
ADSORBENTS: FUNDAMENTALS AND APPLICATIONS

Ralph T. Yang

Dwight F. Benton Professor of Chemical Engineering
University of Michigan



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PREFACE

Since the invention of synthetic zeolites in 1959, innovations in sorbent development and adsorption process cycles have made adsorption a key separations tool in the chemical, petrochemical and pharmaceutical industries. In all future energy and environmental technologies, adsorption will likely play either a key or a limiting role. Some examples are hydrogen storage and CO removal (from hydrogen, to <1 ppm) for fuel cell technology, desulfurization of transportation fuels, and technologies for meeting higher standards on air and water pollutants. These needs cannot be fulfilled by current commercial sorbents.

The past two decades have shown an explosion in the development of new nanoporous materials: mesoporous molecular sieves, zeolites, pillared clays, sol-gel-derived metal oxides, and new carbon materials (carbon molecular sieves, super-activated carbon, activated carbon fibers, carbon nanotubes, and graphite nanofibers). The adsorption properties for most of these new materials remain largely unexplored.

This book provides a single and comprehensive source of knowledge for all commercial and new sorbent materials. It presents the fundamental principles for their syntheses and their adsorption properties as well as their present and potential applications for separation and purification.

Chapter 2 provides a simple formula for calculating the basic forces or potentials for adsorption. Thus, one can compare the adsorption potentials of two different molecules on the same site, or that of the same molecule on two different sites. The calculation of pore size distribution from a single adsorption isotherm is shown in Chapter 4. The effects of pore size and shape on adsorption are discussed in both Chapters 2 and 4. Chapter 3 aims to provide rules for sorbent selection. Sorbent selection is a complex problem because it also depends on the adsorption cycle and the form of sorbent (e.g., granules, powder, or monolith) that are to be used. The attributes sought in a sorbent are capacity, selectivity, regenerability, kinetics, and cost. Hence, Chapter 3 also includes a summary of equilibrium isotherms, diffusion steps, and cyclic processes. Simple sorbent selection criteria are also presented.

The fundamental principles for syntheses/preparation, adsorption properties, and applications of the commercially available sorbents are covered in Chapters 5–7. Mesoporous molecular sieves are discussed, along with zeolites, in Chapter 7.

The sorbent that forms a π -complexation bond with molecules of a targeted component in a mixture is named π -complexation sorbent. The π -complexation bond is a type of weak and reversible chemical bond, the same type that binds oxygen to hemoglobin in our blood. This type of sorbent has been developed in the past decade, largely in the author's laboratory. Because they have shown a tremendous potential for a number of important applications in separation and purification, they are discussed separately in Chapter 8. This chapter also presents their applications for olefin/paraffin separations, olefin purification (by removal of dienes to <1 ppm, separation of CO, as well as aromatics from aliphatics). The particularly promising application of π -complexation sorbents for sulfur removal from transportation fuels (gasoline, diesel, and jet fuels) is discussed in Chapter 10.

Chapter 9 covers carbon nanotubes, pillared clays, and polymeric resins. Polymeric resins are in widespread use for ion exchange, water treatment, and analytical chromatography.

In Chapter 10, sorbents for specific applications in separation and purification are discussed in detail. These include both well-established applications, such as air separation, and potential applications, such as gasoline desulfurization and energy storage (of hydrogen or methane).

In my research on new sorbents and in organizing my thoughts for this book, I have benefited greatly from discussions with a number of researchers in the field, particularly my former students who are now key researchers in industry, as well as my colleagues at SUNY at Buffalo and the University of Michigan.

Thanks are also due to my past and present students and associates, with whom I have had so much pleasure in learning. Finally, I would like to thank Ruby Sowards for her skillful help in the art work and the staff at Wiley for their highly professional editing and publication.

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INTRODUCTORY REMARKS

Separation may be defined as a process that transforms a mixture of substances into two or more products that differ from each other in composition (King, 1980). The process is difficult to achieve because it is the opposite of mixing, a process favored by the second law of thermodynamics. Consequently, the separation steps often account for the major production costs in chemical, petrochemical, and pharmaceutical industries. For many separation processes, the separation is caused by a mass separating agent (King, 1980). The mass separating agent for adsorption is adsorbent, or sorbent. Consequently, the performance of any adsorptive separation or purification process is directly determined by the quality of the sorbent.

Due to the progress made in sorbent and cyclic process developments, adsorption has already become a key separations tool that is used pervasively in industry. Adsorption is usually performed in columns packed with sorbent particles, or fixed-bed adsorbers. The high separating power of chromatography that is achieved in a column is a unique advantage of adsorption as compared with other separation processes. The high separating power is caused by the continuous contact and equilibration between the fluid and sorbent phases. Under conditions free of diffusion limitation, each contact is equivalent to an equilibrium stage or theoretical plate. Usually several hundred to several thousand such equilibrium stages can be achieved within a short column. Thus, adsorption is ideally suited for purification applications as well as difficult separations. Partly because of this unique advantage, adsorption is well-positioned to play a key role in the development of many future energy and environmental technologies. The simulated moving-bed technology is a good example of using adsorption to perform difficult separations, where satisfactory separations are achieved by using sorbents with separation factors as low as 2.

