



## CHAPTER 3

### GAS ADSORPTION

When a gas is brought into contact with a solid, the gas molecules are concentrated at the gas-solid interface by adsorptive forces. The accumulation of a gas at the interface is called "adsorption"; while the gas or adsorbed molecules is known as the "adsorbate" and the solid which has adsorbed them, as the "adsorbent". Adsorption is a dynamic process, in which molecules are continuously coming in contact with the surface, residing there momentarily and then leaving to re-enter the bulk gas phase. In discussing the fundamentals of adsorption it is useful to distinguish between "physical adsorption", involving only relatively weak intermolecular forces, and "chemisorption" which involves essentially the formation of a chemical bond between the adsorbate molecule and the surface of the adsorbent. The general features which distinguish physical adsorption from chemisorption are shown in Table 3.1. Of more practical interest to all the adsorptive separation processes is the reversible, physical adsorption.

It is this process of physical adsorption which is used for selectively concentrating certain compounds out of multicomponent gaseous mixtures. The sorption capacity of an adsorbent depends on two complimentary factors: surface area and porosity. The driving force for all adsorptive gas separation processes lies in the departure from equilibrium. Information on this relationship, or on

Table 3.1 Distinction between physical adsorption and chemisorption.

Physical Adsorption	Chemisorption
Low heat of adsorption (< 2 or 3 times latent heat of evaporation.)	High heat of adsorption (> 2 or 3 times latent heat of evaporation.)
Non specific.	Highly specific.
Monolayer or multilayer. No dissociation of adsorbed species. Only significant at relatively low temperatures.	Monolayer only. May involve dissociation. Possible over a wide range of temperature.
Rapid, non-activated, reversible. No electron transfer although polarization of sorbate may occur.	Activated, may be slow and irreversible. Electron transfer leading to bond formation between sorbate and surface.

the isotherm, is therefore a prerequisite for proper design of the process. These adsorbed materials, since they are held by simple physical forces, can be completely desorbed and recovered unchanged by the application of heat, vacuum or inert gas purge, or by a combination of these methods.

### 3.1 Adsorption Isotherm

An adsorption isotherm is the relationship at constant temperature between the partial pressure of the adsorbate and the amount adsorbed at equilibrium. For a given gas-solid pair, the amount adsorbed at equilibrium is described phenomenologically by (16)

$$v = f(p,T) \quad (3.1)$$

where  $v$  is the amount adsorbed in volume (cc STP/g) and  $p$  is the partial pressure of the adsorbate at the specified temperature  $T$ .

Brunauer et al. (17) have divided the isotherms for physical adsorption into five classes, as illustrated in Fig. 3.1. The isotherms for truly microporous adsorbents, in which the pore size is not very much greater than the molecular diameter of the adsorbate molecule, are normally of type I. This is because with such adsorbents there is a definite saturation limit corresponding to complete filling of the micropores. Occasionally if intermolecular attraction effects are large, an isotherm of type V is observed, as for example in the adsorption of phosphorous vapor on NaX. An isotherm of type IV suggests the formation of two surface layers either on a plane surface or on the wall of a pore very much wider than the molecular diameter of the adsorbate. Isotherms of types II and III are generally observed only in adsorbents in which there is a wide range of pore sizes. In such systems there is a continuous progression with increasing loading from monolayer to multilayer

