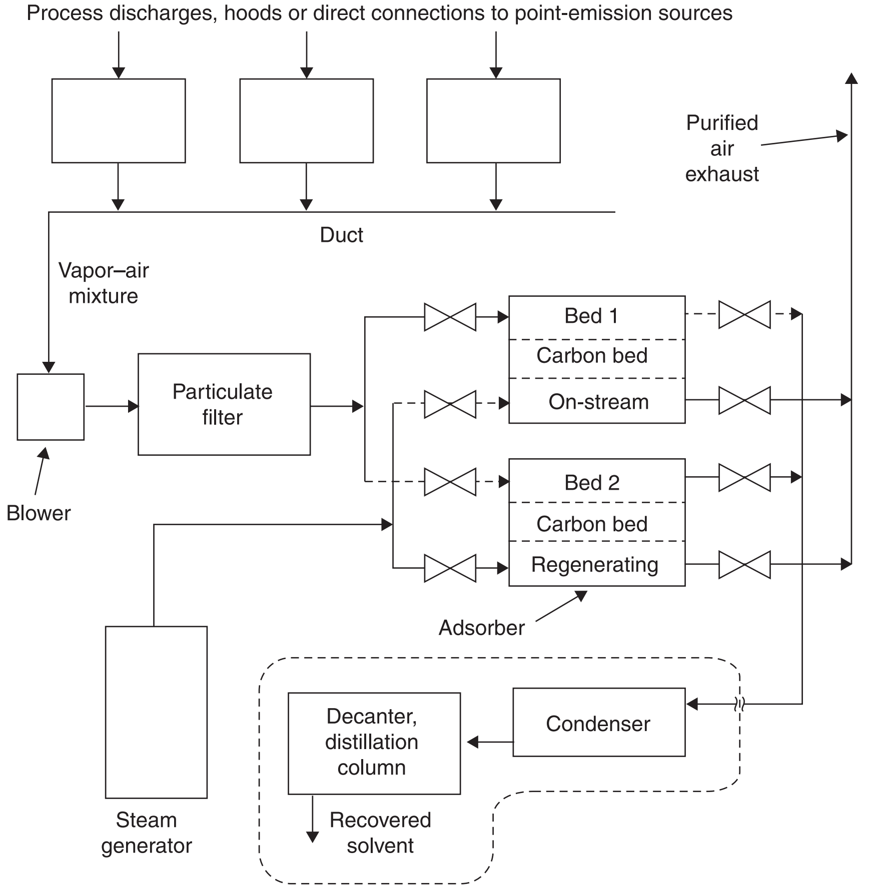

**Figure 11.8** Stationary-bed carbon system with auxiliaries for vapor collection and solvent separation from steam condensate.

required. The effluent steam–solvent mixture from the adsorber is directed through the condenser and the liquified mixture then passes into the decanter and/or distillation column for separation of the solvent from the steam condensate.(3)

Figures 11.9 and 11.10 show two designs of a stationary-bed solvent recovery system.(3) The type shown employs vertical cylindrical bends wherein the solvent-laden air flows axially down through the bed. This particular design is advertised for use in the recovery of solvents used in degreasing and dry cleaning, although equally well-suited for recovery of solvents from other industries. Solvents mentioned are trichloroethylene, tetrachloroethylene, toluene, freon TF, and dichloromethane. Regeneration is accomplished with steam flowing upward through the bed and, since the above-mentioned solvents are essentially immiscible in water, decantation is used to separate the condensed solvent from the steam condensate. The valves

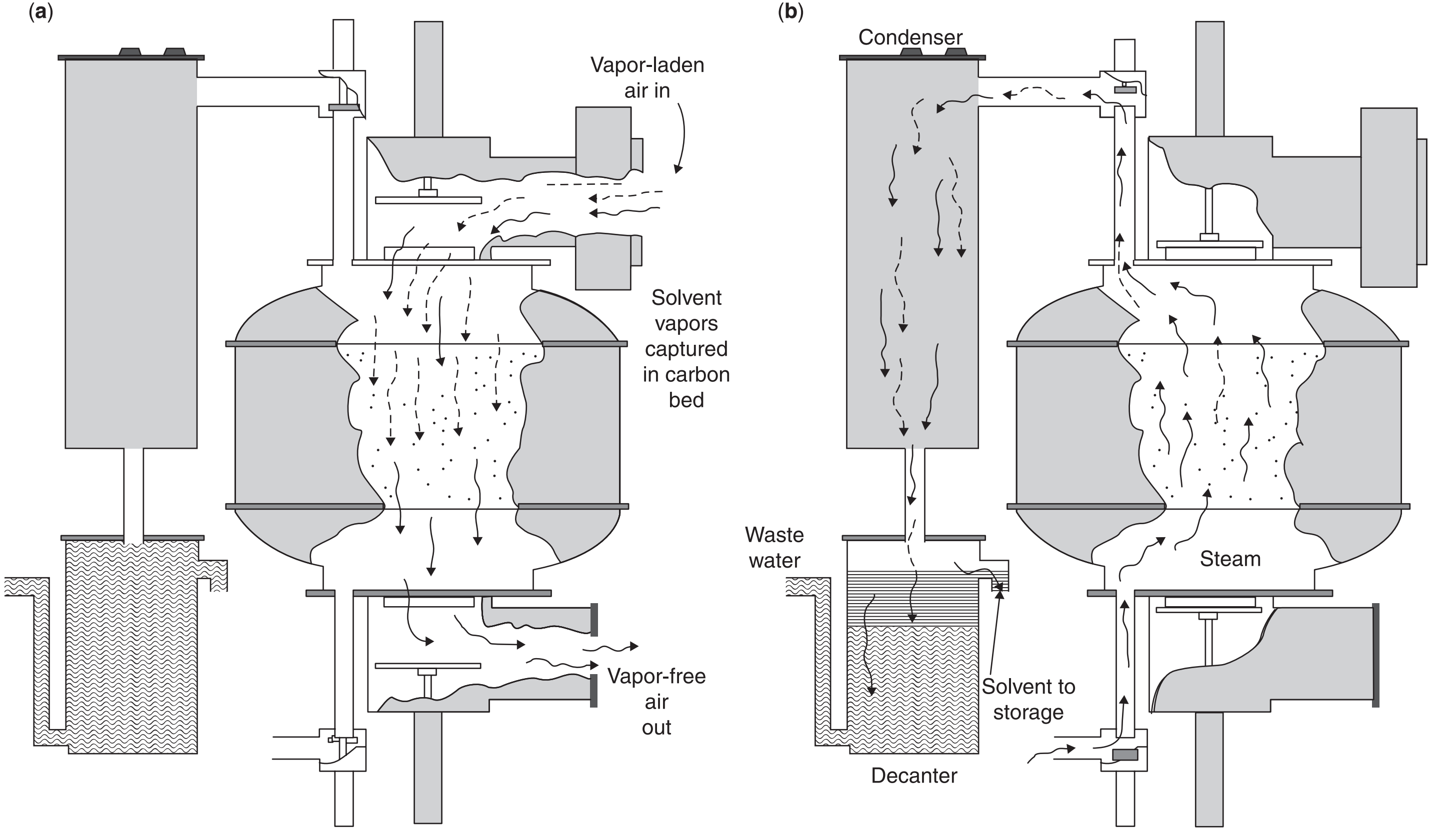

**Figure 11.9** (a) Adsorption cycle; (b) desorption cycle.

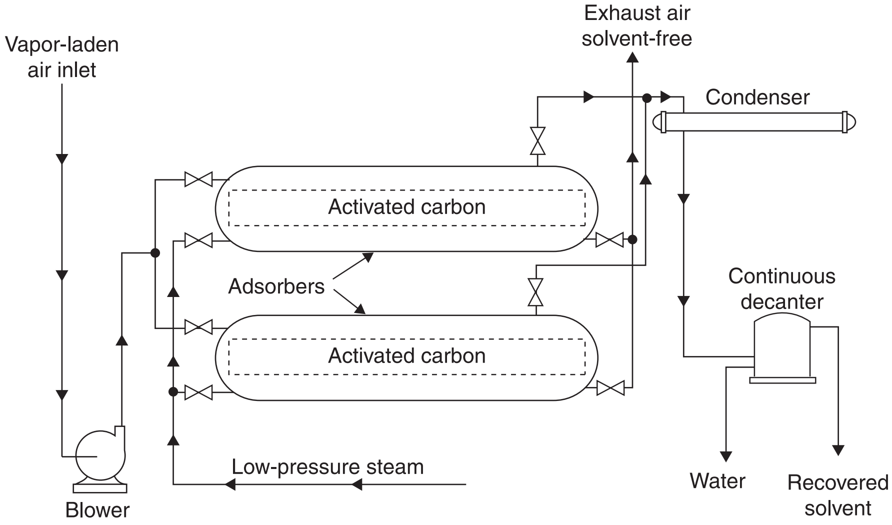

**Figure 11.10** Flow diagram of a solvent recovery system.

are of disk type, opened and closed by air-driven pistons. Water is used as coolant in the condenser. Steam, electric power to drive the blower, and cooling water are three operating-cost items. The cost of steam and cooling water increases with frequency of regeneration.

Figure 11.9 shows the features and arrangement of the component parts of a two-adsorber system. This particular unit is a Vic Model 572 with two adsorber beds used alternately, i.e., while one unit is on-stream adsorbing, the other is regenerating.(4)

Dual adsorber systems can also be operated with both beds on-stream simultaneously, especially when solvent concentrations are low. In this situation, regeneration is less frequent than a full work shift and may be accomplished during off-work hours. Operation in parallel almost doubles the air-handling capacity of the adsorption unit and may be an advantage in terms of operating cost.

