ADSORPTION

1. Introduction

Adsorption is the term used to describe the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid. This is a fundamental property of matter, having its origin in the attractive forces between molecules. The force field creates a region of low potential energy near the solid surface and, as a result, the molecular density close to the surface is generally greater than in the bulk gas. Furthermore, and perhaps more importantly, in a multicomponent system the composition of this surface layer generally differs from that of the bulk gas since the surface adsorbs the various components with different affinities. Adsorption may also occur from the liquid phase and is accompanied by a similar change in composition, although, in this case, there is generally little difference in molecular density between the adsorbed and fluid phases.

The enhanced concentration at the surface accounts, in part, for the catalytic activity shown by many solid surfaces, and it is also the basis of the application of adsorbents for low pressure storage of permanent gases such as methane.

However, most of the important applications of adsorption depend on the selectivity, ie, the difference in the affinity of the surface for different components. As a result of this selectivity, adsorption offers, at least in principle, a relatively straightforward means of purification (removal of an undesirable trace component from a fluid mixture) and a potentially useful means of bulk separation.

2. Fundamental Principles

2.1. Forces of Adsorption. Adsorption may be classified as chemisorption or physical adsorption, depending on the nature of the surface forces. In physical adsorption the forces are relatively weak, involving mainly van der Waals (induced dipole–induced dipole) interactions, supplemented in many cases by electrostatic contributions from field gradient–dipole or –quadrupole interactions. By contrast, in chemisorption there is significant electron transfer, equivalent to the formation of a chemical bond between the sorbate and the solid surface. Such interactions are both stronger and more specific than the forces of physical adsorption and are obviously limited to monolayer coverage. The differences in the general features of physical and chemisorption systems (Table 1) can be understood on the basis of this difference in the nature of the surface forces.

Heterogeneous catalysis generally involves chemisorption of the reactants, but most applications of adsorption in separation and purification processes depend on physical adsorption. Chemisorption is sometimes used in trace impurity removal since very high selectivities can be achieved. However, in most situations the low capacity imposed by the monolayer limit and the difficulty of regenerating the spent adsorbent more than outweigh this advantage. The higher capacities achievable in physical adsorption result from multilayer formation and this is obviously critical in such applications as gas storage, but it is also an important consideration in most adsorption separation processes since the process cost is directly related to the adsorbent capacity.

In very small pores the molecules never escape from the force field of the pore wall even at the center of the pore. In this situation the concepts of

Table 1. **Parameters of Physical Adsorption and Chemisorption**

Parameter	Physical adsorption	Chemisorption
heat of adsorption ($-\Delta H$)	low, <1.5 or 2 times latent heat of evaporation	high, >2 or 3 times latent heat of evaporation
specificity	nonspecific	highly specific
nature of adsorbed phase	monolayer or multilayer, no dissociation of adsorbed species	monolayer only may involve dissociation
temperature range	only significant at relative low temperatures	possible over a wide range of temperature
forces of adsorption	no electron transfer, although polarization of sorbate may occur	electron transfer leading to bond formation between sorbate and surface
reversibility	rapid, nonactivated, reversible	activated, may be slow and irreversible

monolayer and multilayer sorption become blurred and it is more useful to consider adsorption simply as pore filling. The molecular volume in the adsorbed phase is similar to that of the saturated liquid sorbate, so a rough estimate of the saturation capacity can be obtained simply from the quotient of the specific micropore volume and the molar volume of the saturated liquid.

2.2. Selectivity.

Selectivity in a physical adsorption system may depend on differences in either equilibrium or kinetics, but the great majority of adsorption separation processes depend on equilibrium-based selectivity. Significant kinetic selectivity is in general restricted to molecular sieve adsorbents—carbon molecular sieves, zeolites, or zeolite analogues. In these materials the pore size is of molecular dimensions, so that diffusion is sterically restricted. In this regime small differences in the size or shape of the diffusing molecule can lead to very large differences in diffusivity. In the extreme limit one species (or one class of compounds) may be completely excluded from the micropores, thus giving a highly selective molecular sieve separation. The most important example of such a process is the separation of linear hydrocarbons from their branched and cyclic isomers using a 5A zeolite adsorbent. A second example, where the difference in diffusivities is less extreme but still large enough to produce an efficient separation, is air separation over carbon molecular sieve or 4A zeolite, in which oxygen, the faster diffusing component, is preferentially adsorbed.

A degree of control over the kinetic selectivity of molecular sieve adsorbents can be achieved by controlled adjustment of the pore size. In a carbon sieve this may be accomplished by adjusting the burn-out conditions or by controlled deposition of an easily crackable hydrocarbon. In a zeolite, ion exchange offers the simplest possibility but controlled silanation or boration has also been shown to be effective in certain cases (1).

Control of equilibrium selectivity is generally achieved by adjusting the balance between electrostatic and van der Waals forces. This may be accomplished by changing the chemical nature of the surface and also, to a lesser extent, by adjusting the pore size. In carbon adsorbents surface oxidation offers a simple and effective way of introducing surface polarity and thus modifying the selectivity. One example is shown in Figure 1. On an untreated carbon adsorbent n-hexane is adsorbed more strongly than sulfur dioxide, whereas on an oxidized surface the relative affinities are reversed. With zeolite adsorbents, changing the nature of the exchangeable cation by ion exchange or adjusting the silicon–aluminum ratio of the framework, which determines the cation density, are the most common approaches. In some instances the aluminum-free zeolite analogue (a porous crystalline silicate) may be prepared with the same channel geometry but with a nonpolar surface.

Adsorption on a nonpolar surface such as pure silica or an unoxidized carbon is dominated by van der Waals forces. The affinity sequence on such a surface generally follows the sequence of molecular weights since the polarizability, which is the main factor governing the magnitude of the van der Waals interaction energy, is itself roughly proportional to the molecular weight.

2.3. Hydrophilic and Hydrophobic Surfaces.

Water is a small, highly polar molecular and it is therefore strongly adsorbed on a polar surface as a result of the large contribution from the electrostatic forces. Polar adsorbents such as most zeolites, silica gel, or activated alumina therefore adsorb

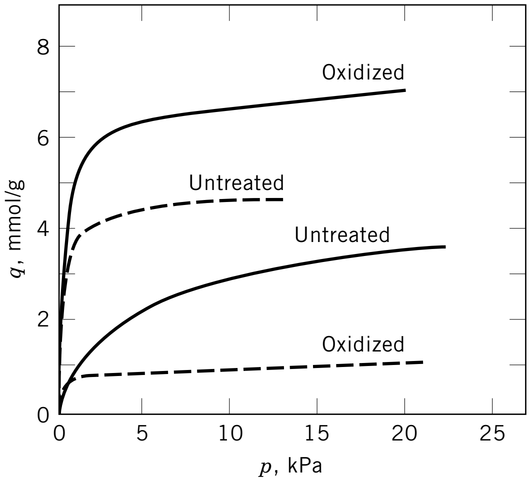


Fig. 1. Equilibrium isotherms for adsorption on activated carbon at 298 K showing the effect of surface modification (2). —, SO_2; – – –, *n*-hexane. To convert kPa to torr multiply by 7.5.

water more strongly than they adsorb organic species, and, as a result, such adsorbents are commonly called hydrophilic. In contrast, on a nonpolar surface where there is no electrostatic interaction water is held only very weakly and is easily displaced by organics. Such adsorbents, which are the only practical choice for adsorption of organics from aqueous solutions, are termed hydrophobic.

The most common hydrophobic adsorbents are activated carbon and silicalite. The latter is of particular interest since the affinity for water is very low indeed; the heat of adsorption is even smaller than the latent heat of vaporization (3). It seems clear that the channel structure of silicalite must inhibit the hydrogen bonding between occluded water molecules, thus enhancing the hydrophobic nature of the adsorbent. As a result, silicalite has some potential as a selective adsorbent for the separation of alcohols and other organics from dilute aqueous solutions (4).

2.4. Capillary Condensation. The equilibrium vapor pressure in a pore or capillary is reduced by the effect of surface tension. As a result, liquid sorbate condenses in a small pore at a vapor pressure that is somewhat lower than the saturation vapor pressure. In a porous adsorbent the region of multilayer physical adsorption merges gradually with the capillary condensation regime, leading to upward curvature of the equilibrium isotherm at higher relative pressure. In the capillary condensation region the intrinsic selectivity of the adsorbent is lost, so in separation processes it is generally advisable to avoid these conditions. However, this effect is largely responsible for the enhanced capacity of macroporous desiccants such as silica gel or alumina at higher humidities.

3. Practical Adsorbents

To achieve a significant adsorptive capacity an adsorbent must have a high specific area, which implies a highly porous structure with very small micropores.

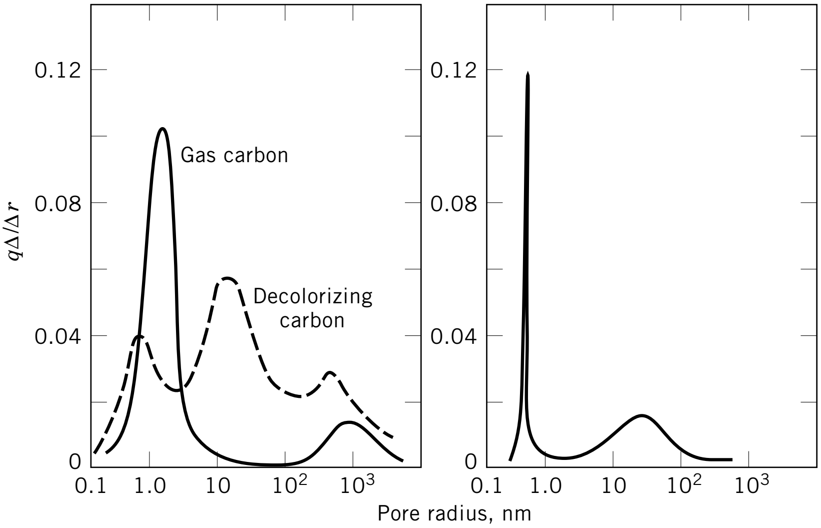


Fig. 2. Pore size distribution of typical samples of activated carbon (small pore gas carbon and large pore decolorizing carbon) and carbon molecular sieve (CMS). $\Delta v/\Delta r$ represents the increment of specific micropore volume for an increment of pore radius.