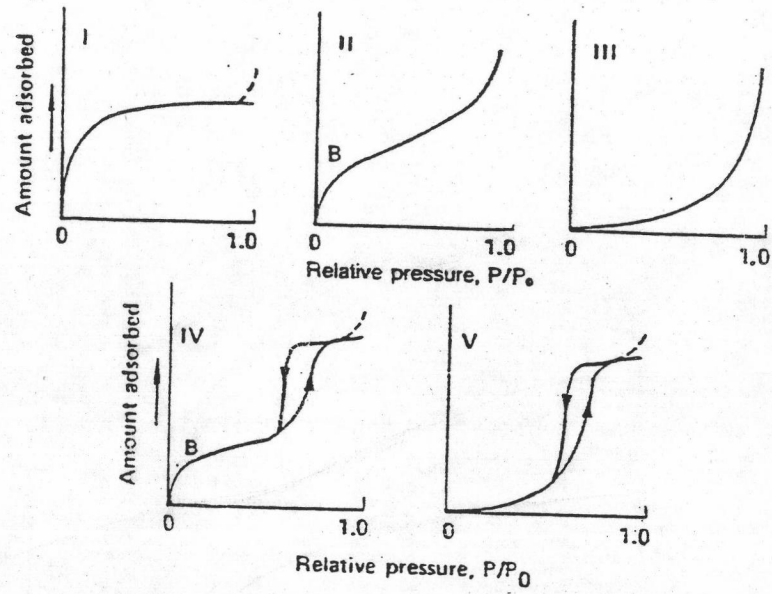


Fig. 3.1 The five type of adsorption isotherms, according to the BDDT classification.

adsorption and then to capillary condensation. The increase in sorption capacity at high pressures is due to capillary condensation occurring in pores of increasing diameter as the pressure is raised.

Many theories and models have been developed to interpret these different types of isotherms. The resulting isotherm equations can then be used to predict the amounts adsorbed based on a limited number of experiments. The numerous isotherm models are based on three different approaches; namely the Langmuir approach, the Gibbs approach, and the potential theory.

### 3.1.1 Langmuir Isotherm :

#### Monolayer Adsorption on Homogeneous Surfaces

The simplest and still the most useful theoretical model, for both physical and chemical adsorption, is the Langmuir isotherm. The basic assumptions on which the model is based are

1. Molecules are adsorbed at a fixed number of well-defined localized sites.
2. Each site can accommodate one and only one adsorbate molecule.
3. All sites are energetically equivalent.
4. There is no interaction (for example, via van der Waals attraction) between molecules adsorbed on neighbouring sites.

Although theoretical derivations of the isotherm may be based on kinetics, statistical thermodynamics or Gibbs isotherm, a relatively simple kinetic approach, originally used by Langmuir, is given below.

Considering the dynamic equilibrium between the adsorbed and gaseous phases (17).

$$\text{Rate of adsorption : } k_a p(1 - \theta)$$

015352

Rate of desorption :  $k_d \Theta$

where  $q_s$  is the total number of sites per unit weight or volume of adsorbent and  $\Theta = q/q_s$  is the fractional coverage. At equilibrium the rates of adsorption and desorption are equal.

$$\Theta / (1 - \Theta) = (k_a/k_d)p = bp \quad (3.2)$$

where  $b = k_a/k_d$  is the adsorption equilibrium constant.

Equation (3.2) may be rearranged to the commonly quoted form.

$$\Theta = q/q_s = bp/(1+bp) \quad (3.3)$$

The expression shows the correct asymptotic behaviour for monolayer adsorption since at saturation  $p \rightarrow \infty$ ,  $q \rightarrow q_s$  and  $\Theta \rightarrow 1.0$ , while at low adsorbate concentrations Henry's law is approached.

$$\lim_{p \rightarrow 0} (q/p) = bq_s = K \quad (3.4)$$

$q_s$  is supposed to represent a fixed number of surface sites and it should therefore be a temperature-independent constant while the temperature dependence of the equilibrium constant should follow a vant Hoff equation:

$$b = b_0 \exp(-\Delta H_0/RT) \quad (3.5)$$

Since adsorption is exothermic ( $\Delta H$  negative),  $b$  should decrease with increasing temperature.

The assumptions of identical sites with no interaction between adsorbed molecules imply that the heat of adsorption is independent of coverage. It follows by differentiation of Eq.(3.1) that the isosteric heat of adsorption ( $-\Delta H_s$ ) is the same as the limiting heat of adsorption ( $-\Delta H_0$ ).

$$(\partial \ln p / \partial T)_q = \Delta H_s / RT^2 = d \ln b / dT = d \ln K / dT = \Delta H_0 / RT^2 \quad (3.6)$$

### 3.2 Diffusion in Porous Solids (17)

Rates of adsorption and desorption in porous adsorbents are generally controlled by transport within the pore network, rather than by the intrinsic kinetics of adsorption at the surface. Since there is generally little, if any, bulk flow through the pores, it is convenient to consider intraparticle transport as a diffusive process and to correlate kinetic data in terms of a diffusivity defined in accordance with Fick's first equation:

$$J = -D(c) \cdot (\partial c / \partial x) \quad (3.7)$$

Such a definition provides a convenient mathematical representation, but it does not imply that the diffusivity is independent of concentration, only that it is not dependent on the concentration gradient. Since the true driving force for any transport process is the gradient of chemical potential, rather than the gradient of concentration, ideal Fickian behavior in which the diffusivity is independent of adsorbate concentration is realized only when the system is thermodynamically ideal.