There are only a handful of generic sorbents that are commercially available. These are the sorbents being used in the current adsorption processes.

Future applications of adsorption are limited by the availability of new and better sorbents. Ideally, the sorbent should be tailored with specific attributes to meet the needs of each specific application. Development of better sorbents can also improve the performance of the current commercial processes. A good example is the invention of the LiX (Si/Al = 1) zeolite (Chao, 1989). Air separation has been performed by pressure swing adsorption, and the generic sorbents 13X (i.e., NaX) and 5A (i.e., CaA) zeolites were used prior to this invention. By switching from NaX to LiX (Si/Al = 1), the productivity of oxygen increased instantly by 1.4–2.7 times and the power consumption reduced by 21–27% depending on the operating conditions used (Leavitt, 1995).

The past two decades have shown an explosion in the developments of new nanoporous materials. Tremendous advances have been made in our capabilities to tailor the porosity and surface chemistry of oxide molecular sieves and new forms of carbon (carbon molecular sieves, super-activated carbon, activated carbon fibers, carbon nanotubes, and graphite nanofibers). However, the potential use of the adsorption properties of these new materials remains largely unexplored.

1.1. EQUILIBRIUM SEPARATION AND KINETIC SEPARATION

The adsorptive separation is achieved by one of three mechanisms: steric, kinetic, or equilibrium effect. The steric effect derives from the molecular sieving properties of zeolites and molecular sieves. In this case only small and properly shaped molecules can diffuse into the adsorbent, whereas other molecules are totally excluded. Kinetic separation is achieved by virtue of the differences in diffusion rates of different molecules. A large majority of processes operate through the equilibrium adsorption of mixture and hence are called equilibrium separation processes.

Steric separation is unique with zeolites and molecular sieves because of the uniform aperture size in the crystalline structure. The two largest applications of steric separation are drying with 3A zeolite and the separation of normal paraffins from iso-paraffins and cyclic hydrocarbons by using 5A zeolite (Yang, 1987). This type of separation is generally treated as equilibrium separation.

Although kinetic separation has had only limited applications, it holds high potentials for many more. It is an option to consider when equilibrium separation is not feasible. Air separation is a good example for which kinetic separation can complement equilibrium separation. Air separation by PSA (i.e., pressure-swing adsorption) using zeolite is based on the preferential adsorption of N₂ over O₂. It is hence used for the production of O₂ from air. N₂ constitutes about 78% of air. If an O₂-selective sorbent is used, air separation can be accomplished with about 1/4 of the work that is needed for the same separation by using zeolite. This is particularly the case with nitrogen production from air. Oxygen diffuses about 30 times faster than nitrogen in carbon molecular sieve. Although the adsorption capacity of carbon molecular sieve is only a fraction of that of zeolite, it is more economical to use carbon molecular sieve for the production of nitrogen from air. Separation of methane from CO₂ has also been performed by kinetic separation

with carbon molecular sieve. The feasibility for propane/propylene separations by using $\text{AlPO}_4\text{-14}$ has been demonstrated (see Chapter 10). The upgrading of natural gas by removal of nitrogen from methane is a large potential application for kinetic separation. This subject will also be discussed in Chapter 10.

For equilibrium separation, the starting point for sorbent design/selection is to examine the fundamental properties of the targeted molecule that is to be adsorbed (compared with the other molecules in the mixture): polarizability, magnetic susceptibility, permanent dipole moment, and quadrupole moment. If the targeted molecule has high polarizability and magnetic susceptibility, but no polarity, carbon with a high surface area would be a good candidate. Sorbents with highly polar surfaces (e.g., activated alumina, silica gel, and zeolites) would be desirable for a targeted molecule that has a high dipole moment (and high polarizability). If the targeted molecule has a high quadrupole moment, sorbents with surfaces that have high electric field gradients are needed. Zeolites are the only such sorbents, as the cations are dispersed above the negatively charged oxides on their surfaces. Cations with high valences (i.e., charges) and small ionic radii would result in strong interactions. The methodology for calculating these interactions is given in Chapter 2 (for all sorbents) and Chapter 7 (for zeolites). The above discussion applies only to the bonding between the targeted molecule and the adsorption site. The targeted molecule also interacts with other atoms on the surfaces of the pore. These interactions are secondary but are also important. Monte Carlo simulation includes pairwise additivity and integrates the interactions over all sites. Sorbent design/selection is a complex problem, because the process for which the sorbent is used needs to be considered at the same time. For purification, particularly ultrapurification, strong adsorption bonds are needed. Strong bond yields high Henry's constant, which leads to ultrahigh product purity. Sorbents that form weak chemical bonds with the targeted molecule can be particularly useful. For this type of sorbents, molecular orbital theory is the most powerful tool for sorbent design, and is discussed in Chapter 8.