The concept of the moving-bed system is illustrated in Figure 11.11. The rotary component of the system consists of four coaxial cylinders. The outer cylinder is impervious to gas flow except at the slots near the left end. They serve as air inlet ports where they are shown uncovered and as steam–vapor outlet ports as shown at the lower left end of the rotary. The carbon bed is retained between two cylinders made of screen or perforated metal and also segmented by partitions placed radially between the two cylinders. The inner cylinder is again impervious to gas flow except at the slots near the right end of the rotary. These slots serve as outlet ports for the discharge air and as inlet ports for the regenerating steam. On each rotation of the rotary, each segment of the bed undergoes adsorption and regeneration. The desorbed solvent can then be separated from the steam by decantation or distillation.(3)

Because of the continuous regeneration capability of the rotary bed, more efficient utilization of the carbon is possible than with stationary-bed systems. In most solvent

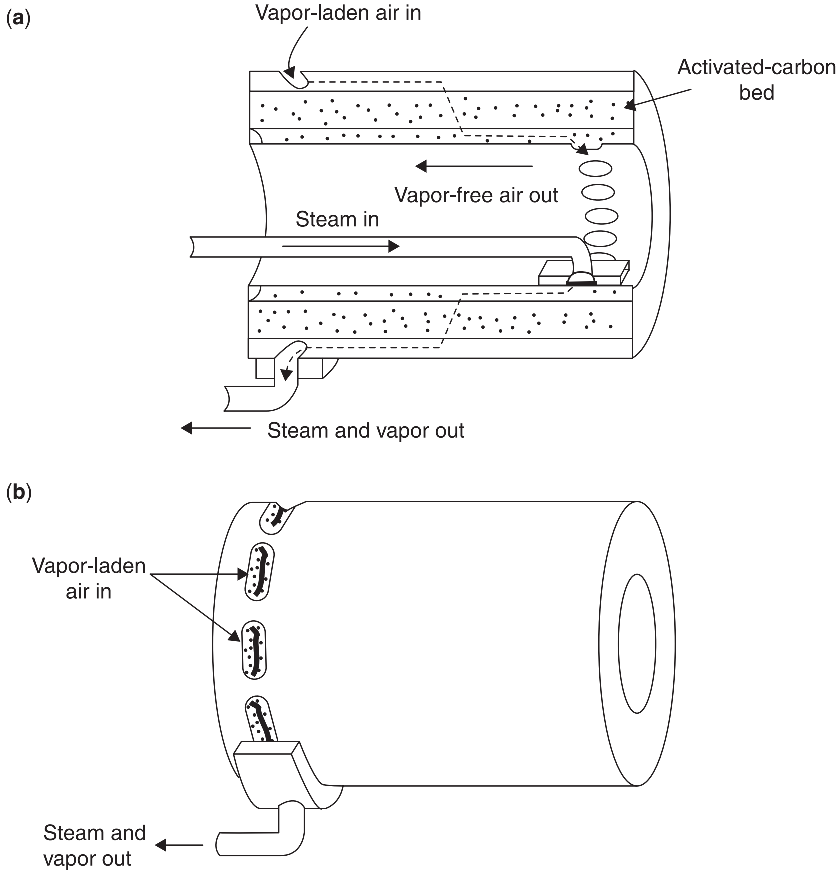

**Figure 11.11** Continuous rotary bed: (a) cross-sectional view; (b) horizontal exterior view.

recovery operations, the adsorption zone and the saturated bed behind it are idle but add to the bulk of the system and increase airflow resistance through the bed. In deep beds of 12 to 36 inches, as required in the stationary-bed systems, a large portion of the bed is idle at any one time.(3) By continuous regeneration, the regeneration time for each segment of the bed is shortened, and thereby shorter bed lengths can be used. This leads to two advantages: a more compact system and a reduced pressure drop. The disadvantages are those associated with wear on moving parts and maintaining seals in contact with moving parts. The use of shorter beds also decreases the steam utilization efficiency.

Figure 11.12 shows a flow diagram for a fluidized-bed solvent recovery system.(3) The carbon is recirculated continuously through the adsorption–regeneration cycle. The spent carbon, saturated with solvent, is elevated to the surge bin and then passed down into the regeneration bed where it is contacted with an upward flow of steam. The regenerated carbon is then metered into the adsorber, where the carbon

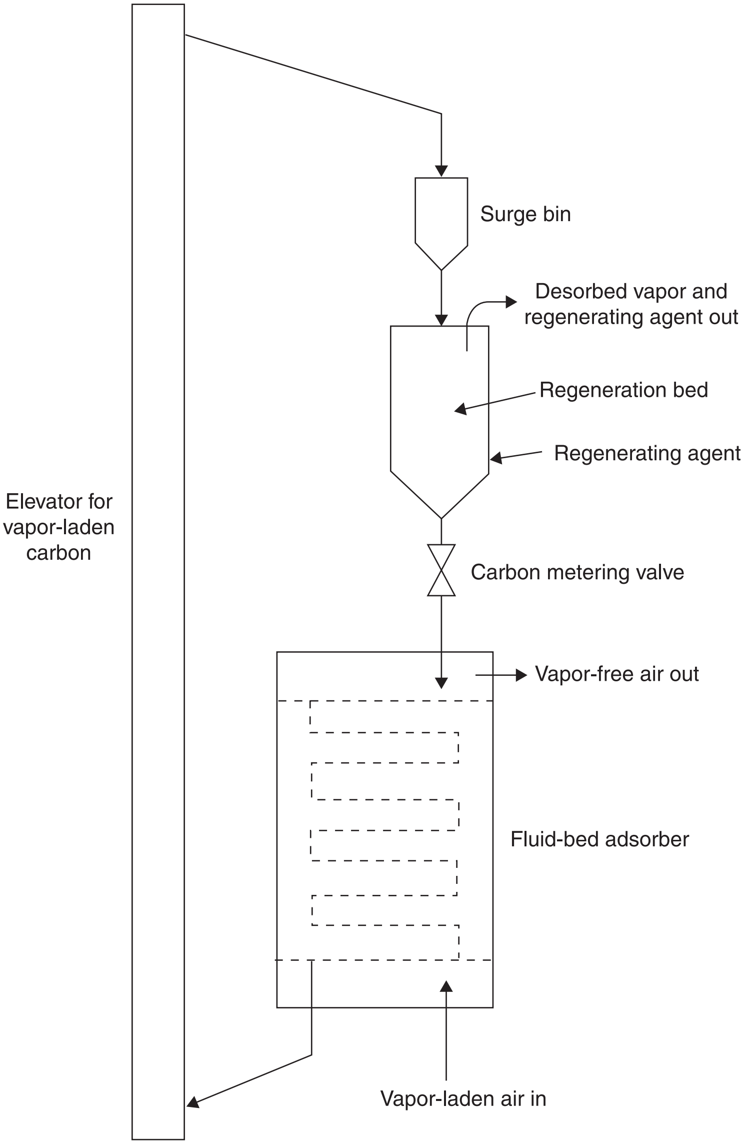

**Figure 11.12** Fluidized-bed solvent recovery system.

traverses nine beds while fluidized with the upward flow of the vapor-laden air. An air velocity of approximately 240 ft/min is required to cause fluidization of the bed. In both the regeneration and adsorption phases, the carbon is moved countercurrent to the gas or vapor. The countercurrent movement increases the efficiency of regeneration (i.e., the steam : solvent ratio is less than for a stationary bed under otherwise comparable conditions). In addition to the beneficial effects of the countercurrent movement, the bed length can be increased to further improve steam utilization.

Countercurrent flow also increases the effective use of the carbon; more solvent can be recovered with less carbon than with stationary- or rotary-bed systems. By adjustments or balance of the carbon and solvent input rates, the total carbon in the adsorber can be made part of the adsorption zone reaching saturation in the lowest bed just before it is discharged into the elevator. Very little of the carbon is then idle; hence, maximum utilization is made of the carbon.

The fact that the carbon has reached saturation when delivered to the regeneration phase is another factor in the reduced steam requirement; in this respect, the fluidized-bed system is most favorable. In rotary-bed operations, the carbon moved into the regeneration phase has reached the lowest state of saturation in the three systems.

When large air volumes are treated and available space for the installation is at a premium, the smaller size and lower initial cost are definite advantages over the stationary-bed system. A serious disadvantage is that of high attrition losses of the carbon caused by the fluidization of the beds. Because of the attrition, filtration of the effluent airstream may be required. The influent airstream need not be highly filtered because plugging of the fluidized beds with particulate matter is minimal. The major manufacturer of these units has given consideration to discontinue operations.

No adsorber system could operate alone without sufficient auxiliary equipment and the components required to collect, transport, and filter vapor-laden airstreams being delivered to the adsorber. Proper design of these components is necessary to provide proper service to the adsorber. The ducts and piping need to be sized properly for required air velocities to optimize the efficiency of the adsorber. If the air velocity is too high, the stationary-bed adsorber may become a fluidized-bed adsorber, or low flows may create severe channeling through the beds. The fan is the catalyst for forcing the gas stream in and out of the unit, so it is important that careful attention to design and sizing is given to this equipment.(5)

Because there are several adsorber configurations, the location of a filter can be varied: before the inlet airstream (in a stationary bed) to reduce possible contamination to the adsorbent, or after the fluidized-bed adsorber to reduce particulate emissions. Monitoring of the filter efficiency can be accomplished by measuring the pressure drop across the filter using either a manometer or pressure gauge.

Compressed-air systems are necessary in some adsorber systems for valve and damper operation. For best results, the air supply should be kept contaminant-free through the use of a filter installed close to the adsorber. The compressed air supply should be equipped with an in-line filter, pressure regulator, and lubricator.

Several devices are installed in series following adsorption for recovery of the solvent after regeneration. Condensers and separators are examples of recovery devices. The condenser is installed just after the system for removal of the heat from the vapors. There are two basic types of condensers: surface condensers and contact condensers. In a surface condenser, the coolant does not contact the vapors or condensate. Most surface condensers are of shell-and-tube configurations. Water flows through the tubes and vapors condense on the shell side. In contact condensers, the coolant vapors and condensate are intimately mixed. These condensers are more flexible, simpler, and considerably less expensive to install. Sizing of this condenser is also more straightforward than the design for surface condensers.

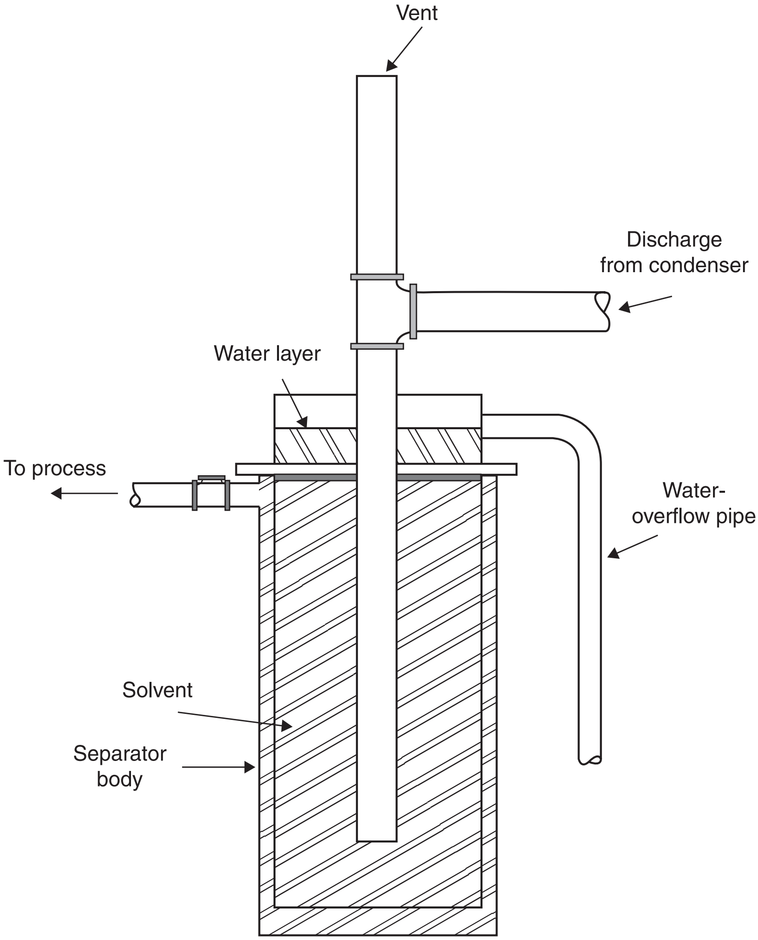

**Figure 11.13** Water separator.

Separators (decanters) are installed following the condenser to separate the contaminant from the water. Figure 11.13 shows a typical separator used with activated carbon bed adsorbers; note, however, that water is generally the heavier phase. Separators work on the principle of gravitational forces where the heavier material to be separated is removed from the bottom of the canister and the lighter material is removed through a line located at the top of the canister. Water separators are more effective with single solvent applications, and only when the solvent is immiscible in water.