Such microporous solids can be produced in several different ways. Adsorbents such as silica gel and activated alumina are made by precipitation of colloidal particles, followed by dehydration (see ALUMINUM COMPOUNDS, ALUMINUM OXIDE (ALUMINA); SILICA, AMORPHOUS SILICA). Carbon adsorbents are prepared by controlled burn-out of carbonaceous materials such as coal lignite, and coconut shells (see CARBON, ACTIVATED CARBON). These procedures generally yield a fairly wide distribution of pore size (Fig. 2). The crystalline adsorbents (zeolite and zeolite analogues) are different in that the dimensions of the micropores are determined by the crystal structure and there is therefore virtually no distribution of micropore size (see MOLECULAR SIEVES). Although structurally very different from the crystalline adsorbents, carbon molecular sieves also have a very narrow distribution of pore size. The adsorptive properties depend on the pore size and the pore size distribution as well as on the nature of the solid surface. A simple classification of some of the common adsorbents according to these features is as follows:

	Pore size distribution	
Surface polarity	Narrow	Broad
polar	zeolites (Al rich)	activated alumina silica gel
nonpolar	carbon molecular sieves silicalite	activated carbon

Despite the difference in the nature of the surface, the adsorptive behavior of the molecular sieve carbons resembles that of the small pore zeolites. As their

Table 2. **Properties and Applications of Amorphous Adsorbents**

Adsorbent	Pore diameter, nm	Particle density, g/cm^3	Specific area, m^2/g	Applications
activated carbon (large pore)	1–10^3 (broad range)	0.6–0.8	200–600	water purification, sugar decolorizing
activated carbon (small pore)	1–10	0.5–0.9	400–1200	removal of light organics
carbon molecular sieve	0.4–0.5, 10–10^2 (bimodal)	0.9–1.0	100–300	air separation (N_2 production)
silica gel (high area)	2–10	1.09	800	general purpose
silica gel (low area)	10–50	0.62	300	
activated alumina	2–10	1.2–1.3	300–400	desiccants

name implies, molecular sieve separations are possible on these adsorbents based on the differences in adsorption rate, which, in the extreme limit, may involve complete exclusion of the larger molecules from the micropores.

Important properties and a number of applications of several commercial adsorbents are summarized in Tables 2–4.

3.1. Amorphous Adsorbents. The amorphous adsorbents (silica gel, activated alumina, and activated carbon) typically have specific areas in the 200–1000-m^2/g range, but for some activated carbons much higher values have been achieved (~1500 m^2/g). The difficulty is that these very high area carbons tend to lack physical strength and this limits their usefulness in many practical applications. The high area materials also contain a large proportion of very small pores, which renders them unsuitable for applications involving adsorption of large molecules. The distinction between gas carbons, used for adsorption of low molecular weight permanent gases, and liquid carbons, which are used for adsorption of larger molecules such as color bodies from the liquid phase, is thus primarily a matter of pore size.

Table 3. **Properties and Application of Polymeric Adsorbents**

Type of polymer	Representative commercial product	Properties	Applications
sulfonated styrene–divinylbenzene copolymers[a] with various degrees of cross-linking	Dowex-50 Amberlite IR120B	pore diameter, porosity, density, etc, vary with degree of hydration or dehydration	sugar separations[b], eg, various fructose, glucose
macroreticular sulfonated styrene–divinylbenzene	Diaion HPK-25	porosity ~0.33, microparticles ~80-μm diameter	removal of NH_3 or light amines[c]

[a] Ion exchanged to Ca^{2+} form.

[b] Liquid-phase operation.

[c] Gas or liquid phase.

Table 4. **Properties and Applications of Crystalline Adsorbents**[a]

Structure	Cation	Typical formula of unit cell or pseudocell	Window	Effective channel diameter, nm	Applications
4A	Na^+	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$	obstructed 8-ring	0.38	desiccant; CO_2 removal; air separation (N_2)
5A	Ca^{2+}	$Ca_5Na_2[(AlO_2)_{12}(SiO_2)_{12}]$	free 8-ring	0.44	linear paraffin separation; air separation (O_2)
3A	K^+	$K_{12}[(AlO_2)_{12}(SiO_2)_{12}]$	obstructed 8-ring	0.29	drying of reactive gases air separation (O_2), removal of mercaptans
13X	Na^+	$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]$	12-ring (free)	0.84	
10X	Ca^{2+}	$Ca_{43}[(AlO_2)_{86}(SiO_2)_{106}]$	12-ring (obstructed)	0.80	
SrBaX	Sr^{2+}, Ba^{2+}	$Sr_{21}Ba_{22}[(AlO_2)_{86}(SiO_2)_{106}]$	12-ring (obstructed)	0.80	separation of C_8 aromatics
KY	K^+	$K_{56}[(AlO_2)_{56}(SiO_2)_{136}]$	12-ring (free)	0.80	
Mordenite	H^+	$H_8[(AlO_2)_8(SO_2)_{40}]$	12-ring (free)	0.70	trapping of Kr from nuclear off-gas trapping of CH_3I from nuclear off-gas
	Ag^+	$Ag_8[(AlO_2)_8(SiO_2)_{40}]$	12-ring (free)	0.70	
AgX	Ag^+	$Ag_{86}[(AlO_2)_{86}(SiO_2)_{106}]$	12-ring (free)	0.84	
silicalite/HZSM5		$(SiO_2)_{96}$	10-ring	0.60	removal of organics in aqueous systems

[a] Structural details can be found in refs. 5 and 6. A simplified description is given in ref. 7.

In a typical amorphous adsorbent the distribution of pore size may be very wide, spanning the range from a few nanometers to perhaps one micrometer. Since different phenomena dominate the adsorptive behavior in different pore size ranges, IUPAC has suggested the following classification:

micropores, <2-nm diameter
mesopores, 2–50-nm diameter
macropores, >50-nm diameter

This division is somewhat arbitrary since it is really the pore size relative to the size of the sorbate molecule rather than the absolute pore size that governs the behavior. Nevertheless, the general concept is useful. In micropores (pores which are only slightly larger than the sorbate molecule) the molecule never escapes from the force field of the pore wall, even when in the center of the pore. Such pores generally make a dominant contribution to the adsorptive capacity for molecules small enough to penetrate. Transport within these pores can be severely limited by steric effects, leading to molecular sieve behavior.

The mesopores make some contribution to the adsorptive capacity, but their main role is as conduits to provide access to the smaller micropores. Diffusion in the mesopores may occur by several different mechanisms, as discussed below. The macropores make very little contribution to the adsorptive capacity, but they commonly provide a major contribution to the kinetics. Their role is thus analogous to that of a super highway, allowing the adsorbate molecules to diffuse far into a particle with a minimum of diffusional resistance.

3.2. Crystalline Adsorbents.

In the crystalline adsorbents, zeolites and zeolite analogues such as silicalite and the microporous aluminum phosphates, the dimensions of the micropores are determined by the crystal framework and there is therefore virtually no distribution of pore size. However, a degree of control can sometimes be exerted by ion exchange, since, in some zeolites, the exchangeable cations occupy sites within the structure which partially obstruct the pores. The crystals of these materials are generally quite small (1–5 μm) and they are aggregated with a suitable binder (generally a clay) and formed into macroporous particles having dimensions large enough to pack directly into an adsorber vessel. Such materials therefore have a well-defined bimodal pore size distribution with the intracrystalline micropores (a few tenths of a nanometer) linked together through a network of macropores having a diameter of the same order as the crystal size (∼1 μm).

3.3. Desiccants.

A solid desiccant is simply an adsorbent which has a high affinity and capacity for adsorption of moisture so that it can be used for selective adsorption of moisture from a gas (or liquid) stream. The main requirements for an efficient desiccant are therefore a highly polar surface and a high specific area (small pores). The most widely used desiccants (qv) are silica gel, activated alumina, and the aluminum rich zeolites (4A or 13X). The equilibrium adsorption isotherms for moisture on these materials have characteristically different shapes (Fig. 3), making them suitable for different applications.

The zeolites have high affinity and high capacity at low partial pressures, shown by the nearly rectangular form of the isotherm. This makes them useful desiccants where a very low humidity or dew point is required. The 3A zeolite is a

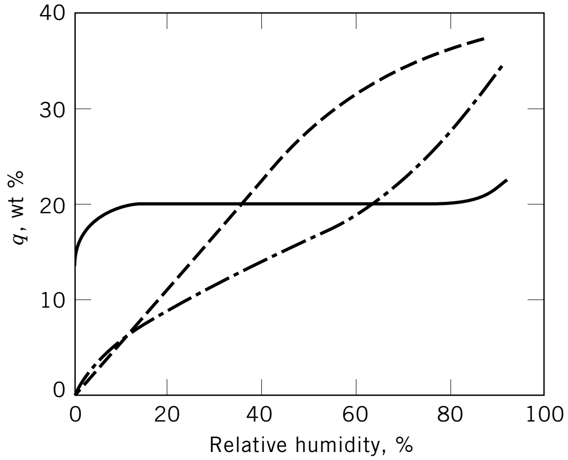


Fig. 3. Adsorption equilibrium isotherms for moisture on three commercial adsorbents: pelletized 4A zeolite (—), silica gel (– – –), and a typical activated alumina (— - —).

molecular sieve desiccant, since its micropores are small enough to exclude most molecules other than water. It is therefore useful for drying reactive gases. The major disadvantage of zeolite desiccants is that a high temperature is required for regeneration (>300°C), which makes their use uneconomic when only a moderately low dew point is required.

Considerable variation in the moisture isotherm for alumina can be obtained by different preparation and pretreatment. However, in general, the initial slope of the isotherm is not as steep as that of a zeolite, indicating a lower moisture affinity at low partial pressure, but the capacity at high humidities is often higher than that of a zeolitic adsorbent. Regeneration temperatures are typically in the 250–350°C range. Alumina adsorbents are also more robust than zeolites and less sensitive to deactivation by organics, but they are generally less suitable than the zeolites where very low humidity is the primary requirement.

The isotherm for silica gel is more nearly linear over a wide range of partial pressure, although the affinity for moisture is lower than that of either alumina or the zeolites. However, a correspondingly lower regeneration temperature is also required. This can be as low as 120°C, making silica gel the most suitable candidate for pressure swing driers, desiccant cooling systems (8), and other applications where low grade heat is used for regeneration of the adsorbent.

3.4. Loaded Adsorbents. Where highly efficient removal of a trace impurity is required it is sometimes effective to use an adsorbent preloaded with a reactant rather than rely on the forces of adsorption. Examples include the use of zeolites preloaded with bromine to trap traces of olefins as their more easily condensible bromides; zeolites preloaded with iodine to trap mercury vapor, and activated carbon loaded with cupric chloride for removal of mercaptans.