For kinetic separation, the pore size needs to be precisely tailored to lie between the kinetic diameters of the two molecules that are to be separated. Many microporous molecular sieves with various pore dimensions have been synthesized (Hartman and Kevan, 1999), which have yet to be used as sorbents.

1.2. COMMERCIAL SORBENTS AND APPLICATIONS

Only four types of generic sorbents have dominated the commercial use of adsorption: activated carbon, zeolites, silica gel, and activated alumina. Estimates of worldwide sales of these sorbents are (Humphrey and Keller, 1997)

Activated carbon	\$1 billion
Zeolites	\$100 million
Silica gel	\$27 million
Activated alumina	\$26 million

Some other reported figures are (according to 2001 demand) zeolites (\$1,070 million), silica gel (\$71 million), activated alumina (\$63 million), and clays (\$16 million) (*Chemical Engineering*, February 2000, p. 59).

Activated carbon has been used as an all-purpose sorbent. It is “hydrophobic.” Its precedent, charcoal, was first used in the sugar industry in England in 1794 to decolorize sugar syrup. The major development of activated carbon took place during World War I, for use in filters to remove chemical agents from air. The commercial activated carbon has taken its present form since the 1930’s (Jankowska et al., 1991). Silica gel and activated alumina are used mainly as desiccants, although many modified forms are available for special purification applications. Synthetic zeolites, the youngest type among the four, were invented by Milton in 1959 (Milton, 1959). The zeolites that are in commercial use today are mainly the types in Milton’s invention, i.e., types A, X, and Y. It is remarkable that most of the \$100 million annual sales of zeolites and the businesses associated with the zeolites are generated by a single invention. Zeolites are used for their special adsorption properties due to their unique surface chemistries and crystalline pore structures. It should be noted, however, that a sizable portion of the commercial zeolites is used for ion exchange and as catalysts.

Polymeric resins are used increasing use in potable water purification, because for some organics they can remove to lower concentration levels than activated carbon does. Acid-treated clays and pillared clays are used for treatments of edible and mineral oils.

Table 1.1 shows examples of commercial applications of these sorbents. Both bulk separation and purification processes are given. Here bulk separation is defined (by Keller, 1983) as having the concentration of the adsorbed component above 10 wt % in the feed. For purification, the concentration of the adsorbed component is generally <2 wt % in the feed. The liquid-phase bulk separations that use the zeolites listed in Table 1.1 are accomplished with the simulated moving bed process. Not included in Table 1.1 are many liquid-phase bioseparations

Table 1.1. Examples of commercial adsorption processes and sorbents used

Separation	Adsorbent
<i>Gas Bulk Separations</i>	
Normal paraffins/isoparaffins, aromatics	Zeolite
N ₂ /O ₂	Zeolite
O ₂ /N ₂	Carbon molecular sieve
CO, CH ₄ , CO ₂ , N ₂ , Ar, NH ₃ /H ₂	Activated carbon followed by zeolite (in layered beds)
Hydrocarbons/vent streams	Activated carbon
H ₂ O/ethanol	Zeolite (3A)
Chromatographic analytical separations	Wide range of inorganic and polymer resin agents

Table 1.1. (continued)

Separation	Adsorbent
<i>Gas Purification</i>	
H ₂ O/olefin-containing cracked gas, natural gas, air, synthesis gas, etc.	Silica, alumina, zeolite (3A)
CO ₂ /C ₂ H ₄ , natural gas, etc.	Zeolite, carbon molecular sieve
Hydrocarbons, halogenated organics, solvents/vent streams	Activated carbon, silicalite, others
Sulfur compounds/natural gas, hydrogen, liquefied petroleum gas (LPG), etc.	Zeolite, activated alumina
SO ₂ /vent streams	Zeolite, activated carbon
Odors/air	Silicalite, others
Indoor air pollutants — VOCs	Activated carbon, silicalite, resins
Tank-vent emissions/air or nitrogen	Activated carbon, silicalite
Hg/chlor-alkali cell gas effluent	Zeolite
<i>Liquid Bulk Separations</i>	
Normal paraffins/isoparaffins, aromatics	Zeolite
<i>p</i> -xylene/ <i>o</i> -xylene, <i>m</i> -xylene	Zeolite
Detergent-range olefins/paraffins	Zeolite
<i>p</i> -Diethyl benzene/isomer mixture	Zeolite
Fructose/glucose	Zeolite
Chromatographic analytical separations	Wide range of inorganic, polymer, and affinity agents
<i>Liquid Purifications</i>	
H ₂ /organics, oxygenated organics, halogenated organics, etc., dehydration	Silica, alumina, zeolite, corn grits
Organics, halogenated organics, oxygenated organics, etc./H ₂ O — water purification	Activated carbon, silicalite, resins
Inorganics (As, Cd, Cr, Cu, Se, Pb, F, Cl, radionuclides, etc.)/H ₂ O — water purification	Activated carbon
Odor and taste bodies/H ₂ O	Activated carbon
Sulfur compounds/organics	Zeolite, alumina, others
Decolorizing petroleum fractions, syrups, vegetable oils, etc.	Activated carbon
Various fermentation products/fermentor effluent	Activated carbon, affinity agents
Drug detoxification in the body	Activated carbon