## DESIGN AND PERFORMANCE EQUATIONS

The movement of vapors through an adsorbent bed is often referred to as a *dynamic process*. The term "dynamic" refers to motion, both in the movement of gas through

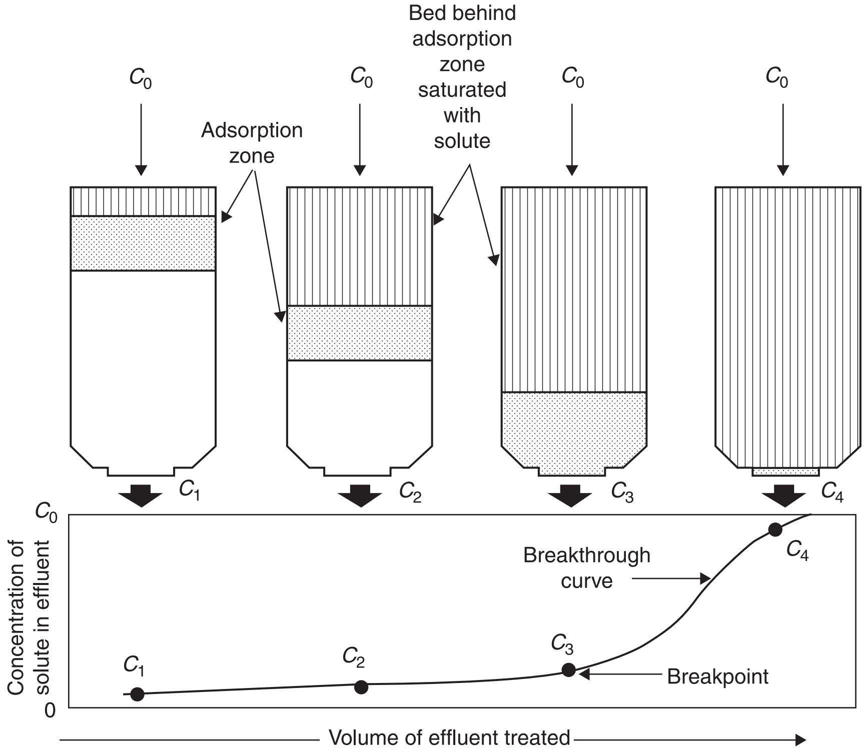

**Figure 11.14** Adsorption wavefront.

the adsorbent bed and the change in vapor concentration(s) as it moves through the bed. There are a variety of configurations in which the solute-ladened air stream and adsorbent are brought into contact. The most common configuration is to pass the air stream down through a fixed volume or bed of adsorbent. Figure 11.14 illustrates how adsorption (mass transfer) occurs as a binary solution containing an adsorbed solute passes down through the bed.

The gas stream containing the solute at an initial concentration $C_0$ is passed down through a (deep) bed of adsorbent material that is free of any solute. Most of the solute is readily adsorbed by the top portion of the bed. The small amount of solute that is left is easily adsorbed in the remaining section of the bed. The effluent from the bottom of the bed is essentially solute-free, denoted as $C_1$.

After a period of time, the top layer of the adsorbent bed becomes saturated with solute. The majority of adsorption (approximately 95%) now occurs in a narrow portion of the bed directly below this saturation section. The narrow zone of adsorption is referred to as the *mass transfer zone* (MTZ). As additional solute vapors pass through the bed, the saturated section of the bed becomes larger and the MTZ moves further down the length of the adsorbent. The actual length of the MTZ remains fairly constant as it travels through the adsorbent bed. Additional adsorption occurs as the vapors pass through the "unused" portion of the bed. The effluent concentration at $C_2$ remains essentially zero, since there is still an unsaturated section of the bed.

Finally, when the lower portion of the MTZ reaches the bottom of the bed, the concentration of solute in the effluent suddenly begins to rise. This is referred to as the *breakthrough point* (or *breakpoint*)—where untreated vapors are being exhausted from the adsorber. If the air stream is not switched to a fresh bed, the concentration of the solute in the outlet will quickly rise until it approaches the initial concentration, illustrated at point $C_4$. It should be noted that in most air pollution control applications even trace amounts of contaminants in the effluent stream are undesirable.(1)

To achieve continuous operation, adsorbers must be either replaced or cycled from adsorption to desorption before breakthrough occurs. In *desorption* or *regeneration*, the adsorbers solute vapors are removed from the used bed in preparation for the next cycle. Most commercial adsorption systems are the regenerable type.

In regard to regenerable adsorption systems, three important terms are used to describe the *equilibrium capacity* (CAP) of the adsorbent bed. These capacity terms are measured in mass of vapor per mass of adsorbent. First, the *breakthrough capacity* (BC) is defined as the capacity of the bed at which unreacted vapors begin to be exhausted. The *saturation capacity* (SAT) is the maximum amount of vapor that can be adsorbed per unit mass of carbon (this is the capacity read from the adsorption isotherm) and thus is equal to CAP. The *working capacity* or *working charge* (WC) is the actual amount adsorbed in the adsorber. Thus, the working capacity is a certain fraction of the saturation capacity. Working capacities can range from 0.1 to 0.7 times the saturation capacity. (*Note*: A smaller capacity increases the amount of carbon required.) This fraction is set by the designer for individual systems by often balancing the cost of carbon and adsorber operation vs preventing breakthrough while allowing for an adequate cycle time.

Another factor in determining the working capacity is that it is uneconomical to desorb all the vapors from the adsorber bed. The small amount of residual vapors left on the bed is referred to as the *HEEL*. This HEEL accounts for a large portion of the difference between the saturation capacity and the working capacity. In some cases, the working capacity can be estimated by assuming it to be equal to the saturation capacity minus the HEEL.

The following equations and procedures may be used to estimate some of the terms described above for an adsorber bed of height $Z$:

$$\mathrm{BC} = [(0.5)(\mathrm{CAP})(\mathrm{MTZ}) + (\mathrm{CAP})(Z - \mathrm{MTZ})]/Z \tag{11.6}$$

$$\begin{aligned}\mathrm{WC} &= [(0.5)(\mathrm{CAP})(\mathrm{MTZ})/Z] + [(\mathrm{CAP})(Z - \mathrm{MTZ})]/Z - \mathrm{HEEL}\\ &= \mathrm{BC} - \mathrm{HEEL}\end{aligned} \tag{11.7}$$

As discussed, the working charge can sometimes be taken to be some fraction of the saturated (equilibrium) capacity of the adsorbent (CAP):

$$\mathrm{WC} = (f)(\mathrm{CAP}) \tag{11.8}$$

with

$$0 \le f \le 1.0 \tag{11.9}$$

## ILLUSTRATIVE EXAMPLE 11.5

Calculate the working capacity of an adsorption bed given the saturation (equilibrium) capacity (CAP), mass transfer zone (MTZ), and HEEL provided. The depth of the adsorption bed is 3 ft, the saturation capacity is 39%, the MTZ is 4 in and the HEEL is 2.5%.

***SOLUTION*:** Calculate the breakthrough capacity, BC.

$$\mathrm{BC} = \frac{0.5(\mathrm{CAP})(\mathrm{MTZ}) + (\mathrm{CAP})(\mathrm{Z} - \mathrm{MTZ})}{Z} \tag{11.6}$$

Substituting,

$$\mathrm{BC} = \frac{0.5(0.39)(4) + (0.39)(36 - 4)}{36} = 0.368 = 36.8\%$$

Calculate the working capacity, WC.

$$\mathrm{WC} = \mathrm{BC} - \mathrm{HEEL} - \mathrm{PF};\ \ \mathrm{PF} = \text{packing factor} \tag{11.7}$$

Substituting,

$$\mathrm{WC} = 36.8 - 2.5 - 0 = 34.3\% \qquad \blacksquare$$

For multicomponent adsorption, the working charge may be calculated from[(6)]

$$\mathrm{WC} = \frac{1.0}{\sum_{i=1}^{n} (w_i/\mathrm{CAP})} \tag{11.10}$$

where $n$ is the number of components, $w_i$ is the mass fraction of $i$ in $n$ components (not including the carrier gas) and $\mathrm{CAP}_i$ is the equilibrium capacity of component $i$. For a two component system ($A$, $B$), the above equation reduces to

$$\mathrm{WC} = \frac{(\mathrm{CAP}_A)(\mathrm{CAP}_B)}{w_A(\mathrm{CAP}_B) + w_B(\mathrm{CAP}_A)} \tag{11.11}$$

## ILLUSTRATIVE EXAMPLE 11.6

Organic vapors in an air stream are to be recovered with an adsorber using activated carbon as the adsorbent. The organic vapor concentrations in the air stream are provided in Table 11.7. Calculate the "theoretical" working capacity and the "actual" capacity given a HEEL of 0.025 (fractional basis) and a fractional packing factor of 0.03 (negative).

***SOLUTION*:** The working capacity is calculated from

$$\mathrm{WC} = \frac{1.0}{\sum_{i=1}^{n} (w_i/\mathrm{CAP})} \tag{11.10}$$

**Table 11.7** Equilibrium Data for Organic Vapor

| $w_i$ (air-free basis) | Mass fraction, $w_i$ (air-free basis) | Equilibrium capacity, lb/lb |
|---|---|---|
| Methane | 0.67 | 0.39 |
| Toluene | 0.05 | 0.08 |
| Propane | 0.25 | 0.40 |
| Diphenyl | 0.02 | 0.11 |
| Benzyl alcohol | 0.01 | 0.16 |

Substituting, one obtains

$$\begin{aligned}\text{WC} &= \frac{1.0}{(0.67/0.39) + (0.05/0.08) + (0.25/0.40) + (0.02/0.11) + (0.01/0.16)} \\ &= \frac{1.0}{1.718 + 0.625 + 0.625 + 0.182 + 0.063} \\ &= 0.3113 = 31.13\%\end{aligned}$$

This represents the "theoretical" or maximum working charge. The actual WC, including the HEEL effect, is

$$\begin{aligned}\text{WC} &= 0.3113 - 0.025 \\ &= 0.2863 = 28.63\%\end{aligned}$$

Including a packing factor leads to

$$\begin{aligned}\text{WC} &= 0.3113 - 0.025 - 0.03 \\ &= 0.2563 = 25.63\%\end{aligned}$$

■

After determining the service time and/or working charge necessary for a particular application, there are several other possible factors to be considered:

**1** The adsorbent particle size
**2** The physical adsorbent bed depth
**3** The gas velocity
**4** The temperature of the inlet gas stream and the adsorbent
**5** The solute concentration to be adsorbed
**6** The solute concentration(s) not to be adsorbed, including moisture
**7** The removal efficiency
**8** Possible decomposition or polymerization on the adsorbent
**9** The frequency of operation
**10** Regeneration conditions
**11** The system pressure

Temperature has an inversely proportional effect on adsorption capacity, such that when temperature increases, the adsorption capacity decreases. The adsorption

**Table 11.8** Adsorbent Heat Capacity Values (Ambient Conditions Btu/ft$^3$ · °F)

| | |
|---|---|
| Activated carbon | 0.25 |
| Alumina | 0.21 |
| Molecular sieve | 0.25 |

process is exothermic. As the adsorption activity moves through the bed, a temperature front follows and heat is transferred to the gas stream. When the gas leaves the area of adsorption activity, the heat exchange reverses (gas will transfer heat to the bed). The temperature differential during the adiabatic operation of the adsorber can be estimated as follows:

$$\Delta T = \frac{6.1}{(C_p/C_i) \times 10^5 + 0.51(C_p/C_{st})} \tag{11.12}$$

where $\Delta T$ is the temperature rise, °F, $C_{st}$ is the saturation capacity of bed at $T + \Delta T$, $C_i$ is the inlet concentration (ppm), and $C_p$ is the volumetric heat capacity of the adsorbent, Btu/ft$^3$ · °F (see Table 11.8).