4. Adsorption Equilibrium

4.1. Henry's Law. Like any other phase equilibrium, the distribution of a sorbate between fluid and adsorbed phases is governed by the principles of thermodynamics. Equilibrium data are commonly reported in the form of an isotherm, which is a diagram showing the variation of the equilibrium adsorbed-phase concentration or loading with the fluid-phase concentration or partial pressure at a fixed temperature. In general, for physical adsorption on a homogeneous surface at sufficiently low concentrations, the isotherm should approach a linear form, and the limiting slope in the low concentration region is commonly known as the Henry's law constant. The Henry constant is simply a thermodynamic equilibrium constant and the temperature dependence therefore follows the usual van't Hoff equation:

$$\lim_{p\longrightarrow 0}\left(\frac{\partial q}{\partial p}\right)_T \equiv K' = K'_0 e^{-\Delta H_0/\mathrm{RT}} \tag{1}$$

in which $-\Delta H_0$ is the limiting heat of adsorption at zero coverage. Since adsorption, particularly from the vapor phase, is usually exothermic, $-\Delta H_0$ is a positive quantity and K' therefore decreases with increasing temperature. A corresponding dimensionless Henry constant (K) may also be defined, based on the ratio of adsorbed and fluid-phase concentrations:

$$\lim_{c\longrightarrow 0}\left(\frac{\partial q}{\partial c}\right)_T \equiv K = K_0 e^{-\Delta U_0/\mathrm{RT}} \tag{2}$$

Since, for an ideal vapor phase, $p = cRT$, these quantities are related by

$$K = RTK'; \qquad -\Delta H_0 = -\Delta U_0 + RT \tag{3}$$

Henry's law corresponds physically to the situation in which the adsorbed phase is so dilute that there is neither competition for surface sites nor any significant interaction between adsorbed molecules. At higher concentrations both of these effects become important and the form of the isotherm becomes more complex. The isotherms have been classified into five different types (9) (Fig. 4). Isotherms for a microporous adsorbent are generally of type I; the more complex forms are associated with multilayer adsorption and capillary condensation.

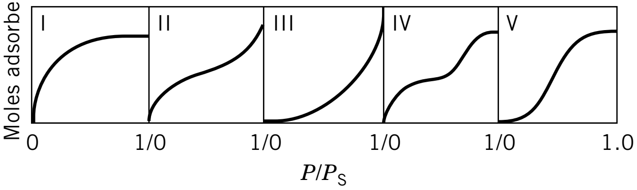


Fig. 4. The Brunaner classification of isotherms (I–V).

4.2. Langmuir Isotherm. Type I isotherms are commonly represented by the ideal Langmuir model:

$$\frac{q}{q_s} = \frac{bp}{1 + bp} \tag{4}$$

where q_s is the saturation limit and b is an equilibrium constant which is directly related to the Henry constant ($K' = bq_s$). The Langmuir model was originally developed to represent monolayer adsorption on an ideal surface, for which q_s corresponds to the monolayer coverage. However, in applying this model to physical adsorption on a microporous solid, the saturation limit becomes the quantity of sorbate required to fill the micropore volume. This expression is of the correct form to represent a type I isotherm, since at low pressure it approaches Henry's law while at high pressure it tends asymptotically to the saturation limit. The equilibrium constant b ($= K'/q_s$) decreases with increasing temperature (eq. 1); therefore, for a given pressure range, the isotherm approaches rectangular or irreversible form at low temperatures (large b) and linear form at high temperatures (small b).

Although very few systems conform accurately to the Langmuir model, this model provides a simple qualitative representation of the behavior of many systems and it is therefore widely used, particularly for adsorption from the vapor phase. According to the Langmuir model the heat of adsorption should be independent of loading, but this requirement is seldom fulfilled in practice. Both increasing and decreasing trends are commonly observed (Fig. 5). For a polar sorbate on a polar adsorbent (ie, a system in which electrostatic forces are dominant) a decreasing trend is normally observed, since the relative importance of

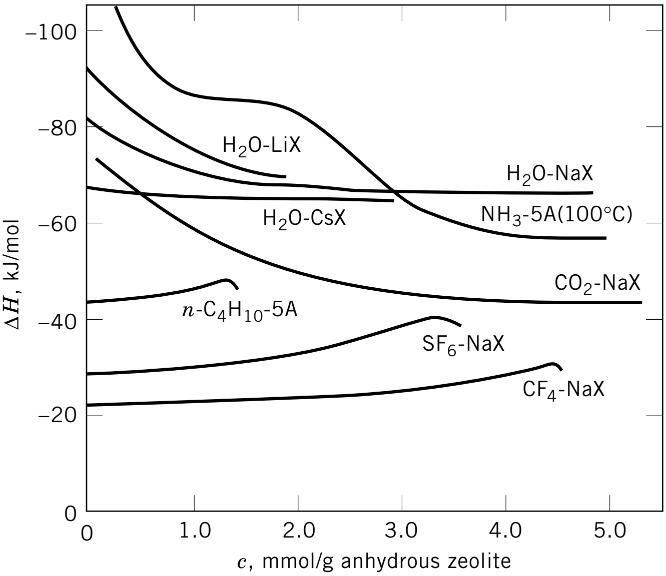


Fig. 5. Variation of isosteric heat of adsorption with adsorbed phase concentration. Reprinted from ref. 10, courtesy of Marcel Dekker, Inc. To convert kJ to kcal divide by 4.184.

the electrostatic contribution declines at high loadings as a result of preferential occupation of the most favorable sites and consequent screening of cations. In contrast, where van der Waals forces are dominant (nonpolar sorbates), a rising trend of heat of adsorption with loading is generally observed. This is commonly attributed to the effect of intermolecular attractive forces, but other explanations are also possible (11). In homologous series such as the linear paraffins the heat of adsorption increases linearly with carbon number (12).

4.3. Freundlich Isotherm. The isotherms for some systems, notably hydrocarbons on activated carbon, conform more closely to the Freundlich equation:

$$q = bp^{1/n} \qquad (n > 1.0) \tag{5}$$

Although the Freundlich expression does not reduce to Henry's law at low concentrations, it often provides a good approximation over a wide range of conditions. This form of equation can be explained as resulting from energetic heterogeneity of the surface. Superposition of a set of Langmuir isotherms with different b values (corresponding to sites of different energy) yields an expression of this form.

4.4. Adsorption of Mixtures. The Langmuir model can be easily extended to binary or multicomponent systems:

$$\frac{q_1}{q_{s1}} = \frac{b_1p_1}{1 + b_1p_1 + b_2p_2 + \cdots}; \qquad \frac{q_2}{q_{s2}} = \frac{b_2p_2}{1 + b_1p_1 + b_2p_2;\ + \cdots} \tag{6}$$

Thermodynamic consistency requires $q_{s1} = q_{s2}$, but this requirement can cause difficulties when attempts are made to correlate data for sorbates of very different molecular size. For such systems it is common practice to ignore this requirement, thereby introducing an additional model parameter. This facilitates data fitting but it must be recognized that the equations are then being used purely as a convenient empirical form with no theoretical foundation.

Equation 6 shows that the adsorption of component 1 at a partial pressure p_1 is reduced in the presence of component 2 as a result of competition for the available surface sites. There are only a few systems for which this expression (with $q_{s1} = q_{s2} = q_s$) provides an accurate quantitative representation, but it provides useful qualitative or semiquantitative guidance for many systems. In particular, it has the correct asymptotic behavior and provides explicit recognition of the effect of competitive adsorption. For example, if component 2 is either strongly adsorbed or present at much higher concentration than component 1, the isotherm for component 1 is reduced to a simple linear form in which the apparent Henry's law constant depends on p_2:

$$q_1 \simeq \left(\frac{b_1q_{s1}}{1 + b_2p_2}\right)p_1 \tag{7}$$

For an equilibrium-based separation, a convenient measure of the intrinsic selectivity of the adsorbent is provided by the separation factor (α_{12}), which is defined by analogy with the relative volatility as

$$\alpha_{12} = \frac{(X_1/Y_1)}{(X_2/Y_2)} \tag{8}$$

where X and Y refer to the mole fractions in the adsorbed and fluid phases, respectively, at equilibrium. For a system that obeys the Langmuir model (eq. 6) it is evident that $\alpha_{12} = b_1/b_2$ and is thus independent of concentration. The Langmuir isotherm is therefore sometimes referred to as the constant separation factor model.

The assumption of a constant separation factor is often a reasonable approximation for preliminary process design but this assumption is often violated in real systems, where some variation of the separation factor with composition is common and more extreme variations involving azeotrope formation ($\alpha = 1.0$ at a particular composition) and selectivity reversal (α varying from greater than 1.0 to less than 1.0 with changing composition) are not uncommon. There have been many attempts to improve the correlation of equilibrium data by using more complex expressions, one of the more widely used being the Langmuir-Freundlich or loading ratio correlation (13):

$$\frac{q_1}{q_s} = \frac{b_1 p_1^{n_1}}{1 + b_1 p_1^{n_1} + b_2 p_2^{n_1} + \cdots}; \qquad \frac{q_2}{q_s} = \frac{b_2 p_2^{n_2}}{1 + b_1 p_1^{n_1} + b_2 p_2^{n_2} + \cdots} \tag{9}$$

This has the advantage that the expressions for the adsorbed-phase concentration are simple and explicit, and, as in the Langmuir expression, the effect of competition between sorbates is accounted for. However, the expression does not reduce to Henry's law in the low concentration limit and therefore violates the requirements of thermodynamic consistency. Whereas it may be useful as a basis for the correlation of experimental data, it should be treated with caution and should not be used as a basis for extrapolation beyond the experimental range.

4.5. Ideal Adsorbed Solution Theory.

Perhaps the most successful approach to the prediction of multicomponent equilibria from single-component isotherm data is ideal adsorbed solution theory (14). In essence, the theory is based on the assumption that the adsorbed phase is thermodynamically ideal in the sense that the equilibrium pressure for each component is simply the product of its mole fraction in the adsorbed phase and the equilibrium pressure for the pure component *at the same spreading pressure*. The theoretical basis for this assumption and the details of the calculations required to predict the mixture isotherm are given in standard texts on adsorption (7) as well as in the original paper (14). Whereas the theory has been shown to work well for several systems, notably for mixtures of hydrocarbons on carbon adsorbents, there are a number of systems which do not obey this model. Azeotrope formation and selectivity reversal, which are observed quite commonly in real systems, are not consistent with an ideal adsorbed phase and there is no way of knowing a priori whether or not a given system will show ideal behavior.

5. Adsorption Kinetics

5.1. Intrinsic Kinetics. Chemisorption may be regarded as a chemical reaction between the sorbate and the solid surface, and, as such, it is an activated process for which the rate constant (k) follows the familiar Arrhenius rate law:

$$k = k_0 e^{-E/RT} \tag{10}$$

Depending on the temperature and the activation energy (E), the rate constant may vary over many orders of magnitude.

In practice the kinetics are usually more complex than might be expected on this basis, since the activation energy generally varies with surface coverage as a result of energetic heterogeneity and/or sorbate-sorbate interaction. As a result, the adsorption rate is commonly given by the Elovich equation (15):

$$q = \frac{1}{k'} \ln(1 + k''t) \tag{11}$$

where k' and k'' are temperature-dependent constants.

In contrast, physical adsorption is a very rapid process, so the rate is always controlled by mass transfer resistance rather than by the intrinsic adsorption kinetics. However, under certain conditions the combination of a diffusion-controlled process with an adsorption equilibrium constant that varies according to equation 1 can give the appearance of activated adsorption.

As illustrated in Figure 6, a porous adsorbent in contact with a fluid phase offers at least two and often three distinct resistances to mass transfer: external film resistance and intraparticle diffusional resistance. When the pore size distribution has a well-defined bimodal form, the latter may be divided into macropore and micropore diffusional resistances. Depending on the particular system and the conditions, any one of these resistances may be dominant or the overall rate of mass transfer may be determined by the combined effects of more than one resistance.