Pore diffusion may occur by several different mechanisms depending on the pore sizes, the concentration, and other conditions. In fine micropores such as the intracrystalline pores of zeolites, the diffusing molecule never escapes from the force field of the adsorbent surface and transport occurs by an activated process involving jumps between adsorption "sites". Such a process is often called "surface diffusion". The more general terms "micropore" or "intracrystalline" diffusion are therefore used here to describe transport in such systems, while diffusion in large pores such that the diffusing molecule escapes from the surface field is referred to as "macropore" diffusion. This distinction between micropore and

macropore diffusion is useful since, in a zeolitic adsorbent, the diameter of the intracrystalline micropores is generally much smaller than that of the smallest intercrystalline macropores.

### 3.2.1 Diffusion in Macropores

Macropore diffusion has been widely studied in connection with its influence on the overall kinetics of heterogeneous catalytic reactions. Four distinct mechanisms of transport may be identified: molecular diffusion, Knudsen diffusion, Poiseuille flow, and surface diffusion. The effective macropore diffusivity is thus a complex quantity which often includes contributions from more than one mechanism. Although the individual mechanisms are reasonably well understood, it is not always easy to make an accurate a priori prediction of the effective diffusivity since this is strongly dependent on the details of the pore structure.

In analyzing macropore diffusion it is usually assumed that the transport occurs only through the pores and the flux through the solid can be neglected. It is therefore convenient to define a pore diffusivity ( $D_p$ ) based on the pore cross-sectional area:

$$J = - \epsilon_p D_p (\partial c / \partial x) \quad (3.8)$$

$D_p$  is smaller than the diffusivity in a straight cylindrical pore as a result of two effects; the random orientation of the pores, which gives a longer diffusion path and a reduced concentration gradient in the direction of flow, and the variation in the pore diameter. Both these effects are commonly accounted for by a "tortuosity factor" ( $\tau$ ):

$$D_p = D / \tau \quad (3.9)$$

where  $D$  is the diffusivity under the same conditions in a straight cylindrical pore. Since the tortuosity is essentially a geometric



factor it should be independent of either temperature or the nature of the diffusing species.

a) Molecular Diffusion (Gases)

If transport within the macropores occurs only by molecular diffusion, the pore diffusivity is given by

$$D_p = D_m / \tau \quad (3.21)$$

where  $D_m$  is the molecular diffusivity which, for gaseous systems, maybe estimated with confidence from the Chapman-Enskog equation. For a binary gas mixture

$$D_m = 0.00158 T^{3/2} (1/M_1 + 1/M_2)^{1/2} / \{P \sigma_{12}^2 \Omega(\epsilon/kT)\} \quad (3.22)$$

where  $M_1, M_2$  are the molecular weights,  $P$  is the total pressure in atmospheres,  $\sigma_{12} = 1/2(\sigma_1 + \sigma_2)$  is the collision diameter from the Lennard-Jones potential, expressed in Angstroms, and  $\Omega$  is a function of  $\epsilon/kT$  where  $\epsilon = \sqrt{\epsilon_1 \epsilon_2}$  is the Lennard-Jones force constant and  $k$  is the Boltzmann constant. Tabulations of the force constants are given by Hirschfelder, Curtis and Bird (18) and by Satterfield (19).

b) Knudsen Diffusion

In molecular diffusion the resistance to flow arises from collisions between diffusing molecules. The effects of the pore is merely to reduce the flux as a result of geometric constraints which are accounted for by the tortuosity factor. Molecular diffusion will be the the dominant transport mechanism whenever the mean free path of the gas (i.e., the average distance travelled between molecular collisions) is small relative to the pore diameter. However, in small pores and at low pressure the mean free path is greater than the pore diameter and collisions of molecules with the pore walls occur more frequently than collisions between

diffusing molecules. Under these conditions the collisions between molecules and pore walls provide the main diffusional resistance and we have what is known as Knudsen diffusion or Knudsen flow.