The design of fixed-bed adsorption systems also requires the need and capability of estimating the pressure drop through the bed. Ergun$^{(7)}$ derived a correlation to estimate the pressure drop for the flow of a fluid through a bed of packed solids when it alone fills the voids in the bed. This correlation is given by the relationship

$$\frac{\Delta P g_c d_p \varepsilon^3}{2Z\rho v^2(1-\varepsilon)} = \frac{75(1-\varepsilon) + 0.875}{\text{Re}} \tag{11.13}$$

where $\Delta P$ is the pressure drop of gas in psf, $Z$ is the depth of packing (ft), $g_c = 4.18 \times 10^8\ \text{ft} \cdot \text{lb}/\text{lb}_\text{f} \cdot \text{h}^2$, $d_p$ is the effective particle diameter (ft), $\varepsilon$ is the fractional void volume in dry-packed bed, $\rho$ is the gas density (lb/ft$^3$), $v$ is the superficial velocity of the gas through the bed (ft/h) and Re is the Reynolds number.

Information on different mesh carbon sizes is presented in Figure 11.15. This data is used in pressure drop calculations.

There is a simpler Ergun equation provided by Union Carbide for molecular sieves:$^{(8)}$

$$\frac{\Delta P}{Z} = \frac{f_T C_T G^2}{\rho d_p} \tag{11.14}$$

where $C_T$ is the pressure drop coefficient (ft · h$^2$/in$^2$), $f_T$ is the friction factor, $G$ is the superficial mass velocity (lb/h · ft$^2$) and the pressure drop is given in psi. The friction factor, $f_T$, is determined from Figure 11.16 as a function of the modified Reynolds number. The pressure drop coefficient, $C_T$, is also determined from the same figure, which has $C_T$ plotted as a function of $\varepsilon$. For molecular-sieve pellets, the effective particle diameter can be obtained from

$$d_p = \frac{d_c}{\frac{2}{3} + \frac{1}{3}(d_c/l_c)} \tag{11.15}$$

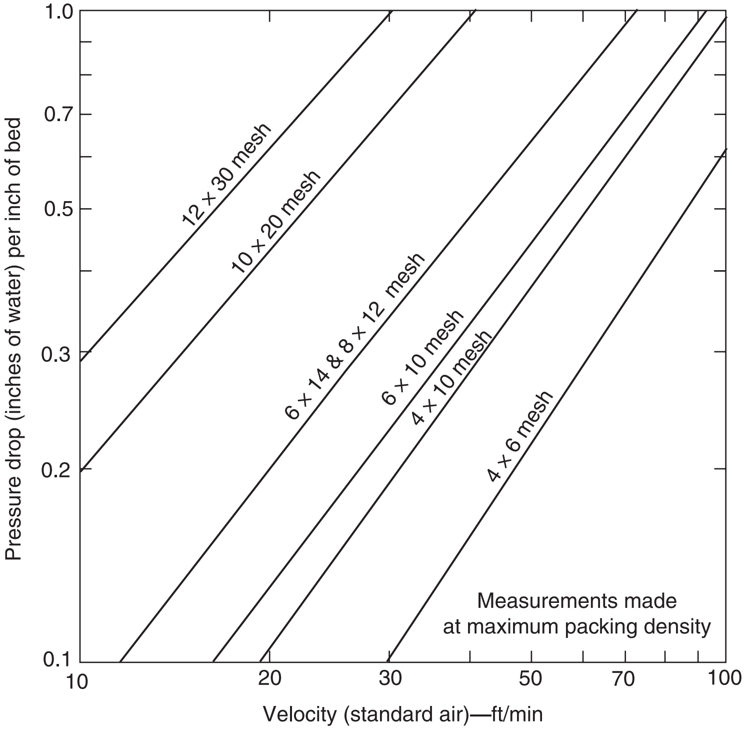

**Figure 11.15** Activated carbon pressure drop curves (EPA chart).

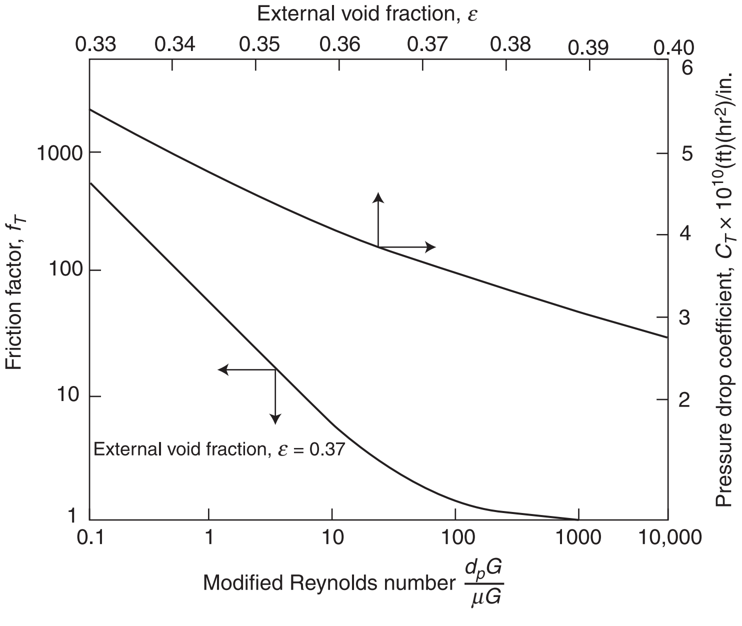

**Figure 11.16** Pressure drop information for molecular sieves.

where $d_c$ is the particle diameter (ft) and $l_c$ is the particle length (ft). Suggested values for $\varepsilon$ and $d_p$ for various sizes of molecular sieves are available in the literature.(1)

This section is concluded with a rather simplified overall design procedure for a system adsorbing an organic that consists of two horizontal units (one on/one off) that are regenerated with steam.(6,9)

**1** Select adsorbent type and size.

**2** Select cycle time; estimate regeneration time; set adsorption time equal to regeneration time; set cycle time to twice the regeneration time; generally, try to minimize regeneration time.

**3** Set velocity; $v$ is usually 80 ft/min, but may be increased to 100 ft/min.

**4** Set steam/solvent ratio.

**5** Calculate (or obtain) WC for above.

**6** Calculate amount of solvent adsorbed during $\frac{1}{2}$ cycle time $(t_{\text{ads}})m_s$.

$$m_s = qc_s t_{\text{ads}}; \quad c_s = \text{inlet solvent concentration} \tag{11.16}$$

**7** Calculate adsorbent mass required, $M_{\text{AC}}$,

$$M_{\text{AC}} = m_s/\text{WC} \tag{11.17}$$

**8** Calculate adsorbent volume requirement,

$$V_{\text{AC}} = M_{\text{AC}}/\rho_B; \quad \rho_B = \text{adsorbent bulk density} \tag{11.18}$$

**9** Calculate the face area of the bed:

$$A_{\text{AC}} = q/V_{\text{AC}} \tag{11.19}$$

**10** Calculate bed height:

$$Z = H = (V/A)_{\text{AC}} \tag{11.20}$$

**11** Set $L/D$ (length-to-diameter) ratio.

**12** Calculate $L$ and $D$ from $A = LD$; constraints: $L < 30$ ft, $D < 10$ ft; $L/D$ of 3 to 4 acceptable if $v < 30$ ft/min.

**13** Design (structurally) to handle if filled with water.

**14** Design vertically if $q < 2500$ actual cubic feet per minute (acfm).

## ILLUSTRATIVE EXAMPLE 11.7

The R&D group at a local adsorbent manufacturer has recently developed a new granulated activated column (GAC) adsorbent, JB26, for the removal of common water pollutants. Some data have been collected on the adsorption isotherm for a few solutes, but extensive tests have not been conducted as of yet. However, a major client is very interested in the new adsorbent and would like to know approximately how long one of its 65 $\text{ft}^3$ units could operate with JB26 before breakthrough would occur.

The following information was given to estimate how many days a 56,000 gal/day unit could run until breakthrough. From limited testing, the isotherm of interest is approximated by

$$Y_T = 0.002C^{3.11}$$

where $Y_T$ is the ratio of lb of adsorbate to lb of adsorbent and $C$ is the adsorbate concentration, mg/L. The bulk density of JB26 is 42 $\text{lb/ft}^3$ and it will treat a stream with an inlet concentration ($C_i$) of 3.5 mg/L. In addition, the breakthrough concentration has been set at 0.5 mg/L.

The breakthrough adsorption capacity typically ranges between 25–50% (assume 50%) of the theoretical capacity, $Y_T$, which is determined from the proposed adsorption isotherm, evaluated at the initial solute concentration in solution, $C_i$. The time to breakthrough is then given by the following equation:

$$t_B = \frac{Y_B M_{\text{AC}}}{8.34q[C_i - (C_B/2)]}$$

where $t_B$ is the time to breakthrough (days), $Y_B$ is the adsorption capacity at breakthrough, $M_{\text{AC}}$ is the mass of carbon in the column (lb), $q$ is the volumetric flow rate of solution (MMgal/day), and $C_B$ is the adsorbate concentration at breakthrough (mg/L).

*Note*: 8.34 lb = 1 MMgal · L/mg.

***SOLUTION*:** The theoretical adsorption capacity $Y_T$ is

$$\begin{aligned} Y_T &= 0.002C^{3.11} \\ &= 0.002(3.5)^{3.11} \\ &= 0.09842 \text{ lb adsorbate/lb adsorbent} \end{aligned}$$

Assume the actual value is 50% of the theoretical value (see comment above). Thus,

$$Y_B = (0.5)(0.09842) = 0.04921 \text{ lb adsorbate/lb adsorbent}$$

The mass of carbon in the unit is

$$\begin{aligned} M_{\text{AC}} &= (65 \text{ ft}^3)(42 \text{ lb/ft}^3) \\ &= 2730 \text{ lb carbon} \end{aligned}$$

The breakthrough time can now be calculated from the breakthrough equation provided above.

$$\begin{aligned} t_B &= \frac{(0.04921)(2730)}{(8.34)(0.56)[3.5 - (0.5/2)]} \\ &= 8.85 \text{ days} \end{aligned}$$

■

## ILLUSTRATIVE EXAMPLE 11.8

A degreaser ventilation stream containing trichloroethylene (TCE) is treated with a horizontal carbon bed adsorber. The adsorber is normally designed to operate at a gas flow of 8000 scfm (60°F, 1 atm), and the concentration of TCE at the adsorber inlet is 1500 ppmv.