5.2. External Fluid Film Resistance. A particle immersed in a fluid is always surrounded by a laminar fluid film or boundary layer through which an adsorbing or desorbing molecule must diffuse. The thickness of this layer, and therefore the mass transfer resistance, depends on the hydrodynamic conditions. Mass transfer in packed beds and other common contacting devices has been widely studied. The rate data are normally expressed in terms of a simple linear rate expression of the form

$$\frac{\partial q}{\partial t} = k_f a(c - c^*) \tag{12}$$

and the variation of the mass transfer coefficient (k_f) with the hydrodynamic conditions is generally accounted for in terms of empirical correlations of the general form

$$\mathrm{Sh} \equiv \frac{2k_f R}{D_m} = f(\mathrm{Re},\ \mathrm{Sc}) \tag{13}$$

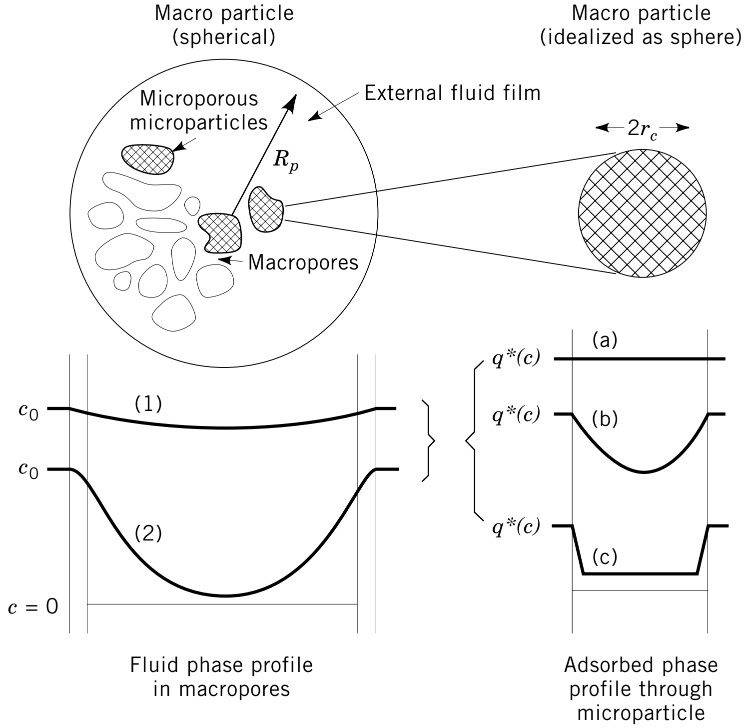


Fig. 6. Concentration profiles through an idealized biporous adsorbent particle showing some of the possible regimes. (1) + (a) rapid mass transfer, equilibrium throughout particle; (1) + (b) micropore diffusion control with no significant macropore or external resistance; (1) + (c) controlling resistance at the surface of the microparticles; (2) + (a) macropore diffusion control with some external resistance and no resistance within the microparticle; (2) + (b) all three resistances (micropore, macropore, and film) significant; (2) + (c) diffusional resistance within the macroparticle and resistance at the surface of the microparticle with some external film resistance.

where Re and Sc are the (particle-based) Reynolds and Schmidt numbers. One of the most widely used correlations, applicable to both gas and liquid systems over a wide range of conditions, is (16)

$$\mathrm{Sh} = \frac{2k_f R}{D_m} = 2.0 + 1.1\,\mathrm{Sc}^{1/3}\mathrm{Re}^{0.6} \tag{14}$$

5.3. Macropore Diffusion. Transport in a macropore can occur by several different mechanisms, the most important of which are bulk molecular diffusion, Knudsen diffusion, surface diffusion, and Poiseuille flow. In liquid systems bulk molecular diffusion is generally dominant, but in the vapor phase the contributions from Knudsen and surface diffusion may be large or even dominant. The contribution from Poiseuille flow, ie, forced flow through the pore under the influence of the pressure gradient, is generally relatively minor since pressure gradients are usually kept small. However, this is not true in the pressurization and blowdown steps of a pressure swing process, where the contribution from Poiseuille flow can be dominant.

A molecule colliding with the pore wall is reflected in a specular manner so that the direction of the molecule leaving the surface has no correlation with that of the incident molecule. This leads to a Fickian mechanism, known as Knudsen diffusion, in which the flux is proportional to the gradient of concentration of partial pressure. The Knudsen diffusivity (D_K) is independent of pressure and varies only weakly with temperature:

$$D_K = 9700\rho\sqrt{T/M} \qquad (\mathrm{cm^2/s}) \tag{15}$$

where ρ is the pore radius (cm) and M the molecular weight. Knudsen diffusion becomes dominant when collisions with the pore wall occur more frequently than collisions between diffusing molecules, ie, when the pore diameter is smaller than the mean free path. Since the mean free path varies inversely with pressure there is a gradual transition from the molecular to the Knudsen regime as the pressure is reduced, but the pressure at which this occurs depends on the pore size. At atmospheric temperature and pressure Knudsen diffusion is dominant in pores of less than about 10 nm diameter. In the intermediate region, which spans the range of the macropores in many commercial adsorbents, both mechanisms are of comparable significance.

The combined effects of Knudsen and molecular diffusion may be estimated approximately from the reciprocal addition rule:

$$\frac{1}{\epsilon_p D_p} = \frac{\tau}{\epsilon_p}\left(\frac{1}{D_K} + \frac{1}{D_m}\right) \tag{16}$$

The factor ε_p takes account of the fact that diffusion occurs only through the pore and not through the matrix; τ is a tortuosity factor which accounts for the increased path length and reduced concentration gradient arising from the random orientation of the pores as well as any other geometric effects. In a typical adsorbent $\tau \sim 3.0$ and $\varepsilon_p \sim 0.3$, so the effect of these two factors is to reduce the diffusivity by about one order of magnitude relative to the value for a straight cylindrical capillary.

5.4. Micropore Diffusion. In very small pores in which the pore diameter is not much greater than the molecular diameter the diffusing molecule never escapes from the force field of the pore wall. Under these conditions steric effects and the effects of nonuniformity in the potential field become dominant and the Knudsen mechanism no longer applies. Diffusion occurs by an activated process involving jumps from site to site, just as in surface diffusion, and the diffusivity becomes strongly dependent on both temperature and concentration.

The true driving force for any diffusive transport process is the gradient of chemical potential rather than the gradient of concentration. This distinction is not important in dilute systems where thermodynamically ideal behavior is approached. However, it becomes important at higher concentration levels and in micropore and surface diffusion. To a first approximation the expression for the diffusive flux may be written

$$J = -Bq\,\partial\mu/\partial z \tag{17}$$

where q is the concentration in the adsorbed phase. Assuming an ideal vapor phase, the expression for the chemical potential is

$$\mu = \mu^{\circ} + RT \ln p \tag{18}$$

where

$$\frac{\partial \mu}{\partial z} = RT \frac{d \ln p}{dq} \frac{\partial q}{\partial z} \tag{19}$$

Combining equations 17 and 18 yields, for the Fickian diffusivity (defined by $J = -D\partial q/\partial z$),

$$D = D_0 \frac{d \ln p}{d \ln q} \tag{20}$$

where $D_0 = BRT$. If the equilibrium relation is linear, $d \ln p/d \ln q = 1.0$ and $D \longrightarrow D_0$. At higher concentrations the equilibrium relationship is nonlinear, and as a result the diffusivity is generally concentration dependent. For the special case of a Langmuir isotherm (eq. 4), $d \ln p / d \ln q = (1 - q/q_s)^{-1}$ so

$$D = \frac{D_0}{1 - q/q_s} \tag{21}$$

A rapid increase in diffusivity in the saturation region is therefore to be expected, as illustrated in Figure 7 (17). Although the corrected diffusivity (D_0) is, in principle, concentration dependent, the concentration dependence of this quantity is generally much weaker than that of the thermodynamic correction factor ($d \ln p / d \ln q$). The assumption of a constant corrected diffusivity is therefore an acceptable approximation for many systems. More detailed analysis shows that the corrected diffusivity is closely related to the self-diffusivity or tracer diffusivity, and at low sorbate concentrations these quantities become identical.

The temperature dependence of the corrected diffusivity follows the usual Eyring expression

$$D_0 = D_{\infty} e^{-E/RT} \tag{22}$$

in which E is the activation energy or the energy barrier between adjacent sites. In small pore zeolites and carbon molecular sieves the dominant contribution to this energy is the repulsive interaction encountered by the molecule in penetrating the concentration in the pore. As a result, the activation energy shows a well-defined correlation with the molecule diameter and the size of the micropore, as illustrated in Figure 8.

More detailed information on micropore diffusion is available in the book by Kärger and Ruthven (18) and in the review article by Krishna and Wesselingh (19) which stresses the usefulness of the Stefan-Maxwell approach to the modelling of diffusion in binary and multicomponent systems.

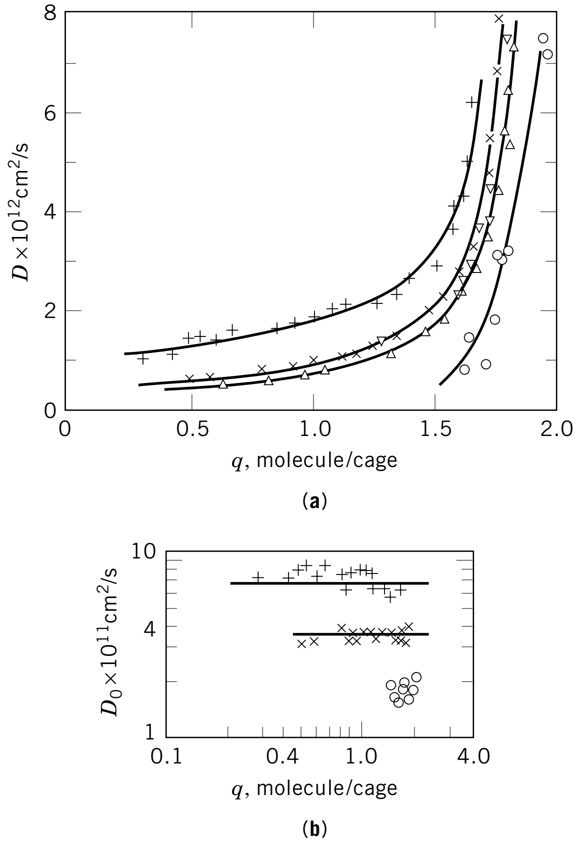


Fig. 7. Variation of (**a**) intracrystalline diffusivity and (**b**) corrected diffusivity (D_0) with sorbate concentration for n-heptane in a commercial sample of 5A zeolite crystals: ○ 409 K; △, ▽, 439 K (ads, des); ×, 462 K; +, 491 K. Reproduced by permission of National Research Council of Canada from ref. 17.