The components that are to be adsorbed are listed first (from Humphrey and Keller, 1997, with permission, and with minor modification).

and purifications accomplished by chromatography in the pharmaceutical and food industries.

1.3. NEW SORBENTS AND FUTURE APPLICATIONS

In the development of new energy technologies, such as fuel cells, adsorption can play a key enabling role. A breakthrough in sorbent development is needed to solve the critical problem of hydrogen storage for hydrogen fuel cells. The best fuel for fuel cells is gasoline (because of its high-energy density, ready availability, and safety in handling). However, to avoid poisoning of the Pt catalyst in the fuel cell, the sulfur content in gasoline needs to be reduced from the present level of ~ 350 ppm to <1 ppm. These challenges cannot be met with the sorbents that are currently available.

Future needs for a clean environment will lead to increasingly higher standards for air and water pollutants. These challenges require better sorbents that are not commercially available. Traditionally, sorbents were developed based on empiricism. To meet the new challenges, tailored sorbents need to be developed based on fundamental principles. Theoretical tools, such as *ab initio* molecular orbital theory and Monte Carlo simulations can be used to speed up the sorbent design. It is one of the goals of this book to help put sorbent design on a more rational basis.

Some of the most challenging problems in separation and purification that require new sorbents are given in Table 1.2. New sorbents that can solve these problems are also given. Details of these new sorbents are discussed in Chapter 10. Further innovations are needed for meeting these and many more future challenges.

Table 1.2. Some future separation and purification applications by new sorbents

Application	Sorbent and Notes
CH ₄ storage for on-board vehicular storage	Super-activated carbon and activated carbon fibers Near or meeting DOE target storage capacity
H ₂ storage for on-board vehicular storage	Carbon nanotubes Possible candidate (?)
N ₂ /CH ₄ separation for natural gas upgrading	Clinoptilolite, Sr-ETS-4 by kinetic separation
Sulfur removal from transportation fuels (gasoline, diesel and jet fuels)	π -complexation sorbents such as Cu(I)Y, AgY
CO removal from H ₂ to <1 ppm for fuel cell applications	π -complexation sorbents such as CuCl/ γ -Al ₂ O ₃ , CuY, and AgY
NO _x removal	Fe-Mn-Ti oxides, Fe-Mn-Zr oxides, Cu-Mn oxides
Removal of dienes from olefins (to <1 ppm)	π -complexation sorbents such as Cu(I)Y, AgY

Table 1.2. (continued)

Application	Sorbent and Notes
C_3H_6/C_3H_8 (+hydrocarbons) separation	π -complexation sorbents such as CuCl/ γ - Al_2O_3 , $AgNO_3/SiO_2$, $AgNO_3/clays$
C_2H_4/C_2H_6 (+hydrocarbons) separation	π -complexation sorbents such as CuCl/ γ - Al_2O_3 , $AgNO_3/SiO_2$, $AgNO_3/clays$

Details are given in Chapters 8, 9, and 10.

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FUNDAMENTAL FACTORS FOR DESIGNING ADSORBENT

Selection or synthesis of adsorbents for a target adsorbate molecule is based on the adsorption isotherm. With the availability of high-speed computing, it is now possible to calculate the adsorption isotherms based on: (1) interaction potentials and (2) structure/geometry of the adsorbent. Let us begin with a review of the basic forces between the adsorbent and adsorbate, paying particular attention to adsorbent design.

2.1. POTENTIAL ENERGIES FOR ADSORPTION

Adsorption occurs when the interaction potential energy ϕ is equal to the work done to bring a gas molecule to the adsorbed state. As a first approximation, the adsorbed state is assumed to be at the saturated vapor pressure.

$$-\phi = -\Delta G = \int_P^{P_0} V dP = RT \ln \frac{P_0}{P} \quad (2.1)$$

where ΔG is the free energy change and P_0 is the saturated vapor pressure. Hence P is the pressure when adsorption occurs for the given ϕ (ϕ is actually the sorbate–sorbate interaction energy on the liquid surface).