The capture efficiency of the adsorber is 99% ($E_c = 0.99$) under normal design conditions. Design parameters are as follows:

Actual conditions: 25 psia, 90°F
SAT = 35%
$Z$ = depth of bed = 2.5 ft
$L$ = length of adsorber = 2.5 ft
$D$ = diameter of adsorber = 8 ft
MTZ = 5 in
HEEL = 2.0%
Bulk density of carbon bed = 35 lb/ft$^3$

Determine the time before breakthrough occurs.

***SOLUTION*:** The calculations are provided below:

$$q = 8000\left(\frac{14.7}{25}\right)\left(\frac{90+460}{60+460}\right)$$

$$= 4975 \text{ acfm}$$

$$q_{\text{TCE}} = (1500 \times 10^{-6})(4975)$$

$$= 7.46 \text{ acfm}$$

$$\dot{m}_{\text{TCE}} = \frac{P(\text{MW})q_{\text{TCE}}}{RT} = \frac{(25)(131.5)(7.46)}{(10.73)(90+460)}$$

$$= 4.16 \text{ lb/min}$$

$$\text{BC} = \frac{0.5(C_s)(\text{MTZ}) + (C_s)(Z - \text{MTZ})}{Z} \tag{11.6}$$

$$= \frac{0.5(0.35)\left(\frac{5}{12}\right) + (0.35)\left[2.5 - \left(\frac{5}{12}\right)\right]}{2.5}$$

$$= 0.32$$

$$\text{WC} = \text{BC} - \text{HEEL} \pm \text{SF (safety factor)} \tag{11.7}$$

$$= 0.32 - 0.02 - 0$$

$$= 0.30 = 30\%$$

$$V_{\text{AC}} = (25)(8)(2.5)$$

$$= 500 \text{ ft}^3$$

$$M_{\text{AC}} = V_{\text{AC}}\rho_B \tag{11.8}$$

$$= (500)(35)$$

$$= 17{,}500 \text{ lb}$$

$$t \text{ (to saturation)} = \frac{(\text{WC})(M_{\text{AC}})}{\dot{m}_{\text{TCE}}E_{\text{c}}}$$

$$= \frac{(0.30)(17{,}500)}{(4.16)(0.99)}$$

$$= 1275 \text{ min} \approx 21 \text{ hr}$$

■

## ILLUSTRATIVE EXAMPLE 11.9

Refer to Illustrative Example 11.8. Recalculate the time before breakthrough occurs, based on the following transient condition. The adsorber system is on line for one hour at the previous (normal) design conditions when the inlet concentration of TCE rises to an average value of 2500 ppmv because of a malfunction in the degreaser process. The efficiency also drops to 97.5% during this time. Assume that the SAT remains the same.

***SOLUTION*:** For these transient conditions

$$\begin{aligned} m_{\text{TCE}}\ (\text{in carbon}) &= (0.30)(500)(35) = (0.30)(17{,}500) \\ &= 5250\ \text{lb}_{\text{TCE}},\ \text{maximum} \\ m_{\text{TCE}}\ (\text{flow, first hour}) &= (4.16)(60)(0.99) \\ &= 247.1\ \text{lb}_{\text{TCE}}\ \text{captured} \end{aligned}$$

The remaining capacity of the bed is now available for adsorption after the first hour,

$$\begin{aligned} m_{\text{TCE}}\ (\text{after first hour}) &= 5250 - 247.1 \\ &= 5003\ \text{lb}_{\text{TCE}} \\ t\ (\text{to transient saturation}) &= t_{\text{ts}} = \frac{5003}{\dot{m}_{\text{TCE}\cdot\text{transient}}(0.975)} \\ \dot{m}_{\text{TCE}\cdot\text{transient}} &= (4.16)(2500/1500) \\ &= 6.93\ \text{lb/min} \\ t_{\text{ts}} &= \frac{5003}{(6.93)(0.975)} \\ &= 740\ \text{min} = 12.34\ \text{h} \end{aligned}$$

The time to breakthrough, following the transient period, is

$$\begin{aligned} t_B &= t + t_{\text{ts}} \\ &= 60 + 740.1 \\ &= 800.1\ \text{min} = 13.34\ \text{h} \end{aligned}$$

Thus, the time to breakthrough has been reduced from 21 to 13.3 h. ■

## ILLUSTRATIVE EXAMPLE 11.10

Theodore Consultants has been selected by Flynn Chemicals Inc. to design an adsorber that treats a degreaser ventilation stream containing trichloroethylene (TCE). Flynn Chemicals has provided basic operating data to Theodore Consultants and requires the use of activated carbon as an adsorbent. Determine the volume of activated carbon required to treat the gas and the height of the adsorption column. Operating data is provided as follows:

TCE MW = 131.5 g/gmol

Standard conditions = 1 atm, 65°F

Operating conditions = 25 psia and 75°F
Bulk density or activated carbon = $38 \text{ lb/ft}^3$
Working capacity of activated carbon = 25 lb TCE per 100 lb carbon
Flow rate of air stream = 12,000 scfm
Inlet concentration of TCE = 2000 ppm

The adsorption column cycle is set at 5 hr in the adsorption mode, 2 hr in the heating and desorbing mode, 2 hr in cooling, and 1 hr in standby. The adsorber recovers 96% of TCE by weight. A horizontal unit with a cross sectional area of 5 ft by 20 ft is recommended.

***SOLUTION*:** Convert the standard flow rate to actual flow rate using the ideal gas law:

$$\begin{aligned} q_A &= q_S\left(\frac{T_A}{T_S}\right)\left(\frac{P_S}{P_A}\right) \\ &= 12{,}000\left(\frac{75+460}{65+460}\right)\left(\frac{14.7}{25}\right) = 7190.4 \text{ acfm} = 4.3\times 10^5 \text{ acfh} \end{aligned}$$

The flow rate of TCE is therefore:

$$\begin{aligned} q_{\text{TCE}} &= y_{\text{TCE}}q_A = \frac{2000}{10^6}(4.3\times 10^5) = 860 \text{ acfh} \\ \dot{m}_{\text{TCE}} &= q\rho = 860[25(131.5)/(10.73)(535)] = 492.5 \text{ lb/h} \\ \dot{m}_{\text{TCE,adsorbed}} &= (492.5)(0.96)(5) = 2364 \text{ lb} \\ V_{\text{AC}} &= \frac{\dot{m}_{\text{TCE,adsorbed}}}{\text{WC}(\rho_B)} = \frac{2364}{0.25(38)} = 248.8 \text{ ft}^3 \\ Z &= \frac{V_{\text{AC}}}{A_{\text{AC}}} = \frac{248.8}{5(20)} = 2.49 \approx 2.50 \text{ ft} \end{aligned}$$

■

## ILLUSTRATIVE EXAMPLE 11.11

Gas emissions are being collected from a landfill and must be treated before being released into the environment. There are several options for treatment. As one of the project engineers, you have been given the task to look at the use of a horizontal activated carbon adsorber to collect the methane in the gas stream (assume 95% removal). Perform the following calculations:

1. Mass of $CH_4$ collected per operating period
2. Mass of activated carbon needed
3. Depth of AC bed

The following data are provided:

Flow rate = 11,000 acfh
Operating pressure of the adsorber = 1 atm
Operating temperature of the adsorber = 70°F

Time between regeneration = 24 h

Gas stream contains (by mole fraction): $N_2$ 0.10

$CH_4$ 0.50

$CO_2$ 0.40

Bulk density of activated carbon = 30 lb/ft$^3$

Width of AC bed = 15 ft

Length of AC bed = 20 ft

CAP = 0.39 lb $CH_4$/lb AC

HEEL = 0.05 lb $CH_4$/lb AC

***SOLUTION*****:** The mass flow rate of the methane is (applying the ideal gas law)

$$\begin{aligned}\dot{m}_{\mathrm{M}} &= (0.5)(11{,}000)(14.7)(16)/(10.73)(530)\\ &= 227\ \mathrm{lb/h}\end{aligned}$$

For the mass of methane collected in one day,

$$\begin{aligned}m_{\mathrm{M}} &= 0.95(227)(24)\\ &= 5176\ \mathrm{lb}\end{aligned}$$

A key assumption that should be made here is that only the methane contributes to the WC:

$$\begin{aligned}\mathrm{WC} &= 0.39 - 0.05\\ &= 0.34\end{aligned}$$

The mass of carbon required is

$$\begin{aligned}M_{\mathrm{AC}} &= m_{\mathrm{M}}/\mathrm{WC} \qquad (11.17)\\ &= 5176/0.34\\ &= 15{,}224\ \mathrm{lb}\end{aligned}$$

To complete the calculations,

$$\begin{aligned}V_{\mathrm{AC}} &= M_{\mathrm{AC}}/\rho_B \qquad (11.18)\\ &= 15{,}224/30\\ &= 508\ \mathrm{ft}^3\end{aligned}$$

$$\begin{aligned}Z &= V_{\mathrm{AC}}/A_{\mathrm{AC}} \qquad (11.20)\\ &= 508/(15)(20)\\ &= 1.7\ \mathrm{ft}\\ &= 20.4\ \mathrm{in}\end{aligned}$$

■

## ILLUSTRATIVE EXAMPLE 11.12

A vertical 10-ft-diameter vessel is used to adsorb 40 ppm benzene and 30 ppm pyridine from an air stream at 1 atm and 70°F. The superficial velocity through the vessel is 64 fpm. The adsorbent is 4 × 6 mesh activated carbon having a bulk density 30 lb/ft$^3$. Inlet concentrations (lb/lb) indicate that the equilibrium capacities for benzene and pyridine are 0.12 and 0.19, respectively. The working charge can be assumed equal to 80% of the ideal value.

Determine the pressure drop and the amount of adsorbent in the bed if the bed is in operation for 5 days a week, 24 hr a day.