5.5. Sorption Rates in Batch Systems. Direct measurement of the uptake rate by gravimetric, volumetric, or piezometric methods is widely used as a means of measuring intraparticle diffusivities. Diffusive transport within a particle may be represented by the Fickian diffusion equation, which, in spherical coordinates, takes the form

$$\frac{\partial q}{\partial t} = D\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\,\frac{\partial q}{\partial r}\right) \tag{23}$$

For a step change in sorbate concentration at the particle surface ($r = R$) at time zero, assuming isothermal conditions and diffusion control, the expression for the uptake curve may be derived from the appropriate solution of this differential equation:

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\,e^{-n^2\pi^2 Dt/R^2} \tag{24}$$

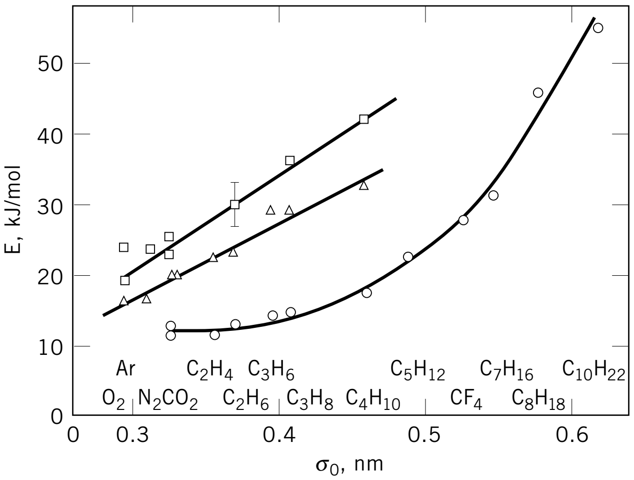


Fig. 8. Variation of activation energy with kinetic molecular diameter for diffusion in 4A zeolite (□), 5A zeolite (○), and carbon molecular sieve (MSC-5A) (△). Kinetic diameters are estimated from the van der Waals co-volumes. From ref. 7. To convert kJ to kcal divide by 4.184.

or, in the initial region,

$$\frac{m_r}{m_\infty} = \frac{6}{\sqrt{\pi}} \left(\frac{Dt}{R^2}\right)^{1/2} \tag{25}$$

The time constant R^2/D, and hence the diffusivity, may thus be found directly from the uptake curve. However, it is important to confirm by experiment that the basic assumptions of the model are fulfilled, since intrusions of thermal effects or extraparticle resistance to mass transfer may easily occur, leading to erroneously low apparent diffusivity values.

In certain adsorbents, notably partially coked zeolites and some carbon molecular sieves, the resistance to mass transfer may be concentrated at the surface of the particle, leading to an uptake expression of the form

$$\frac{m_t}{m_\infty} = 1 - e^{-k_s t} \tag{26}$$

in place of equation 24. The difference between surface resistance and intraparticle diffusion control is easily apparent from the form of the uptake curves (see Fig. 9). Since both D and k_s are generally concentration dependent, it is preferable to make differential measurements over small concentration steps in order to simplify the interpretation of the experimental data.

For a macroporous sorbent the situation is slightly more complex. A differential balance on a shell element, assuming diffusivity transport through the macropores with rapid adsorption at the surface (or in the micropores), yields

$$\epsilon_p \frac{\partial c}{\partial t} + (1 - \epsilon_p) \frac{\partial q}{\partial t} = \epsilon_p D_p \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r}\right) \tag{27}$$

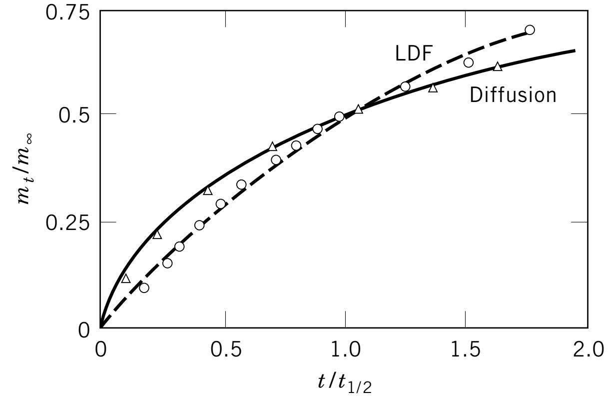


Fig. 9. Uptake curves for N_2 in two samples of carbon molecular sieve showing conformity with diffusion model (eq. 24) for sample 1 (△), and with surface resistance model (eq. 26) for example 2 (○); LDF = linear driving force. Data from ref. 20.

Assuming a linear equilibrium relationship (over the range of the small concentration step, $q^* = Kc$), this becomes

$$\frac{\partial c}{\partial t} = \frac{\epsilon_p D_p}{1 + (1 - \epsilon_p)K} \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \tag{28}$$

which is of the same form as equation 23 but with an effective diffusivity given by

$$D = \frac{\epsilon_p D_p}{1 + (1 - \epsilon_p)K} \tag{29}$$

For adsorption from the vapor phase, K may be very large (sometimes as high as 10^7) and then clearly the effective diffusivity is very much smaller than the pore diffusivity. Furthermore, the temperature dependence of K follows equation 2, giving the appearance of an activated diffusion process with $E \approx (-\Delta U)$.

As a result of these difficulties the reported diffusivity data show many apparent anomalies and inconsistencies, particularly for zeolites and other microporous adsorbents. Discrepancies of several orders of magnitude in the diffusivity values reported for a given system under apparently similar conditions are not uncommon. Since most of the intrusive effects lead to erroneously low values, the higher values are probably the more reliable.

6. Adsorption Column Dynamics

In most adsorption processes the adsorbent is contacted with fluid in a packed bed. An understanding of the dynamic behavior of such systems is therefore needed for rational process design and optimization. What is required is a mathematical model which allows the effluent concentration to be predicted for any defined change in the feed concentration or flow rate to the bed. The flow pattern can generally be represented adequately by the axial dispersed plug-flow model, according to which a mass balance for an element of the column yields, for the basic differential equation governing the dynamic behavior,

$$-D_L \frac{\partial^2 c_i}{\partial z^2} + \frac{\partial}{\partial z}(vc_i) + \frac{\partial c_i}{\partial t} + \left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \bar{q}_i}{\partial t} = 0 \tag{30}$$

The term $\partial \overline{q}_i/\partial t$ represents the overall rate of mass transfer for component i (at time t and distance z) averaged over a particle. This is governed by a mass transfer rate expression which may be thought of as a general functional relationship of the form

$$\frac{\partial \bar{q}}{\partial t} = f(c_i, c_j, \ldots, q_i, q_j, \ldots) \tag{31}$$

This rate equation must satisfy the boundary conditions imposed by the equilibrium isotherm and it must be thermodynamically consistent so that the mass transfer rate falls to zero at equilibrium. It may be a linear driving force expression of the form

$$\frac{\partial \bar{q}}{\partial t} = k_s(q_i^* - \bar{q}_i) \tag{32}$$

where $q^*{}_i(c_i, c_j, \ldots)$ represents the equilibrium adsorbed phase concentration of component i, or it may be a set of diffusion equations with their associated boundary conditions.

For an isothermal system the simultaneous solution of equations 30 and 31, subject to the boundary conditions imposed on the column, provides the expressions for the concentration profiles $c_i(z,t)$, $\overline{q}_i(z,t)$ in both phases. If the system is nonisothermal, an energy balance is also required and since, in general, both the equilibrium concentration and the rate coefficients are temperature dependent, all equations are coupled. Analytical solutions are possible only for the simpler cases: single-component isothermal systems with linear or rectangular equilibrium isotherms. In the general case of a multicomponent nonisothermal system, numerical solutions offer the only practical approach.

The form of the response for an adiabatic three-component system (two adsorbable components in an inert carrier) is illustrated in Figure 10. In general, if there are n components (counting both heat and nonadsorbing species as components), the response contains $(n-1)$ transitions or mass transfer zones, separated by $(n-2)$ plateaus between the initial and final states. When the change imposed at the column inlet involves an increase in the concentration of the more strongly adsorbed species, the concentration at the intermediate plateau will exceed both its initial concentration and its final steady-state concentration. This phenomenon, known as roll-up, results from displacement by the more strongly adsorbed species, which travels more slowly through the column.

6.1. Equilibrium Theory. The general features of the dynamic behavior may be understood without recourse to detailed calculations since the overall

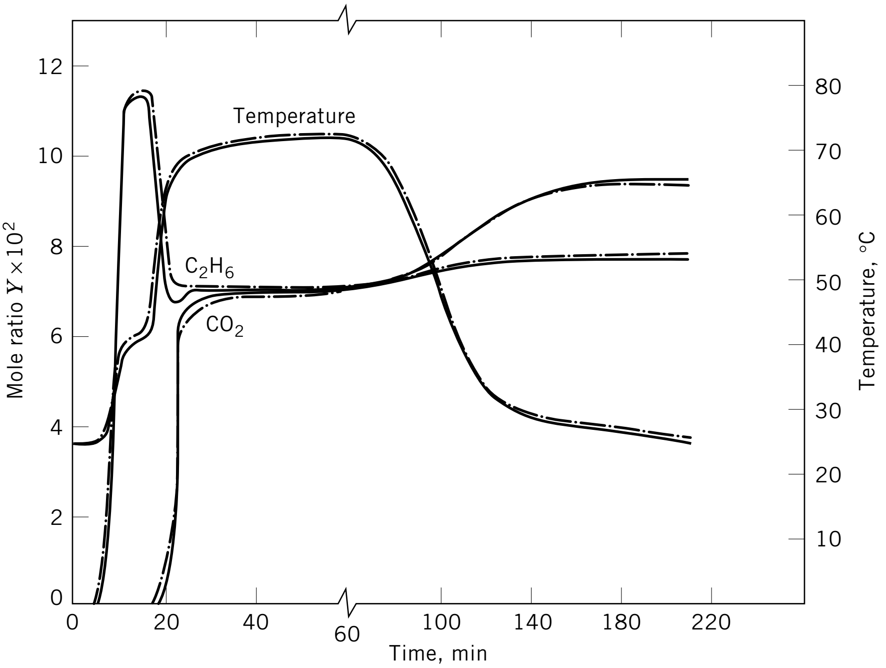


Fig. 10. Comparison of theoretical (—) and experimental (—·) concentration and temperature breakthrough curves for sorption of C_2H_6–CO_2 mixtures from a N_2 carrier on 5A molecular sieve. Feed: 10.5% CO_2, 7.03% C_2H_6 (molar basis) at 24°C, 116.5 kPa (1.15 atm). Column length, 48 cm. Theoretical curves were calculated numerically using the linear driving force model with a Langmuir equilibrium isotherm. Experimental data are from ref. 21. From ref. 22, courtesy of Pergamon Press.