The total potential between the adsorbate molecules and the adsorbent is the sum of the total adsorbate–adsorbate and the adsorbate–adsorbent interaction potentials:

$$\phi_{\text{total}} = \phi_{\text{adsorbate–adsorbate}} + \phi_{\text{adsorbate–adsorbent}} \quad (2.2)$$

The adsorbent has only a secondary effect on the adsorbate–adsorbate interaction. For this reason, we will focus our attention on the second term, adsorbate–adsorbent potential, and refer to this term as ϕ .

The three basic types of contributions to the adsorbate–adsorbent interactions are dispersion, electrostatic, and chemical bond. The latter, chemical bond, has been explored for adsorption only recently. Weak chemical bonds, particularly the broad type of bonds involving π electrons or π -complexation, offer promising possibilities for designing new and highly selective sorbents. The subject of π -complexation sorbents will be discussed separately, in Chapter 8. For physical adsorption, the adsorbate–adsorbent potential is

$$\phi = \phi_D + \phi_R + \phi_{Ind} + \phi_{F\mu} + \phi_{\dot{F}Q} \quad (2.3)$$

where ϕ_D = dispersion energy, ϕ_R = close-range repulsion energy, ϕ_{Ind} = induction energy (interaction between electric field and an induced dipole), $\phi_{F\mu}$ = interaction between electric field (F) and a permanent dipole (μ), $\phi_{\dot{F}Q}$ = interaction between field gradient (\dot{F}) and a quadrupole (with quadrupole moment Q).

The first two contributions ($\phi_D + \phi_R$) are “nonspecific” (Barrer, 1978), which are operative in all sorbate–sorbent systems. The last three contributions arise from charges (which create electric fields) on the solid surface. (This is a simplified view, because an adsorbate molecule with a permanent dipole can also induce a dipole in the sorbent if the sorbent is a conductor [Masel, 1996]). For activated carbon, the nonspecific interactions dominate. For metal oxides, zeolites, and ionic solids, the electrostatic interactions often dominate, depending on the adsorbate. For adsorbate with a quadrupole, the net interaction between a uniform field and the quadrupole is zero. However, the quadrupole interacts strongly with the field gradient, thus the term $\phi_{\dot{F}Q}$.

The individual contributions to the total potential have been reviewed and discussed in detail in the literature (Barrer, 1978; Masel, 1996; Razmus and Hall, 1991; Gregg and Sing, 1982; Steele, 1974; Adamson and Gast, 1997; Rigby et al., 1986; Israelachvili, 1992; Young and Crowell, 1962; Ross and Olivier, 1964). Their functional forms are summarized below. All interactions are given between an atom (or a charge) on the surface and the adsorbate molecule.

Dispersion:

$$\phi_D = -\frac{A}{r^6} \quad (2.4)$$

Repulsion:

$$\phi_R = +\frac{B}{r^{12}} \quad (2.5)$$

Field (of an ion) and induced point dipole:

$$\phi_{Ind} = -\frac{1}{2}\alpha F^2 = -\frac{\alpha q^2}{2r^4(4\pi\epsilon_0)^2} \quad (2.6)$$

Field (of an ion) and point dipole:

$$\phi_{F\mu} = -F\mu \cos \theta = -\frac{q\mu \cos \theta}{r^2(4\pi \epsilon_0)} \quad (2.7)$$

Field gradient (\dot{F}) and linear point quadrupole:

$$\phi_{\dot{F}Q} = \frac{1}{2}Q\dot{F} = -\frac{Qq(3 \cos^2 \theta - 1)}{4r^3(4\pi \epsilon_0)} \quad (2.8)$$

where A and B are constants, α = polarizability, F = electric field, q = electronic charge of ion on surface, ϵ_0 = permittivity of a vacuum, μ = permanent dipole moment, θ = angle between the direction of the field or field gradient and the axis of the dipole or linear quadrupole, Q = linear quadrupole moment (+ or -). The important parameter, r , is the distance between the centers of the interacting pair. It can be shown that the field-quadrupole interaction is always zero for all θ .

The dispersion and repulsion interactions form the Lennard–Jones potential (Barrer, 1978; Masel, 1996; Razmus and Hall, 1991; Gregg and Sing, 1982; Steele, 1974; Adamson and Gast, 1997; Rigby, et al., 1986), with an equilibrium distance (r_0) at which point $\phi_D + \phi_R = 0$. This distance is taken as the mean of the van der Waals radii of the interacting pair. Once the attractive, dispersion constant, A , is known, B is readily obtained by setting $d\phi/dr = 0$ at r_0 . Hence, $B = Ar_0^6/2$. Interestingly, at r_0 , $\phi_D = -2\phi_R$. The most commonly used expression for calculating A is the Kirkwood–Müller formula:

$$A = \frac{6mc^2\alpha_i\alpha_j}{(\alpha_i/\chi_i) + (\alpha_j/\chi_j)} \quad (2.9)$$

where m is the mass of electron, c is the speed of light, χ is the magnetic susceptibility, and i and j refer to the two interacting atoms or molecules. For ϕ_{Fu} and $\phi_{\dot{F}Q}$, the maximum potentials are obtained when the dipole or quadrupole is arranged linearly with the charge on the surface.