***SOLUTION*:** Preliminary calculations are provided below:

$$\begin{aligned} A_{\mathrm{AC}} &= (\pi/4)D^2 = (0.7854)(10)^2 \\ &= 78.54\ \mathrm{ft}^2 \\ q &= (64)(78.54) \\ &= 5027\ \mathrm{ft}^3/\mathrm{min} \end{aligned}$$

Applying the ideal gas law yields

$$\begin{aligned} \rho_B &= \frac{(1)(78.11)}{(530)(0.7302)}; \quad \mathrm{MW}_B = 78.11 \\ &= 0.20\ \mathrm{lb/ft}^3 \\ \rho_P &= 0.20\ \mathrm{lb/ft}^3; \quad \mathrm{MW}_P = 79.1 \end{aligned}$$

The volume and mass of each organic are now calculated:

$$\begin{aligned} V_B &= (5027)(60)(24)(5)(40/10^6) \\ &= 1448\ \mathrm{ft}^3 \\ m_B &= (1448)(0.2) \\ &= 290\ \mathrm{lb} \\ V_P &= (5027)(60)(24)(5)(30/10^6) \\ &= 1086\ \mathrm{ft}^3 \\ m_P &= (1086)(0.2) \\ &= 217\ \mathrm{lb} \end{aligned}$$

The total mass adsorbed is

$$\begin{aligned} m_T &= m_B + m_P = 290 + 217 \\ &= 507\ \mathrm{lb} \end{aligned}$$

Calculate the two mass fractions:

$$\begin{aligned} w_B &= 290/507 \\ &= 0.57 \\ w_P &= 217/507 \\ &= 0.43 \end{aligned}$$

Noting that $\mathrm{CAP}_B = 0.12$ and $\mathrm{CAP}_P = 0.19$ and applying Equation (11.11), one obtains

$$\begin{aligned} \mathrm{WC}_\mathrm{I} &= \frac{(\mathrm{CAP}_B)(\mathrm{CAP}_P)}{(w_B)(\mathrm{CAP}_P) + (w_P)(\mathrm{CAP}_B)} \\ &= \frac{(0.12)(0.19)}{(0.571)(0.19) + (0.428)(0.12)} \\ &= 0.143 \end{aligned}$$

The actual WC is

$$\begin{aligned} \mathrm{WC} &= (0.143)(0.8) \\ &= 0.114 \end{aligned}$$

The mass and volume of carbon are therefore

$$\begin{aligned} M_\mathrm{AC} &= 507/0.114 \\ &= 4447 \text{ lb} \\ V_\mathrm{AC} &= 4447/30 \\ &= 148 \text{ ft}^3 \end{aligned}$$

The height is given by

$$Z = \frac{V_\mathrm{AC}}{A_\mathrm{AC}}$$

Substituting gives

$$\begin{aligned} Z &= 148/78.54 \\ &= 1.89 \text{ ft} \\ &= 22.6 \text{ in} \approx 23 \text{ in} \end{aligned}$$

■

## ILLUSTRATIVE EXAMPLE 11.13

A printing company must reduce and recover the amount of toluene it emits from its Rotograve printing operation. The company submits some preliminary information on installing a carbon adsorption system. You, the primary consultant, are given the following information:

Airflow = 20,000 acfm (77°F, 1 atm)
Adsorption capacity for toluene = 0.175 lb toluene/lb activated carbon
Operation occurs at 10% of LEL (lower explosivity limit) for toluene in the exit air from printer
LEL for toluene = 1.2%
Toluene molecular weight = 92.1
Carbon bulk density (4 × 6 mesh) = 30 $\mathrm{lb/ft^3}$
Working charge = 60% of saturation capacity
Regeneration just under one hour; assume 1.0 hr
Maximum velocity through adsorber = 100 fpm (ft/min)

Determine the minimum size of adsorber you would recommend for a 1 × 1 system. Calculations should include the pertinent dimensions of the adsorber, the amount of carbon, the depth of the bed and an estimate of the pressure drop. Also calculate the fan horsepower if the blower/motor efficiency is 58%.

***SOLUTION*:** Initially, base the calculations on a 1 hr regeneration time so that 1 hr of adsorption is available. Key calculations and results are provided below for the toluene (TOL) and activated carbon (AC). Design for operation at 10% of LEL.

$$
\begin{aligned}
q_{\mathrm{TOL}} &= (20{,}000)(0.10)(0.012) \\
&= 24 \text{ acfm} \\
\dot{m}_{\mathrm{TOL}} &= \frac{(24)(492/537)(92.1)(60)}{359} \\
&= 338 \text{ lb/h} \\
p_{\mathrm{TOL}} &= (24/20{,}000)(14.7) \\
&= (0.0012)(14.7) \\
&= 0.01764 \text{ psia} \\
\mathrm{SAT} &= 17.5\% = 0.175 \text{ lb}_{\mathrm{TOL}}/\text{lb}_{\mathrm{AC}} \\
\mathrm{WC} &= (0.175)(0.60) \\
&= 0.105 \text{ lb}_{\mathrm{TOL}}/\text{lb}_{\mathrm{AC}} \\
&= 10.5 \text{ lb}_{\mathrm{TOL}}/100 \text{ lb}_{\mathrm{AC}} \\
M_{\mathrm{AC}} &= (338/0.105)(1.0) \\
&= 3220 \text{ lb}_{\mathrm{AC}} \text{ for one bed} \\
&= 6440 \text{ lb}_{\mathrm{AC}} \text{ for both beds} \\
V_{\mathrm{AC}} &= 3220/30 = 107 \text{ ft}^3 \\
A_{\mathrm{AC}} &= 20{,}000/100 = 200 \text{ ft}^2 \\
Z &= 107/200 \\
&= 0.535 \text{ ft} = 6.4 \text{ in}
\end{aligned}
$$

Suggest a horizontal 10-ft diameter × 20-ft-long design.

Refer to Figure 11.15. At 100 ft/min, $\Delta P = 0.625$ in $H_2O$/in bed. Therefore

$$
\begin{aligned}
\Delta P_{\mathrm{total}} &= (0.625)(6.4) \\
&= 4.0 \text{ in } \mathrm{H_2O} \\
\mathrm{HP} &= q\Delta P/E_f; \quad E_f = \text{blower fractional efficiency} \\
&= \frac{(20{,}000)(4.0)(5.2)}{(0.58)(33{,}000)} \\
&= 22 \text{ HP}
\end{aligned}
$$

*Note*: This represents a marginal design since $H$ is only slightly higher than 0.5 ft. ■

## ILLUSTRATIVE EXAMPLE 11.14

You have been asked to design a system to recover a 1.3% by volume acetone mixture in air. The air stream flow rate is $4.32 \times 10^7$ acfd (actual $\text{ft}^3$/day) at 20°C and 1 atm. Your boss has given you plenty of latitude but suggests working within the operating conditions and design procedure suggested by the eminent Dr. L. Theodore. The most immediate adsorbent equilibrium data available indicates that the equilibrium capacity for acetone in the 4.0–8.0% relative saturation range ($0.04 < p_i/p_i' < 0.08$) is 0.35. It has been further suggested to employ 4 × 6 mesh carbon as the adsorbent and to operate with a 2-hr regeneration period. The average particle diameter can be assumed to be 0.0091 ft. The apparent and bulk density for all types of carbon particles available are 45 lb/ft$^3$ and 26 lb/ft$^3$, respectively. Assume $v = 80$ fpm and WC = 0.8 (CAP). Also provide horsepower ($E_f = 0.65$) requirements (use the EPA chart, Fig. 11.15).

***SOLUTION*:** First, calculate the relative saturation (RS) of the acetone on the gas stream:

$$\begin{aligned}\text{RS} &= y_A P/p_A' = p_A/p_A' \\ &= (0.013)(760)/170 \\ &= 0.0581 = 5.81\%\end{aligned}$$

The equilibrium capacity is therefore 0.35, i.e.,

$$\text{CAP} = 0.35$$

Following the usual design procedure

$$\begin{aligned}q &= 4.32 \times 10^7/1440 \\ &= 30{,}000 \text{ acfm}\end{aligned}$$

For $v = 80$ ft/min

$$\begin{aligned}A_{\text{AC}} &= 30{,}000/80 \\ &= 375 \text{ ft}^2 \\ \dot{m}_{\text{A}} &= (0.013)(4.32 \times 10^7)(50)(273/293)/359 \\ &= 72{,}878 \text{ lb/day}\end{aligned}$$

In a 2-hr period

$$\begin{aligned}m_{\text{A}} &= (72{,}878)(2/24) \\ &= 6073 \text{ lb}\end{aligned}$$

The working charge is

$$\begin{aligned}\text{WC} &= (0.35)(0.8) \\ &= 0.28\end{aligned}$$

Therefore

$$\begin{aligned}M_{\text{AC}} &= 6073/0.28 \\ &= 21{,}689 \text{ lb} \\ V_{\text{AC}} &= 21{,}689/26 \\ &= 834 \text{ ft}^3 \\ Z &= V_{\text{AC}}/A_{\text{AC}} = 834/375 \\ &= 2.22 \text{ ft} = 27 \text{ in}\end{aligned}$$

From Figure 11.15

$$\begin{aligned}\Delta P/Z &= 0.44 \text{ in } H_2O/\text{in bed}\\ \Delta P &= (0.44)(27)\\ &= 11.9 \text{ in } H_2O\end{aligned}$$

Finally,

$$\begin{aligned}\text{HP} &= (30{,}000)(11.9)/(33{,}000)(0.65)\\ &= 16.6\end{aligned}$$

■

## ILLUSTRATIVE EXAMPLE 11.15

Small volatile organic compound (VOC) emission sources often use activated carbon that is available in small drums often referred to as canisters. An example of this is a modified form of Carbtrol model G-1, which is suitable for low airflow rates. The drum is not regenerated on site; it is returned to the manufacturer and a new drum delivered.

A small pilot scale reactor uses this modified model G-1 adsorber to capture methylene chloride emissions in a 50 acfm nitrogen purge source. The following operating and design data are provided:

Volumetric flow rate of nitrogen purge = 50 acfm
Molecular weight of methylene chloride = 85
Operating temperature = 70°F
Operating pressure = 1.0 atm
Saturation capacity = 30 lb $CH_2Cl_2/100$ lb C
Methylene chloride concentration = 500 ppm
Weight of carbon in drum = 200 lb
Height of adsorbent in drum = 24 in
Adsorption time = 6 h
Mass transfer zone (MTZ) = 2 in
HEEL = negligible

Based on the above data and information, estimate the number of purge streams that this G-1 model adsorber canister can treat to breakthrough.