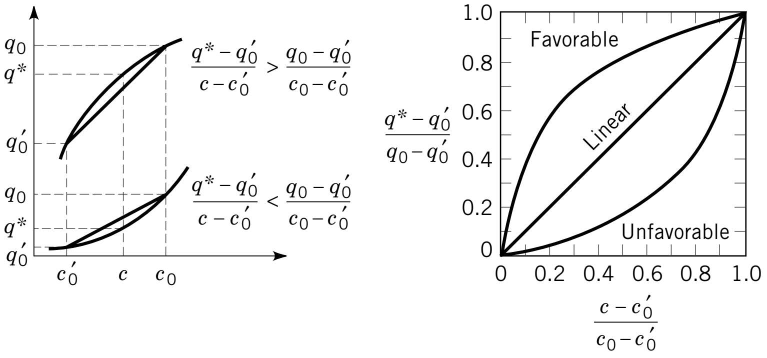
pattern of the response is governed by the form of the equilibrium relationship rather than by kinetics. Kinetic limitations may modify the form of the concentration profile but they do not change the general pattern. To illustrate the different types of transition, consider the simplest case: an isothermal system with plug flow involving a single adsorbable species present at low concentration in an inert carrier, for which equation 30 reduces to

$$v\frac{\partial c}{\partial z}+\frac{\partial c}{\partial t}+\left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \bar{q}}{\partial t}=0 \tag{33}$$

Assuming local equilibrium, $\bar{q}=f(c)$ where this function represents the isotherm equation, this becomes

$$\frac{v}{1+((1-\epsilon)/\epsilon)f'(c)}\,\frac{\partial c}{\partial z}+\frac{\partial c}{\partial t}=0 \tag{34}$$

where $f'(c)=dq^*/dc$ is simply the slope of the equilibrium isotherm at concentration c.



(**a**) (**b**)

Fig. 11. (**a**) Equilibrium isotherm and (**b**) dimensionless equilibrium diagram showing favorable, linear, and unfavorable isotherms.

Equation 34 has the form of the kinematic wave equation and represents a transition traveling with the wave velocity w, given by

$$w = \left(\frac{\partial z}{\partial t}\right)_c = \frac{v}{1 + ((1-\epsilon)/\epsilon)f'(c)} \tag{35}$$

For a linear system $f'(c) = K$, so the wave velocity becomes independent of concentration and, in the absence of dispersive effects such as mass transfer resistance or axial mixing, a concentration perturbation propagates without changing its shape. The propagation velocity is inversely dependent on the adsorption equilibrium constant.

For a nonlinear system the behavior depends on the shape of the isotherm. If the isotherm is unfavorable (Fig. 11), $f'(c)$ increases with concentration so that w decreases with concentration. This leads to a spreading profile, as illustrated in Figure 12**b**. However, if the isotherm is favorable (in the direction of the concentration change), an entirely different situation arises. Then $f'(c)$ decreases with concentration so that w increases with concentration. This would lead to the physically unreasonable overhanging profiles shown in Figure 12**a**. In fact, what happens is that the continuous solution is replaced by the equivalent shock transition so that response becomes a shock wave which propagates at a steady velocity w' given by

$$w' = \frac{v}{1 + ((1-\epsilon)/\epsilon)(\Delta q/\Delta c)} \tag{36}$$

where $\Delta q/\Delta c$ represents the ratio of the concentration changes in the adsorbed and fluid phases.

6.2. Constant Pattern Behavior. In a real system the finite resistance to mass transfer and axial mixing in the column lead to departures from the idealized response predicted by equilibrium theory. In the case of a favorable isotherm the shock wave solution is replaced by a constant pattern solution. The

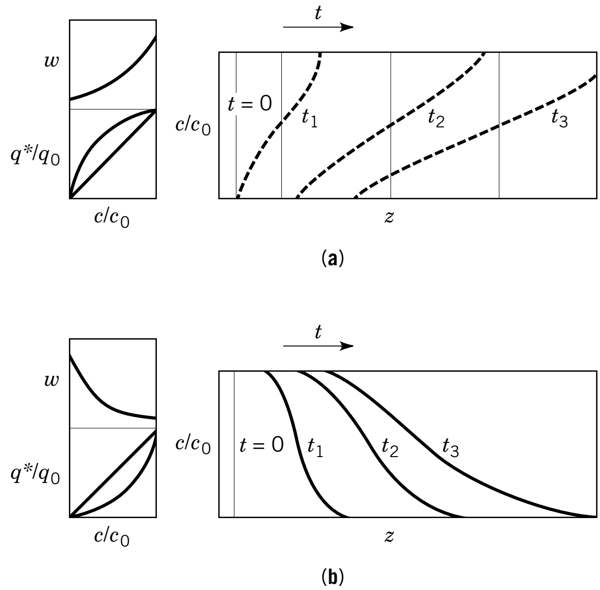


Fig. 12. (**a**) Development of the physically unreasonable overhanging concentration profile and the corresponding shock profile for adsorption with a favorable isotherm and (**b**) development of the dispersive (proportionate pattern) concentration profile for adsorption with an unfavorable isotherm (or for desorption with a favorable isotherm). From ref. 7.

concentration profile spreads in the initial region until a stable situation is reached in which the mass transfer rate is the same at all points along the wave front and exactly matches the shock velocity. In this situation the fluid-phase and adsorbed-phase profiles become coincident, as illustrated in Figure 13. This represents a stable situation and the profile propagates without further change in shape—hence the term constant pattern. The form of the concentration profile under constant pattern conditions may be easily deduced by integrating the mass transfer rate expression subject to the condition $c/c_0 = q/q_0$, where q_0 is the adsorbed phase concentration in equilibrium with c_0.

The distance required to approach the constant pattern limit decreases as the mass transfer resistance decreases and the nonlinearity of the equilibrium isotherm increases. However, when the isotherm is highly favorable, as in many adsorption processes, this distance may be very small, a few centimeters to perhaps a meter.

6.3. Length of Unused Bed. The constant pattern approximation provides the basis for a very useful and widely used design method based on the concept of the length of unused bed (LUB). In the design of a typical adsorption process the basic problem is to estimate the size of the adsorber bed needed to remove a certain quantity of the adsorbable species from the feed stream, subject to a specified limit (c') on the effluent concentration. The length of unused bed, which measures the capacity of the adsorber which is lost as a result of the spread of the concentration profile, is defined by

$$\mathrm{LUB} = (1 - q'/q_0)L = (1 - t'/\bar{t})L \tag{37}$$

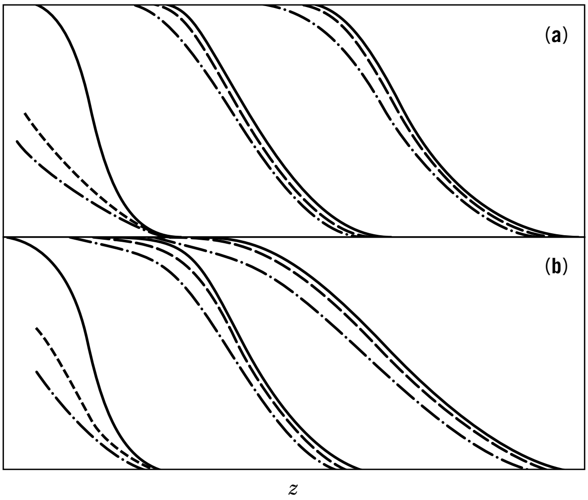


Fig. 13. Schematic diagram showing (**a**) approach to constant pattern behavior for a system with a favorable isotherm and (**b**) approach to proportionate pattern behavior for a system with an unfavorable isotherm. y axis: c/c_0, —; $\bar{q}/q_0$, -; c^*/c_0, —·. From ref. 7.

where q' is the capacity at the break time t' and $\bar{t}$; is the stoichiometric time (see Fig. 14). The values of t', $\bar{t}$, and hence the LUB are easily determined from an experimental breakthrough curve since, by overall mass balance,

$$\bar{t} = \frac{L}{v}\left[1+\left(\frac{1-\epsilon}{\epsilon}\right)\left(\frac{q_0}{c_0}\right)\right] = \int_0^\infty \left(1-\frac{c}{c_0}\right) dt \tag{38}$$

$$t' = \frac{L}{v}\left[1+\left(\frac{1-\epsilon}{\epsilon}\right)\left(\frac{q'}{c_0}\right)\right] = \int_0^{t'} \left(1-\frac{c}{c_0}\right) dt \tag{39}$$

Under constant pattern conditions the LUB is independent of column length although, of course, it depends on other process variables. The procedure is therefore to determine the LUB in a small laboratory or pilot-scale column packed with the same adsorbent and operated under the same flow conditions. The length of column needed can then be found simply by adding the LUB to

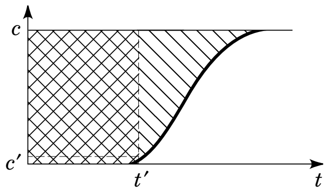


Fig. 14. Sketch of breakthrough curve showing break time t' and the method of calculation of the stoichiometric time $\bar{t}$; and LUB. From ref. 7. ╲╲╲ = the integral of equation 38; ◇◇◇ = the integral of equation 39.

the length calculated from equilibrium considerations, assuming a shock concentration front.

One potential problem with this approach is that heat loss from a small scale column is much greater than from a larger diameter column. As a result, small columns tend to operate almost isothermally whereas in a large column the system is almost adiabatic. Since the temperature profile in general affects the concentration profile, the LUB may be underestimated unless great care is taken to ensure adiabatic operation of the experimental column.

6.4. Proportionate Pattern Behavior. If the isotherm is unfavorable, the stable dynamic situation leading to constant pattern behavior can never be achieved. The situation is shown in Figure 13**b**. The equilibrium adsorbed-phase concentration lies above rather than below the actual adsorbed-phase profile. As the mass transfer zone progresses through the column it broadens, but the limiting situation, which is approached in a long column, is simply local equilibrium at all points ($c = c^*$) and the profile therefore continues to spread in proportion to the length of the column. This difference in behavior is important since the LUB approach to design is clearly inapplicable under these conditions.

Favorable and unfavorable equilibrium isotherms are normally defined, as in Figure 11, with respect to an increase in sorbate concentration. This is, of course, appropriate for an adsorption process, but if one is considering regeneration of a saturated column (desorption), the situation is reversed. An isotherm which is favorable for adsorption is unfavorable for desorption and vice versa. In most adsorption processes the adsorbent is selected to provide a favorable adsorption isotherm, so the adsorption step shows constant pattern behavior and proportionate pattern behavior is encountered in the desorption step.