The dispersion potential, Eq. 2.4, was derived by F. London in 1930, starting from Eq. 2.6, and summarized by Adamson and Gast, 1997. The repulsion term, Eq. 2.5, was not rigorously derived. Equation 2.6 can be obtained from $\mu = \alpha F$, where μ is the induced dipole moment and α is, by definition, the polarizability. The derivation of Eqs. 2.7 and 2.8 is straightforward.

2.2. HEAT OF ADSORPTION

In 2.1, we summarized the different contributions to the potential energy for the interactions between an adsorbate molecule (or atom) and an atom on the solid surface. Pairwise additivity is generally assumed when calculating the interaction

energy between the adsorbate molecule and all atoms on the surface. The task is then to add the interactions, pairwise, with all atoms on the surface, by integration.

It can be shown (Barrer, 1978; Ross and Olivier, 1964) that the isosteric heat of adsorption (ΔH) at low coverage is related to the sorbate–sorbent interaction potential (ϕ) by

$$\Delta H = \phi - RT + F(T) \quad (2.10)$$

where $F(T)$ arises due to the vibrational and translational energies of the adsorbate molecule, and for monatomic classical oscillators, $F(T) = 3RT/2$ (Barrer, 1978). For ambient temperature, $\Delta H \approx \phi$.

2.3. EFFECTS OF ADSORBATE PROPERTIES ON ADSORPTION: POLARIZABILITY (α), DIPOLE MOMENT (μ), AND QUADRUPOLE MOMENT (Q)

For a given sorbent, the sorbate–sorbent interaction potential depends on the properties of the sorbate. Among the five different types of interactions, the nonspecific interactions, ϕ_D and ϕ_R , are nonelectrostatic. The most important property that determines these interactions (and also ϕ_{Ind}) is the polarizability, α . On a surface without charges, such as graphite, $\phi_{Ind} = 0$. The value of α generally increases with the molecular weight because more electrons are available for polarization. From the expressions for ϕ_D , ϕ_R , and ϕ_{Ind} , it is seen that these energies are nearly proportional to α . The dispersion energy also increases with the magnetic susceptibility, χ , but not as strongly as α .

Table 2.1 summarizes interaction energies for a number of sorbate–sorbent pairs. Here, groupings are made for the theoretical nonelectrostatic ($\phi_D + \phi_R + \phi_{Ind}$) and the electrostatic ($\phi_{F\mu} + \phi_{\dot{F}Q}$) energies.

The nonelectrostatic energies depend directly on the polarizability of the sorbate molecule; χ makes a contribution to the dispersion energy, and χ also increases with molecular weight.

Two types of sorbents are included in Table 2.1, one without electric charges on the surface (graphitized carbon) and one with charges (three zeolites). On carbon, dispersion energy dominates. On zeolites, the permanent dipole and quadrupole can make significant contributions toward, and indeed can dominate, the total energy. N_2 has a moderately strong quadrupole but no permanent dipole, hence $\phi_{F\mu} = 0$. From Table 2.1, it is seen that $\phi_{\dot{F}Q}$ accounts for about 1/3 of the energies on chabazite and Na-Mordenite. Na-X zeolite contains more Na^+ ions because its Si/Al ratio is lower than the other two zeolites. Consequently $\phi_{\dot{F}Q}$ contributes about 1/2 of the interaction energies for N_2 on Na-X. The other sorbate molecules included in Table 2.1 both have strong dipoles and quadrupoles (except H_2O , which has a strong dipole only). For adsorption of these molecules on zeolites, the ($\phi_{F\mu} + \phi_{\dot{F}Q}$) interactions clearly dominate.

A comparison of N_2 and O_2 holds particular interest for the application of air separation. Both molecules are nonpolar and have very similar polarizabilities and magnetic susceptibilities. However, their quadrupole moments differ by nearly

Table 2.1. Contributions (theoretical) to initial (near zero loading) heat of adsorption

Sorbent	Sorbate*	$\alpha \times 10^{24}$ cm ³ /molec.	$-\Delta H$	$-(\phi_D + \phi_R + \phi_{Ind})^{**}$	$-(\phi_{F\mu} + \phi_{FQ})$
Graphitized Carbon	Ne	0.396	0.74	0.73	0
	Ar	1.63	2.12	1.84	0
	Kr	2.48	2.8	2.48	0
	Xe	4.04	3.7	3.1	0
Chabazite	N ₂	1.74	8.98	6.45	2.55
	N ₂ O	3.03	15.3	9.07	6.18
	NH ₃	2.2	31.5	7.5	23.8
Na-Mordenite	N ₂	1.74	7.0	4.5	2.50
	CO ₂	2.91	15.7	6.73	8.93
Na-X	N ₂	1.74	6.5	3.10	3.4
	CO ₂	2.91	12.2	4.20	7.98
	NH ₃	2.2	17.9	3.75	14.2
	H ₂ O	1.45	≈33.9	2.65	≈31.3

*Permanent dipole moments (μ , debye): N₂O = 0.161, NH₃ = 1.47, H₂O = 1.84, all others = 0.