***SOLUTION*:** Calculate the working charge, WC, of the carbon drum (canister):

$$\begin{aligned}\text{WC} &= [0.5(\text{CAP})(\text{MTZ}) + (\text{CAP})(Z - \text{MTZ})]/Z \qquad (11.7)\\ &= [0.5(0.3)(2) + (0.3)(24 - 2)]/24 = 0.2875\end{aligned}$$

The drum capacity in lb of methylene chloride is therefore

$$\text{DC} = \text{WC}(W_C) = 0.2875(200) = 57.5 \text{ lb}$$

Determine the mole fraction of methylene chloride in the purge stream and the volumetric flow rate of methylene chloride in acfh:

$$y_{\text{MEC}} = \frac{500}{10^6} = 0.0005$$

$$q_{\text{MEC}} = y_{\text{MEC}}q = 0.0005(50)(60) = 1.5 \text{ acfh}$$

Calculate the density of the methylene chloride vapor in lb/ft$^3$ using the ideal gas law:

$$\rho_{\text{MEC}} = \frac{P(\text{MW})}{RT} = \frac{1(85)}{0.73(70+460)} = 0.220 \text{ lb/ft}^3$$

Calculate the weight of methylene chloride emitted per batch:

$$W = q_{\text{MEC}}\rho_{\text{MEC}}(6 \text{ hr/batch}) = 1.5(0.220)(6) = 1.98 \text{ lb/batch}$$

Determine the maximum number of purges $N$ per canister:

$$N = \text{DC}/W = 57.5/1.98 = 29$$

■

## ILLUSTRATIVE EXAMPLE 11.16

Consider the adsorber system in Figure 11.17. It is designed to operate with a maximum discharge concentration of 50 ppm. Once the unit is installed and running, it operates with a

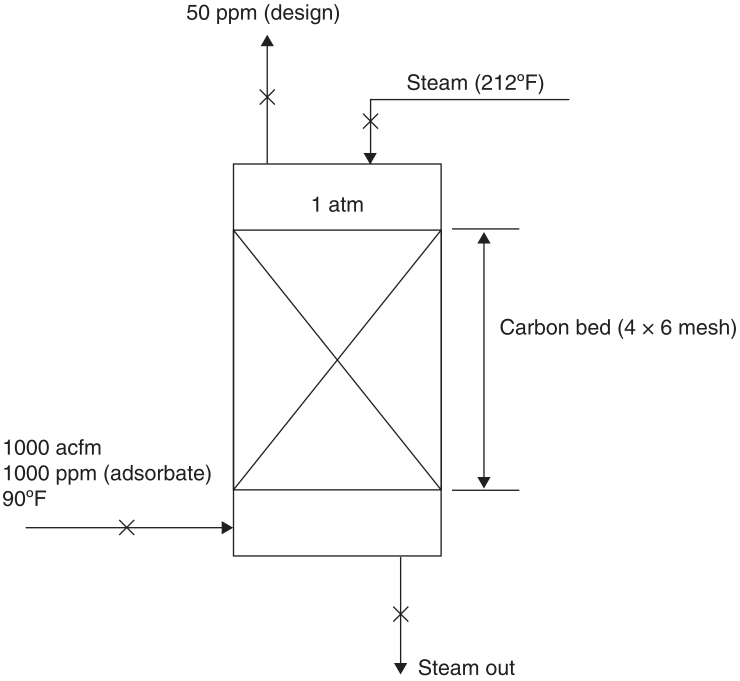

**Figure 11.17** Adsorber not in compliance.

discharge of 60 ppm. Rather than purchase a new unit, what options are available to bring the unit into compliance with the specified design concentration?

***SOLUTION*:** This is obviously an open-ended problem.(6) The suggestions and options (if possible) recommended for adsorbers can be found in an Illustrative Example 20.5 in Chapter 20. ■

## REGENERATION

Adsorption processes in practice use various techniques to accomplish regeneration or desorption. The adsorption–desorption cycles are usually classified into four types, used separately or in combination. This important topic is now considered in more detail.

1. *Thermal swing cycles* using either direct heat transfer by contacting the bed with a hot fluid or indirect transfer through a surface, and reactivating the adsorbent by raising the temperature. A temperature between 300 and 600°F is usually reached, the bed is flushed with a dry purge gas or reduced in pressure, and then it is returned to adsorption conditions. High design loadings on the adsorbent can usually be obtained, but a cooling step is needed.
2. *Pressure swing cycles* use either a lower pressure or vacuum to desorb the bed. The cycle can be operated at nearly isothermal conditions with no heating or cooling steps. The advantages include fast cycling with reduced adsorber dimensions and adsorbent inventory, direct production of a high purity product, and the ability to utilize gas compression as the main source of energy.
3. *Purge gas stripping cycles* use an essentially nonadsorbent purge gas to desorb the bed by reducing the partial pressure of the adsorbed component. Such stripping is more efficient at higher operating temperatures and lower operating pressures. The use of a condensable purge gas has the advantages of reduced power requirements, which are gained by using a liquid pump instead of a blower, and an effluent stream that can be condensed to separate the desorbed material by simple distillation.
4. *Displacement cycles* use an adsorbable purge to displace the previously adsorbed material on the bed. The stronger the adsorption of the purge, the more completely the bed is desorbed using lesser amounts of purge, but the more difficult it becomes subsequently to remove the adsorbed purge itself from the bed.

When deciding whether to employ a regenerative system, several factors should be considered. The principal consideration is that of economics. It is important to establish if recovery of the adsorbate will be cost-effective or if regeneration of the adsorbent is the prime consideration. If solvent recovery is the main objective, the design should be based on past experimental data to establish the ratio of sorbent fluid to recoverable adsorbent at different working capacities. Most systems today employ steam as the regenerating medium, but some of the new systems use a hot inert gas such as nitrogen.

A short discussion on steam systems is now provided. A well-designed system will have a steam consumption in the range of 1 to 4 lb of steam per pound of recovered solvent. The steam entering the bed not only introduces heat but creates adsorption and capillary action of the moisture, which supplies additional heat for the desorption process. Certain parameters should be considered in the design of this stripping process:

1. Minimize the time required for regeneration. If continuous adsorption and recovery are required, multiple systems have to be installed.
2. The short regeneration time requires a higher steaming rate, thus increasing the heat duty of the condenser system.
3. The steam flow should be in a direction opposite to that of adsorption to prevent the possible accumulation of polymerizable substances.
4. To enable fast stripping and efficient heat transfer, it is necessary to sweep out the carrier gas from the adsorber and condenser system as fast as possible.
5. A larger fraction of the heat content of the steam is used to heat the adsorber vessel and the adsorbent; thus, it is essential that the steam condenses quickly in the bed. The steam should contain only a slight super-heat to allow condensation.
6. It is advantageous to use a low-retentivity carbon to enable the adsorbate to be stripped out easily. When empirical data is not available, the following heat requirements have to be taken into consideration: heat to the adsorbent and vessel, heat of adsorption and heat capacity of adsorbate leaving the adsorbent, latent and heat capacity of water vapor accompanying the adsorbate, heat in condensate steam, and, radiation and convection heat loss.

During the desorbing cycle, condensation and adsorption will take place in the adsorbent bed, increasing the moisture content of the adsorbent. Also, a certain portion of the solute will remain; this is referred to as the aforementioned “HEEL.” To achieve a minimum efficiency drop from successive adsorption cycles, a drying and cooling cycle should occur before returning to the “adsorb” mode. When using high adsorbate concentrations, it may be desirable to leave some moisture; a moisture-free bed is desired with other solutes.

In air pollution control applications where the pollutant concentrations are low, and, in addition, the pollutants may have no recovery value, steam regeneration may not be the best regenerating agent. Because of the adsorption at low concentrations, the vapors may be held tightly by the adsorbent, and, relative to the amounts of pollutant adsorbed, the amount of steam required would be large. Under these conditions, even slightly soluble organic compounds would be completely dissolved in the steam condensate. For these circumstances, the more economical approach is to regenerate using an inert noncondensable gas such as nitrogen or air, or if there is a danger of explosion, regenerate with an inert noncondensable gas such as flue gas. For example, miscible pollutants such as the solvents 4-methyl-2-pentanone and propanone would completely dissolve in large amounts of steam condensate. Their recovery by distillation would not be economical, thus creating a disposal problem if water pollution is be avoided. In these cases, the solution to the problem is to regenerate the adsorbent with a noncondensable gas and burn the released vapors immediately in a small thermal incinerator.

## ILLUSTRATIVE EXAMPLE 11.17

Use the accompanying graph in Figure 11.18 to solve the following problem. Estimate the mass of $CO_2$ that can be adsorbed by 100 lb of Davison 4A Molecular Sieve from a discharge gas mixture at 77°F and 40 psia containing 10,000 ppmv (by volume) $CO_2$.

***SOLUTION*:** Calculate the mole fraction of $CO_2$ in the discharge gas mixture:

$$\begin{aligned} y_{CO_2} &= \text{ppm}/10^6 \\ &= 10{,}000/10^6 \\ &= 0.01 \end{aligned}$$

Also determine the partial pressure of $CO_2$ in psia and mm Hg:

$$\begin{aligned} p_{CO_2} &= y_{CO_2}P \\ &= (0.01)(40) \\ &= 0.4 \text{ psia} \\ &= (0.4)(760/14.7) \\ &= 20.7 \text{ mm Hg} \end{aligned}$$

Estimate the adsorbent capacity, SAT, at 77°F. Refer to Figure 11.18.

$$\text{SAT} = 9.8 \text{ lb } CO_2/100 \text{ lb sieve (from Fig. 11.18).}$$ ■

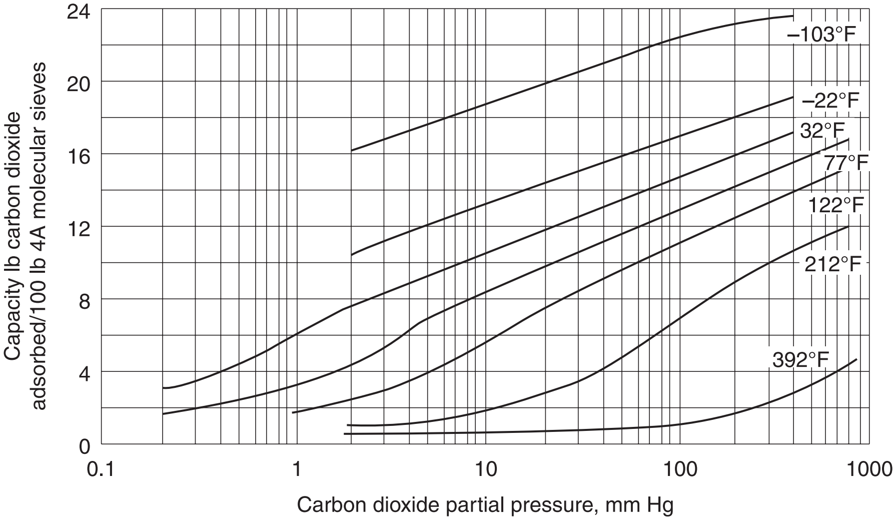

**Figure 11.18** Vapor–solid equilibrium isotherms.

## ILLUSTRATIVE EXAMPLE 11.18

Refer to Illustrative Example 11.17. What percentage of this adsorbed vapor would be recovered by passing superheated steam at a temperature of 392°F through the adsorbent until the partial pressure of the $CO_2$ in the stream leaving is reduced to 1.0 mm Hg?

***SOLUTION*:** Estimate the adsorbent capacity at 392°F and 1.0 mm Hg. Note that this represents the HEEL:

$$\text{HEEL} = 0.8 \text{ lb } CO_2/100 \text{ lb sieve}$$

The amount of $CO_2$ recovered is therefore

$$\begin{aligned} CO_2 \text{ recovered} &= 9.8 - 0.8 \\ &= 9.0 \text{ lb } CO_2/100 \text{ lb sieve} \end{aligned}$$

The percent recovery is

$$\begin{aligned} \% \text{ recovery} &= (9.0/9.8)100 \\ &= 91.8\% \end{aligned}$$

Note that this represents the percent recovery relative to the HEEL. ■

## ILLUSTRATIVE EXAMPLE 11.19

Refer to Illustrative Example 11.17. What is the residual $CO_2$ partial pressure in a gas mixture at 77°F in contact with the freshly stripped sieve in the previous example?