6.5. Detailed Modeling Results. The results of a series of detailed calculations for an ideal isothermal plug-flow Langmuir system are summarized in Figure 15. The solid lines show the form of the theoretical breakthrough curves for adsorption and desorption, calculated from the following set of model equations and expressed in terms of the dimensionless variables ζ, τ, and β:

Differential Balance for Column

$$v\frac{\partial c}{\partial z}+\frac{\partial c}{\partial t}+\left(\frac{1-\epsilon}{\epsilon}\right)\frac{\partial \bar{q}}{\partial t}=0 \tag{40}$$

Rate Equation

$$\frac{\partial \bar{q}}{\partial t}=k(q^*-\bar{q}) \tag{41}$$

Equilibrium Isotherm

$$\frac{q^*}{q_s}=\frac{bc}{1+bc} \tag{42}$$

Initial Conditions

$$\begin{aligned}&\bar{q}(z,\,0)=c(z,\,0)=0 \quad \text{(adsorption)}\\&\bar{q}(z,\,0)=q_0,\; c(z,\,0)=c_0 \quad \text{(desorption)}\end{aligned} \tag{43}$$

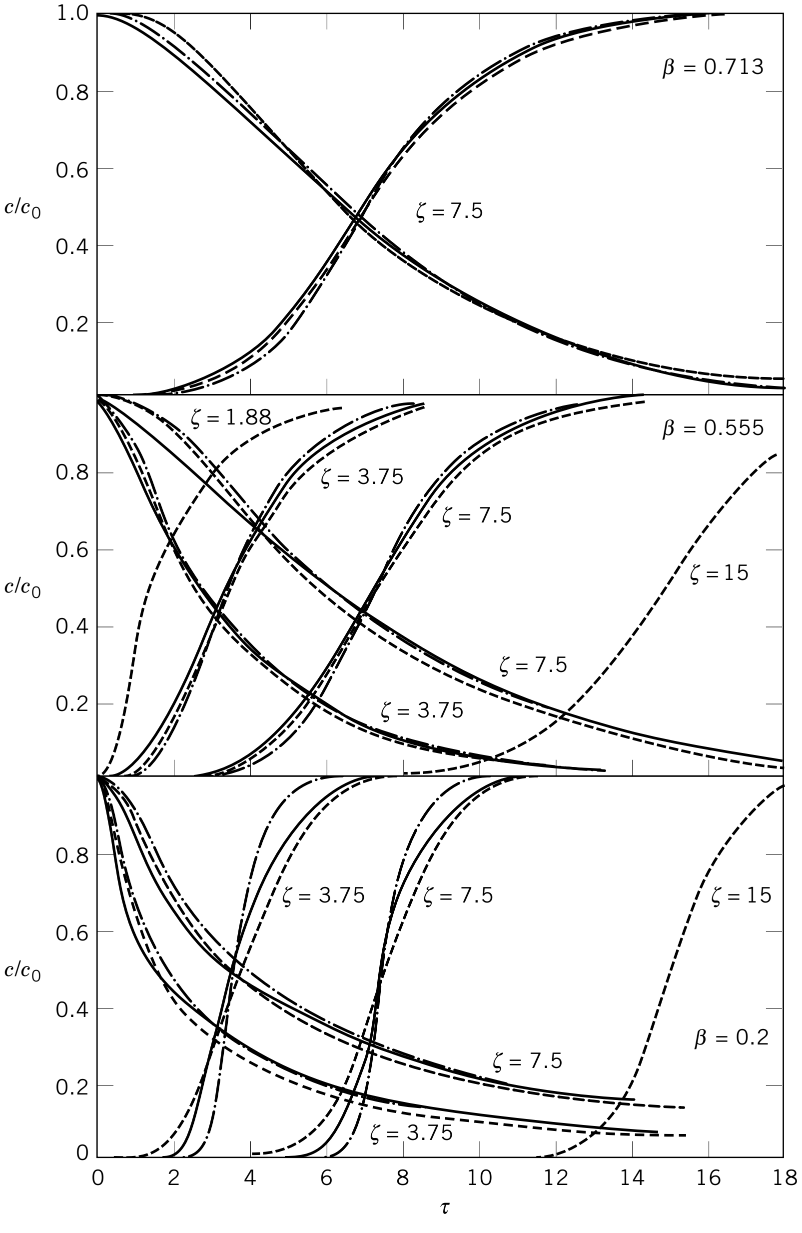


Fig. 15. Theoretical breakthrough curves for a nonlinear (Langmuir) system showing the comparison between the linear driving force (—), pore diffusion (-), and intracrystalline diffusion (—·) models based on the Glueckauf approximation (eqs. 40–45). From Ref. 7.

Boundary Conditions

$$\begin{aligned} c(0,t) &= c_0 \quad \text{(adsorption)} \\ c(0,t) &= 0 \quad \text{(desorption)} \end{aligned} \tag{44}$$

Bed Length Parameter

$$\zeta = \frac{z}{v}\left(\frac{q_0}{c_0}\right)\left(\frac{1-\epsilon}{\epsilon}\right)$$

Dimensionless Time

$$\tau = k\left(t - \frac{z}{v}\right) \tag{45}$$

Nonlinearity Parameter

$$\beta = 1 - \frac{q_0}{q_s} = \frac{1}{1+bc_0}$$

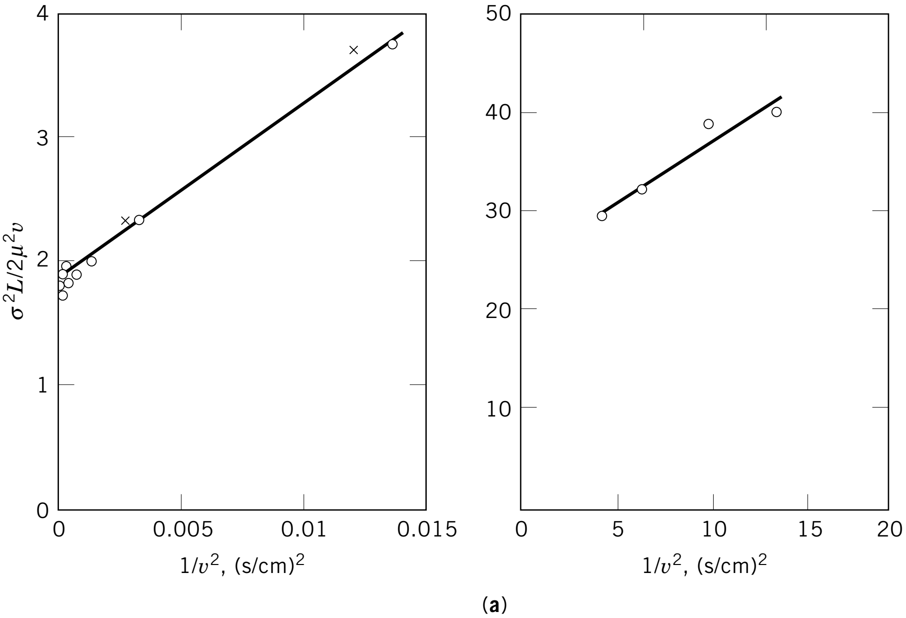
Also shown are the corresponding curves calculated for the same system assuming a diffusion model in place of the linear rate expression. For intracrystalline diffusion $k = 15D_0/r_c^2$, whereas for macropore diffusion $k = (15\epsilon_p D_p/R_p^2)(c_0/q_0)$, in accordance with the Glueckauf approximation (23).

For linear or moderately nonlinear systems ($\beta \longrightarrow 1.0$) there is little difference in the response curves for all three models, thus verifying the validity of the Glueckauf approximation. Differences between the models, however, become more significant for a highly nonlinear isotherm ($\beta \longrightarrow 0$). For linear or near linear systems the adsorption and desorption curves are mirror images, but as the isotherm becomes more nonlinear the adsorption and desorption curves become increasingly asymmetric. The adsorption curve approaches its limiting constant pattern form whereas the desorption curve approaches the limiting proportionate pattern form. In the long-time region the desorption curve is governed entirely by equilibrium, so that the curves for all three rate models again become coincident.

The main conclusion to be drawn from these studies is that for most practical purposes the linear rate model provides an adequate approximation and the use of the more cumbersome and computationally time consuming diffusing models is generally not necessary. The Glueckauf approximation provides the required estimate of the effective mass transfer coefficient for a diffusion controlled system. More detailed analysis shows that when more than one mass transfer resistance is significant the overall rate coefficient may be estimated simply from the sum of the resistances (7):

$$\frac{1}{kK} = \frac{R}{3k_f} + \frac{R^2}{15KD_c} + \frac{R^2}{15\epsilon_p D_p} \tag{46}$$

6.6. Adsorption Chromatography. The principle of gas-solid or liquid-solid chromatography may be easily understood from equation 35. In a linear multicomponent system (several sorbates at low concentration in an inert carrier) the wave velocity for each component depends on its adsorption equilibrium constant. Thus, if a pulse of the mixed sorbate is injected at the column inlet, the different species separate into bands which travel through the column at their



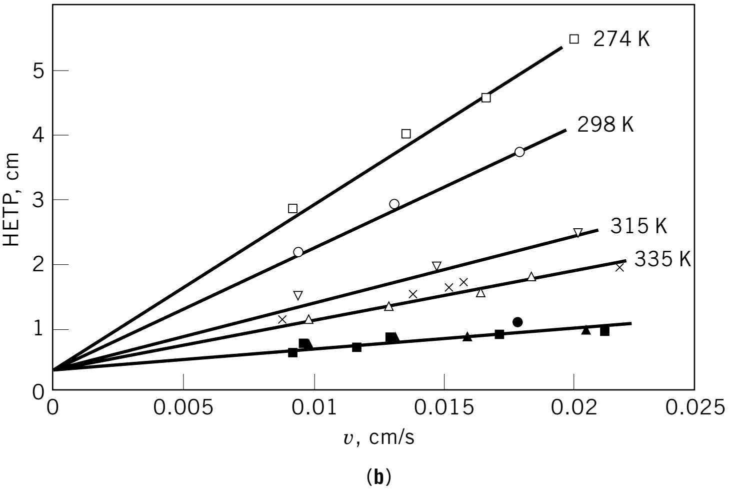


Fig. 16. Plots showing (**a**) variation of ($\varsigma^2 L/2\mu^2 v$) with $1/v^2$ for O_2 (left plot, ×, 0.84 – 0.72 mm = 20 – 25 mesh; ○, 0.42 – 0.29 mm = 40 – 50 mesh) and N_2 (right plot, on 3.2-mm pellets) in Bergbau-Forschung carbon molecular sieve and (**b**) variation of HETP with liquid velocity (interstitial) for fructose (solid symbols), and glucose (open symbols) in a column packed with KX zeolite crystals. From refs. 24 and 25.

characteristic velocities, and at the outlet of the column a sequence of peaks corresponding to the different species is detected. Measurement of the retention time ($\bar{t}$) under known flow conditions thus provides a simple means of determining the equilibrium constant (Henry constant):

$$\int_0^\infty \frac{ct\,dt}{\int_0^\infty c\,dt} = \bar{t} = \frac{L}{v}\left[1 + \left(\frac{1-\epsilon}{\epsilon}\right)K\right] \tag{47}$$

In an ideal system with no axial mixing or mass transfer resistance the peaks for the various components propagate without spreading. However, in any real system the peak broadens as it propagates and the extent of this broadening is directly related to the mass transfer and axial dispersion characteristics of the column. Measurement of the peak broadening therefore provides a convenient way of measuring mass transfer coefficients and intraparticle diffusivities. The simplest approach is to measure the second moments of the response peak over a range of flow rates:

$$\sigma^2 \equiv \int_0^\infty \frac{c(t-\bar{t})^2\,dt}{\int_0^\infty c\,dt} \tag{48}$$

Solution of the model equations shows that, for a linear isothermal system and a pulse injection, the height equivalent to a theoretical plate (HETP) is given by

$$H = \frac{\sigma^2}{\bar{t}^2}L = \frac{2D_L}{v} + \frac{2v}{kK}\left(\frac{\epsilon}{1-\epsilon}\right)\left[1 + \frac{\epsilon}{(1-\epsilon)K}\right]^{-2} \tag{49}$$

where $1/kK$ is the overall mass transfer resistance defined by equation 46.