Quadrupole moments (Q , erg^{1/2} cm^{5/2} × 10²⁶): N₂ = -1.5, N₂O = -3.0, NH₃ = -1.0, CO₂ = -4.3, all others ≈0.

**For graphitized carbon, $\phi_{Ind} = 0$.

Experimental, $-\Delta H$, kcal/mol (Barrer, 1978; Ross and Olivier, 1964).

a factor of 4 ($Q = -0.4$ esu for O₂ and -1.5 esu for N₂). As a result, the adsorption isotherms of N₂ and O₂ on carbon are similar, whereas the isotherm of N₂ is much higher than that of O₂ on zeolites. The contribution of interaction between the field gradient and the quadrupole moment of N₂ accounts for about 1/2 of the total energy for N₂ adsorption on Na-X zeolite, as mentioned above. The $\phi_{F\mu}$ energy for O₂ is approximately 1/4 of that for N₂ (see Eq. 2.8).

2.4. BASIC CONSIDERATIONS FOR SORBENT DESIGN

2.4.1. Polarizability (α), Electronic Charge (q), and van der Waals Radius (r)

For van der Waals (dispersion) interactions, the polarizabilities of the sorbate molecule and the atoms on the sorbent surface are both important (see Eq. 2.9). In electrostatic interactions, for a given sorbate molecule, the charges and van der Waals radii of the surface atoms are important. The roles of these parameters are discussed separately.

For a given sorbate molecule, its dispersion interaction potential with a surface atom increases with the polarizability of that surface atom. The polarizability increases with atomic weight for elements in the same family, and decreases with increasing atomic weight for elements in the same row of the periodic table as the outer-shell orbitals are being increasingly filled. The polarizabilities of

Table 2.2. Polarizabilities (α) of ground state atoms and ions (in 10^{-24} cm^3)

Atom	α	Atom	α	Atom	α
C	1.76	K	43.4	Co	7.5
N	1.10	Rb	47.3	Ni	6.8
O	0.802	Cs	59.6		
F	0.557	Mg	10.6	Li ⁺	0.029
S	2.90	Ca	22.8	Na ⁺	0.180
Cl	2.18	Sr	27.6	K ⁺	0.840
Br	3.05	Ba	39.7	Ca ²⁺	0.471
I	5.35	Al	6.8	Sr ²⁺	0.863
		Si	5.38	Ba ²⁺	1.560
Li	24.3	Fe	8.4		
Na	24.08				

selected atoms are given in Table 2.2. It can be seen that the alkali and alkaline earth metal atoms have very high polarizabilities. Hence these elements, when present on the surface, can cause high dispersion potentials. When these elements are present as cations, however, the polarizabilities are drastically reduced. The polarizabilities of selected cations are also included in Table 2.2 for comparison.

For electrostatic interactions, the charges (q) and the van der Waals radii of the surface atoms (or ions) are most important. For ionic solids with point charges distributed on the surface, the positive and negative fields can partially offset when spaced closely. However, anions are normally bigger than cations. Consequently, the surface has a negative electric field. All electrostatic interaction potentials are proportional to q ($\Phi_{F\mu}$ and Φ_{FQ}) or q^2 (Φ_{Ind}) and are inversely proportional to r^n (where $n = 2-4$, see Eqs. 2-8). Here, r is the distance between the centers of the interacting pair, which should be the sum of the van der Waals radii of the two interacting atoms. Hence, the van der Waals radii of the ions on the surface are important. The strong effects of charge (q) and ionic radius of the cation on the adsorption properties of ion-exchanged zeolites will be discussed in Chapter 7.

Because the ionic radius determines the distance r , it has a strong effect on the electrostatic interactions. The ionic radii of selected cations are given in Table 2.3. The ionic radius is a crucially important factor when considering ion-exchanged zeolites and molecular sieves as sorbents.