***SOLUTION*:** Estimate the partial pressure of $CO_2$ in mm Hg in equilibrium at 77°F with sieve containing 0.8 lb $CO_2$/100 lb sieve (the HEEL):

$$p_{CO_2} \approx 0.05 \text{ mm Hg}$$

The equilibrium $CO_2$ partial pressure may be converted to ppm:

$$\begin{aligned} \text{ppm} &= (p_{CO_2}/P)10^6 \\ &= (0.05)(14.7/760)(10^6)/40 \\ &= 24.1 \end{aligned}$$

This represents the discharge ppm following regeneration. The reader is left the exercise of calculating the percent recovery based on inlet and outlet concentrations (ppm).

The data in the isotherm diagram were extrapolated in order to solve parts of this and the two previous examples. This is poor practice. In actual applications, data should be obtained at the operating condition for both the adsorption and regeneration phases. Also note that the last calculation can be extremely critical for some applications. It provides information on the concentration of the adsorbate in the clean gas discharge stream. Note that this can rarely be predicted a priori. ■

As noted earlier, in order to maintain the concentration of the clean gas discharge stream at its lowest value, the regeneration step is almost always conducted in a direction opposite that for adsorption. A residual concentration gradient exists in the bed after regeneration, with the minimum value located at the inlet side of the regenerating stream. If one adsorbs down and regenerates up—as is typically done—the bottom of the bed will contain a smaller HEEL, thus providing more efficient recovery.

Adsorbing down provides an additional advantage. Fine particles, impurities, polymeric materials, and high molecular weight hydrocarbons will be deposited/captured at the inlet or top side of the bed. If the performance of the bed is reduced because of this, one need only replace a small portion of the bed (an easy skimming operation) rather than replace the entire bed.

## ILLUSTRATIVE EXAMPLE 11.20

A two-bed carbon adsorption system is used to control the odors being emitted from a drum-filling operation. The material being drummed is a high-purity grade of pyridine ($C_5H_5N$) that has a human odor detection level of 100 ppm. It has been reported that odor has been detected from outside the drumming area when the equipment is in service, i.e., when drums are being filled. Discussions with operating personnel have indicated that the adsorption system is the source of the odor. You are requested to determine if the adsorption equipment/emission is in fact the source of the odor or if the equipment is capable of containing/controlling the pyridine emission. Design and actual operating data are provided below:

1. The adsorption units are twin horizontal units with face dimensions for flow of 5 × 12 ft. Each unit contains new 4 × 6 mesh activated carbon B that was installed one month ago. The measured bed height is 12 inches.
2. The carbon manufacturer maintains that the breakthrough capacity of the carbon is 0.49 lb pyridine/lb carbon and that the carbon has a bulk density of 25 lb/ft$^3$.
3. Laboratory tests performed by plant personnel indicate that the carbon contains a HEEL of approximately 0.03 lb pyridine/lb carbon when regenerated with 4.0 lb of steam/lb pyridine at 10 psig.
4. The ventilation blower for the drum-filling station has a flow of 5000 acfm at 25°C and 14.7 psia and contains a pyridine concentration of 2000 ppm (toxicology data from plant hygienist).
5. The drum-filling operation operates on a 24-h/day basis and the adsorption units are operated on an 8-h adsorption, 5-h regeneration cycle, with 3 h for cooling and stand-by. The steam used during the 5-h regeneration cycle was determined to be 2725 lb (mass flowmeter).
6. The adsorption unit was designed based on a pressure drop through the bed following the relationship

   $$\Delta P = 0.37Z(v/100)^{1.56}$$

   where $Z$ is the bed depth in inches, $v$ is the velocity in ft/min, and the pressure drop is in inches of water. The measured operating pressure drop is 3.3 inches of water.
7. The fractional fan efficiency is 0.58.

To evaluate the adsorber's performance, please determine the following:

1. The mass of pyridine to be captured in the adsorption period
2. The working capacity of the carbon B
3. The mass and volume of carbon that should be used in each unit
4. The required bed height
5. The design pressure drop through the bed using the required bed height for full capture
6. The horsepower requirement for this process
7. The required steam to regenerate the bed to the HEEL level of 0.03 lb pyridine/lb carbon

***SOLUTION*:** Calculate the mole fraction of pyridine (P) in the gas stream:

$$\begin{aligned} y_P &= 2000/10^6 \\ &= 0.0020 \end{aligned}$$

Calculate the volumeteric flow rate of P in acfm:

$$\begin{aligned} q_P &= y_P q \\ &= (0.0020)(5000) \\ &= 10.0 \text{ acfm} \end{aligned}$$

Determine the density of the P vapor at the operating conditions:

$$\begin{aligned} \rho_P &= \frac{P(MW)}{RT} = \frac{(14.7)(79)}{(10.73)(537)} \\ &= 0.2015 \text{ lb/ft}^3 \end{aligned}$$

The mass of P collected during the adsorption period is then

$$\begin{aligned} m_P &= (10)(0.2015)(8)(60) \\ &= 967.2 \text{ lb} \end{aligned}$$

Estimate the working capacity (WC) of carbon B for this system:

$$\begin{aligned} \text{WC} &= \text{BC} - \text{HEEL} \\ &= 0.49 - 0.03 \\ &= 0.46 \text{ lb P/lb carbon B} \end{aligned}$$

Calculate the mass of carbon that should be used for each unit:

$$\begin{aligned} M_{AC} &= m_P/\text{WC} \\ &= 967.2/0.46 \\ &= 2103 \text{ lb carbon B} \end{aligned}$$

The volume of activated carbon $V_{AC}$ is

$$\begin{aligned} V_{AC} &= M_{AC}/\rho_B \\ &= 2103/25 \\ &= 84.1\ \text{ft}^3 \end{aligned}$$

The cross-sectional area $A_{AC}$ of the carbon that is presently available for flow is

$$A_{AC} = (5)(12) = 60\ \text{ft}^2$$

Since the bed height is 12 inches or 1.0 ft, the actual volume currently employed is 60 $\text{ft}^3$. Because this is below the required 84 $\text{ft}^3$, the odor problem exists. Thus, the equipment is not capable of controlling the emission to eliminate the odor.

The "required" height of the adsorbent in the unit may now be calculated

$$\begin{aligned} Z &= V_{AC}/A_{AC} \\ &= 84.1/60 \\ &= 1.40\ \text{ft} \\ &= 16.8\ \text{inches} \\ &\approx 17.0\ \text{inches} \end{aligned}$$

Estimate the pressure drop across the required adsorbent in inches of $H_2O$ using the recommended pressure drop equation:

$$\begin{aligned} \Delta P = 0.37Z\left(\frac{v}{100}\right)^{1.56} &= 0.37Z\left(\frac{q/A_{AC}}{100}\right)^{1.56} \\ &= (0.37)(17)\left(\frac{5000/60}{100}\right)^{1.56} \\ &= 4.73\ \text{in}\ H_2O \end{aligned}$$

The total pressure drop across the bed in $\text{lb}_f/\text{ft}^2$ is then

$$\begin{aligned} \Delta P_{\text{total}} &= (4.73)(5.2) \\ &= 24.6\ \text{lb}_f/\text{ft}^2 \end{aligned}$$

while the HP requirement is

$$\begin{aligned} \text{HP} &= \frac{(24.6)(5000)}{(60)(550)(0.58)} \\ &= 6.43 \end{aligned}$$

Finally, the steam requirement for regeneration is

$$\begin{aligned} m_{\text{steam}} &= (4.0)(967.2) \\ &= 3869\ \text{lb steam during regeneration} \end{aligned}$$

Note that the actual operating steam rate (2725 lb for 5 hr) is also below the required value. ■

## ILLUSTRATIVE EXAMPLE 11.21

Benzene is to be recovered from a dilute mixture with air by adsorption on a 6 × 10 mesh activated carbon ($\rho_B = 30\ \text{lb/ft}^3$). The gas enters the adsorber at a rate of 6500 $\text{ft}^3/\text{h}$ (60°F, 1.0 atm) and contains 3.8% by volume benzene. A two-bed unit (one on, one off) is used, adsorbing at 80°F and 1.0 atm, where approximately 95% of the benzene is removed. Experience indicates that a superficial gas velocity through the adsorber of 25 ft/min is satisfactory. The adsorption time is 4 h. Regeneration is to be accomplished with 150 psia saturated steam and 15% excess carbon is used in the beds. During operation, the activated carbon will retain 0.3 lb benzene per lb carbon at 80°F. Determine the following:

1. The amount of carbon needed in each bed.
2. The gas flow area of each bed.
3. The dimensions of the adsorber.
4. The pressure drop across the bed (refer to Fig. 11.15).
5. The heat required to heat the vessel to the 150 psia steam temperature is 90,000 Btu and the heat of desorption (with sensible heat) is 40 Btu/lb benzene. The heat capacity of carbon is approximately 0.25 Btu/lb · °F. How much steam must be theoretically supplied for regeneration of the bed?

***SOLUTION***

1. Key calculations are provided below:

$$\begin{aligned}
q &= 6500(540/520)\\
&= 6750\ \text{acfh}\\
q_B &= (0.038)(6750)\\
&= 256.5\ \text{ft}^3/\text{h}\\
\dot{m}_B &= (256.5)(78/379)(520/540)\\
&= 50.83\ \text{lb/h}\\
\dot{m}_B/4\ \text{h} = m_B &= (50.83)(0.95)(4)\\
&= 193.2\ \text{lb B}\\
M_{\text{AC}} &= (193.2/0.3)1.15\\
&= 740.5\ \text{lb AC}
\end{aligned}$$

2. The face area of the bed may now be calculated:

$$\begin{aligned}
V_{\text{AC}} &= 740.5/30 = 24.68\ \text{ft}^3\\
A_{\text{AC}} &= 6750/(25)(60)\\
&= 4.5\ \text{ft}^2
\end{aligned}$$

**3** The dimensions of the bed are (assuming a vertical column)

$$\begin{aligned} Z &= 24.68/4.5 \\ &= 5.5 \text{ ft} \end{aligned}$$

$$\begin{aligned} D &= (4.5/0.785)^{1/2} \\ &= 2.4 \text{ ft} \end{aligned}$$

**4** From Figure 11.15, one obtains

$$\begin{aligned} \Delta P &= 0.145 \text{ in } H_2O/\text{in bed} \\ \Delta P_{\text{total}} &= (0.145)(5.5)(12) \\ &= 9.57 \text{ in } H_2O \end{aligned}$$

**5** To heat the bed (*b*)

$$\begin{aligned} Q_b &= (0.25)(740.5)(359 - 80) \\ &= 51{,}650 \text{ Btu} \end{aligned}$$

To desorb (*d*)

$$\begin{aligned} Q_d &= (40)(193.2) \\ &= 7727 \text{ Btu} \end{aligned}$$

Therefore,

$$\begin{aligned} Q_{\text{total}} &= 90{,}000 + 51{,}650 + 7727 \\ &= 149{,}400 \text{ Btu} \end{aligned}$$

The steam requirement SR is

$$\begin{aligned} \text{SR} &= Q_{\text{total}}/\Delta H_{\text{vap}} \\ &= 149{,}400/862 \\ &= 173 \text{ lb steam} \end{aligned}$$

for each 4 hour cycle. In actual practice, more steam would probably be required. ■

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