For liquid systems D_L/v is approximately independent of velocity, so that a plot of H versus v provides a convenient method of determining both the axial dispersion and mass transfer resistance. For vapor-phase systems at low Reynolds numbers D_L is approximately constant since dispersion is determined mainly by molecular diffusion. It is therefore more convenient to plot H/v versus $1/v^2$, which yields D_L as the slope and the mass transfer resistance as the intercept. Examples of such plots are shown in Figure 16.

7. Applications

The applications of adsorbents are many and varied and may be classified as nonregenerative uses, in which the adsorbent is used once and discarded, and regenerative applications, in which the adsorbent is used repeatedly in a cyclic manner involving sequential adsorption and regeneration steps.

Nonregenerative uses
Desiccant in dual pane windows
Odor removal in health care products

Desiccant in refrigeration and air conditioning systems
Cigarette filters

Regenerative uses
Water purification (some systems)
Removal of trace impurities from gases or liquid streams
Bulk separations (gas or liquid)
Low pressure storage of methane
Desiccant cooling (open-cycle air conditioning)

In terms of tonnage usage, some of the nonregenerative applications, notably as desiccants in dual pane windows, in cigarette filters, and in water purification, are surprisingly important, but most of the important chemical engineering applications are regenerative since, with a few notable exceptions, the cost of the adsorbent is too great to allow nonregenerative use.

The application of adsorbents (generally high area activated carbon) as a means of storing methane fuel (natural gas) at relatively high density under moderate pressure is relatively new. With current technology, capacities of about 180 m^3 STP/m^3 at 3 MPa (30 atm) pressure are achievable (26) but somewhat higher capacities are needed to compete with liquid fuels for motor vehicles. However, depending on the cost of crude oil and the potential for improvement of the adsorbent, this technology could become important in the future.

Open-cycle desiccant cooling is another area of emerging technology (8). Rather than cooling and dehumidifying by mechanical work, as in a conventional air conditioning system, in an open-cycle desiccant system dehumidification is achieved directly, while cooling is achieved by controlled evaporation. The energy input is in the form of the heat required to regenerate the desiccant. A significant advantage of this system is that it can be designed to operate with a low regeneration temperature, thus making it possible to utilize low grade heat or even solar heat to drive the system.

7.1. Adsorption Separation and Purification Processes. The main area of current application of adsorption is in separation and purification processes. Many different ways of operating such processes have been devised and it is helpful to consider the various systems according to the mode of fluid-solid contact (see Fig. 17). In a cyclic batch process at least two beds are employed and each bed is successively saturated with the preferentially adsorbed species (or class of species) during the adsorption step and then regenerated during a desorption step in which the direction of mass transfer is reversed to remove the adsorbed species from the bed. In the continuous countercurrent process the adsorbent can be regarded as circulating continuously between the adsorption and desorption beds, in both of which fluid and solid contact in countercurrent flow. More commonly, as in the Sorbex type of process, the adsorbent is not physically circulated but the same effect is achieved in a fixed adsorbent bed equipped with multiple inlet and outlet ports to which the fluid streams are directed in sequence. Such systems can achieve a close approximation to counter-current flow without the problems inherent in circulating the solid adsorbent. However, the system is relatively expensive, so it is generally used only for difficult separations (low separation factor) which cannot be carried out efficiently in a simple batch process.

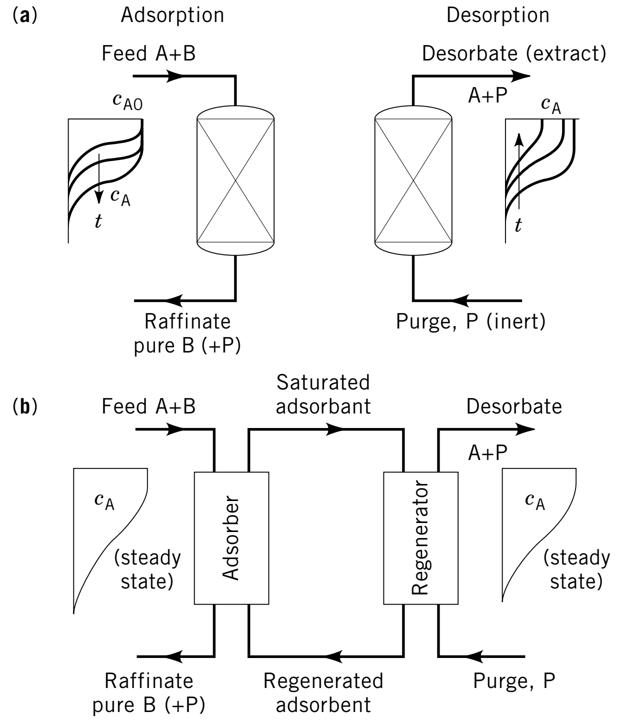


Fig. 17. The two basic modes of operation for an adsorption process: (**a**) cyclic batch system; (**b**) continuous countercurrent system with adsorbent recirculation. From ref. 7.

The other major difference between adsorption processes lies in the method by which the adsorbent bed is regenerated. The advantages and disadvantages of three different methods—temperature swing, pressure swing, and displacement—are summarized in Table 5. For efficient removal of trace impurities it is normally essential to use a highly selective adsorbent on which the sorbate is strongly held. Temperature swing regeneration is therefore generally used in such applications. However, in bulk separations all three regeneration methods are widely used.

7.2. Adsorbent Contactors. The randomly packed bed of adsorbent particles (with axial flow) is the workhorse of adsorption process technology. Such a contactor is cheap and robust and offers the important advantage of relatively low resistance to mass transfer. However, the pressure drop is relatively high so for applications such as VOC removal or desiccant cooling, which involve large flows of dilute gas streams, the energy losses can be prohibitive. It has been shown that a monolithic or parallel passage contactor with sufficiently small holes or spacing between the adsorbent layers has more favorable characteristics, in terms of the pressure drop per theoretical stage, and therefore, for such applications, offers an attractive alternative to the randomly packed bed (27). Processes based on parallel passage contactors, often constructed in the form of a slowly rotating wheel to allow continuous cycling between a cold adsorption

Table 5. **Factors Governing Choice of Regeneration Method**[a]

Method	Advantages	Disadvantages
thermal swing	good for strongly adsorbed species; small change in T gives large change in q^*	thermal aging of adsorbent
	desorbate may be recovered at high concentration	heat loss means inefficiency in energy usage
	gases and liquids	unsuitable for rapid cycling, so adsorbent cannot be used with maximum efficiency
		in liquid systems the latent heat of the interstitial liquid must be added
pressure swing	good where weakly adsorbed species is required at high purity	very low P may be required
	rapid cycling—efficient use of adsorbent	mechanical energy more expensive than heat
		desorbate recovered at low purity
displacement desorption	good for strongly held species	product separation and recovery needed (choice of desorbent is crucial)
	avoids risk of cracking reactions during regeneration	
	avoids thermal aging of adsorbent	

[a] Ref. 7.

zone and a hot regeneration zone, have been developed by several manufacturers including Dürr and Seibu-Geiken.

7.3. Process Design. As with any chemical engineering process, the choice of process type and the details of the design are dictated primarily by economic considerations, subject to the overriding requirements of safety and reliability. Although the principles of adsorption processes are well understood, most practical designs still rely on a good deal of empiricism since factors such as the aging and deterioration of an adsorbent under practical operating conditions are difficult to predict except from experience.

In general the sophistication of the design procedures is closely related to the level of sophistication of the process. In the simple thermal swing, batch type processes for removal of trace impurities the beds are generally sized on the basis of equilibrium capacity and LUB with a suitable allowance for aging of the adsorbent. The desorption or regeneration temperature is generally selected on the basis of equilibrium data as the minimum temperature which will allow the required specification of the purity of the raffinate product to be easily met. Use of a higher regeneration temperature generally gives a purer product but only at the cost of increased energy consumption and reduction of the service life of the adsorbent. The quantity of purge gas is estimated in two ways: from the overall heat balance with the required temperature rise and from the mass balance with the assumption of equilibrium at the bed outlet. Depending on the particular system and the process conditions, either of these considerations may be limiting. In general, when regeneration is carried out by purging at atmospheric pressure, the purge requirement is determined by the heat balance, but when the regeneration is carried out at elevated pressure, the mass balance is often the major constraint.

The design of pressure swing systems is also largely dependent on the scale-up of pilot-plant units, although, with such systems, the use of a detailed numerical simulation to guide the optimization of the operating conditions is more common. This is true also of countercurrent and simulated countercurrent processes where the initial design is commonly based on a simple McCabe-Thiele diagram (28) (see ADSORPTION, LIQUID SEPARATION).

7.4. Notation

a	ratio of external surface area to particle volume
b	Langmuir equilibrium constant
B	mobility
c	sorbate concentration in fluid phase
c_0	initial value of c
D	diffusivity
D_e	effective diffusivity
D_m	molecular diffusivity
D_K	Knudsen diffusivity
D_L	axial dispersion coefficient
D_0	corrected diffusivity
D_∞	preexponential factor
D_p	pore diffusivity
E	activation energy
$-\Delta H_0$	limiting heat of adsorption
K	dimensionless equilibrium constant
K_0	preexponential factor
K'	Henry's law constant
K'_0	preexponential factor
k	rate constant
k_0	preexponential factor
k', k''	constants in Elovich equation
k_f	fluid film mass transfer coefficient
k_s	surface mass transfer coefficient
L	bed length
M	molecular weight
m_t	mass adsorbed (or desorbed) at time t
m_∞	mass adsorbed (or desorbed) at $t \longrightarrow \infty$
p	partial pressure of sorbate
q	adsorbed phase concentration
q_0	initial value of q
$\bar{q}$	adsorbed phase concentration averaged over a particle
q^*	equilibrium value of q
q_s	saturation limit in Langmuir expression
r	radial coordinate
R	radius of adsorbent particle
R	gas constant
t	time
$\bar{t}$	mean residence time or stoichiometric time
t'	break time
T	temperature
$-\Delta U$	change of interval energy on adsorption
v	interstitial fluid velocity
w	wave velocity

w'	shock velocity
z	distance
α	separation factor
ε	voidage of adsorbent bed
ε_p	porosity of particle
μ	chemical potential
ρ	mean pore radius
σ^2	variance of pulse response
τ	tortuosity factor

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