2.4.2. Pore Size and Geometry

The potentials discussed above are those between two molecules/atoms. The interactions between a molecule and a flat solid surface are greater because the molecule interacts with all adjacent atoms on the surface, and these interactions are assumed pairwise additive. When a molecule is placed between two flat surfaces, i.e., in a slit-shaped pore, it interacts with both surfaces, and the potentials on the two surfaces overlap. The extent of the overlap depends on

Table 2.3. Ionic Radii, r_i (Å)

Ion	r_i	Ion	r_i
Li ⁺	0.68	Al ³⁺	0.51
Na ⁺	0.97	Ce ³⁺	1.03
K ⁺	1.33	Cu ⁺	0.96
Rb ⁺	1.47	Cu ²⁺	0.72
Cs ⁺	1.67	Ag ⁺	1.26
Mg ²⁺	0.66	Ag ²⁺	0.89
Ca ²⁺	0.99	Au ⁺	1.37
Sr ²⁺	1.12	Ni ²⁺	0.69
Ba ²⁺	1.34	Ni ³⁺	0.62

Table 2.4. Theoretical threshold pressure for adsorption in different pore sizes and shapes

Pore Size (Å)	P/P_0 for Slit-Shaped	P/P_0 for Cylindrical Shape	P/P_0 for Spherical Shape
4	6.3×10^{-7}	1.3×10^{-12}	3.2×10^{-51}
5	9.1×10^{-6}	2.9×10^{-10}	1.1×10^{-42}
6	3.5×10^{-5}	8.3×10^{-9}	2.5×10^{-36}
7	1.2×10^{-4}	6.5×10^{-8}	6.2×10^{-32}
9	6.1×10^{-4}	3.5×10^{-6}	3.1×10^{-24}
12	2.6×10^{-3}	2.3×10^{-5}	1.2×10^{-20}
15	6.1×10^{-3}	3.2×10^{-4}	1.7×10^{-16}
20	1.4×10^{-2}	1.2×10^{-3}	6.1×10^{-13}

N₂ on carbon at 77 K. $P_0 = 1$ atm.

the pore size. For cylindrical and spherical pores, the potentials are still greater because more surface atoms interact with the adsorbate molecule.

The effects of the pore size and pore geometry are best illustrated by Table 2.4. Table 2.4 lists the threshold pressure for adsorption in different pore sizes and geometries for N₂ on carbon. The calculation was based on the Horvath–Kawazoe (HK) model (Horvath and Kawazoe, 1983), using the corrected version by Rege and Yang (2000). The corrected HK model has been shown to give pore dimensions from N₂ isotherms that agreed well with the actual pore dimension for a number of materials, including carbon and zeolites (Rege and Yang, 2000). The model is based on equating the work done for adsorption (Eq. 2.1) to the total sorbate–sorbent and sorbate–sorbate interactions. The sorbate–sorbent interactions are the sum over all sorbent surface atoms using the Lennard–Jones potentials. A detailed discussion of the HK models, as well as other models, are given

in Chapter 4 for calculating pore size distribution from a single isotherm. The results in Table 2.4 exhibit the remarkable attraction forces acting on the adsorbate molecule due to the overlapping potentials from the surrounding walls. The same carbon atom density on the surface was assumed for all geometries, i.e. $3.7 \times 10^{15} \text{ 1/cm}^2$. The experimental data on two molecular sieve carbons agreed with predictions for slit-shaped pores. Scarce or no experimental data are available for cylindrical pores and spherical pores of carbon. Data on these shapes may become available with the availability of carbon nanotubes and fullerenes (if an opening to the fullerene can be made).

As expected, the total interaction energies depend strongly on the van der Waals radii (of both sorbate and sorbent atoms) and the surface atom densities. This is true for both HK type models (Saito and Foley, 1991; Cheng and Yang, 1994) and more detailed statistical thermodynamics (or molecular simulation) approaches (such as Monte Carlo and Density Functional Theory). By knowing the interaction potential, molecular simulation techniques enable the calculation of adsorption isotherms (see for example, Razmus and Hall, 1991; Cracknell et al., 1995; Barton et al. 1999).

NOTATION

<i>A</i>	constant in the 6–12 potential
<i>B</i>	constant in the 6–12 potential; dispersion constant
<i>c</i>	speed of light
<i>C</i>	dispersion constant; average number of sorbate molecules per cage in zeolite
<i>E</i>	interaction energy
<i>F</i>	electric field strength
<i>G</i>	Gibbs free energy
<i>h</i>	Planck constant
<i>H</i>	enthalpy
<i>k</i>	Boltzmann constant
<i>m</i>	mass of electron
<i>P</i>	total pressure
<i>P</i> ₀	saturation vapor pressure
<i>q</i>	electronic charge of ion or surface
<i>Q</i>	heat of adsorption; linear quadrupole moment
<i>r</i>	distance between centers of pair; pore radius
<i>r</i> _i	ionic radius
<i>R</i>	gas constant
<i>T</i>	temperature
<i>V</i>	molar volume
α	polarizability
γ	activity coefficient
ε	potential energy field over surface; emittivity

θ	angle between field and dipole; fractional surface coverage;
μ	permanent dipole moment; chemical potential
ρ	density
ϕ	potential energy function
χ	magnetic susceptibility
ω	lateral interaction energy

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