When a molecule strikes the pore wall, it does not bounce like a tennis ball. Rather the molecule is instantaneously adsorbed and re-emitted in a random direction. The direction in which the molecule is emitted bears no relation to its original direction before the collision and it is this randomness which provides the characteristic feature of a diffusive process.

The Knudsen diffusivity may be estimated from the expression

$$D_K = 9700 r (T/M)^{1/2} \quad (\text{cm}^2 \text{s}^{-1}) \quad (3.12)$$

where  $r$  is the mean pore radius (cm),  $T$  is in Kelvin, and  $M$  is the molecular weight of the diffusing species. It is evident that in the Knudsen regime each species diffuses independently so that the diffusivity does not depend on either composition or total gas concentration. The temperature dependence is slight and there is the usual inverse dependence on the square root of molecular weight.

#### c) Surface Diffusion

Both the Knudsen and molecular diffusion mechanisms involve flow through the gas phase within the pore. There is in addition the possibility of a direct contribution to the flux from transport through the physically adsorbed layer on the surface of the macropore, and this is referred to as "surface diffusion". Although the mobility of the adsorbed phase will generally be much smaller than that of the gas phase, the concentration is very much higher; so, under conditions such that the thickness of the adsorbed layer is appreciable, a significant contribution to the flux is

possible. Significant physical adsorption is thus seen as a prerequisite for the contribution from surface diffusion to be noticeable, and this requires temperatures not too far above the boiling point of the species considered. At high temperatures the thickness of the adsorbed layer decreases and any surface flux becomes small compared with the flux through the gas phase.

Direct measurement of surface diffusion is not feasible since the flux due to diffusion through the gas phase is always present in parallel. In order to study surface diffusion it is therefore necessary to eliminate the gas phase contribution. The normal procedure, which is illustrated by the study of Schneider and Smith (3), involves making measurements over a wide range of temperatures. The flux through the gas phase is determined from the high temperature measurements since under these conditions the surface flux can be neglected. The flux through the gas phase at the lower temperature is then found by extrapolation and subtracted from the measured flux in order to estimate the surface flux. Surface diffusion is significant only in small diameter pores in which the flux through the gas phase can generally be attributed entirely to Knudsen diffusion, and this simplifies considerably the extrapolation.

#### d) Poiseuille Flow

If there is a difference in total pressure across a particle, then there will be a direct contribution to the adsorption flux from forced laminar flow through the macropores. This effect is generally negligible in a packed bed since the pressure drop over an individual particle is very small. The effect may be of greater significance in the direct laboratory measurement of uptake rates in a vacuum system. From Poiseuille's equation it may

be shown that the equivalent diffusivity is given by

$$D = P r^2 / 8 \mu^2 \quad (3.13)$$

where  $P$  is the absolute pressure (dyne/cm<sup>2</sup>),  $\mu$  is the viscosity in poise, and  $r$  is the mean pore radius in cm. Any flux due to Poiseuille flow simply adds to the diffusional flux through the pore.

### 3.2.2 Micropore Diffusion

Intracrystalline or micropore diffusion is an activated process and the temperature dependence can generally be correlated by an Eyring equation:

$$D = D_0 \exp(-E/RT) \quad (3.14)$$

Micropore diffusion in zeolites and carbon molecular sieves has been widely studied. The subject has been reviewed by Barrer (20), Karger et al. (21), and Ruthven (17), but the picture presented by the published literature is confusing. Most of the earlier reported diffusivities were derived from uptake measurements and the extent to which uptake rates may be affected by extraneous heat and mass transfer resistances was not always fully appreciated. However, by the application of other experimental techniques such as chromatography and NMR methods as well as by more detailed adsorption rate measurements with larger zeolite crystals, the general features of the diffusional behavior have now been established for several systems.

### 3.3 Industrial Adsorbents

In principle, all microporous materials can be used as adsorbents for gas purification and separation. For example, bone chars, coal clays, calcined clays, activated carbon, inorganic gels such as silica gel and activated alumina, molecular sieve carbon and molecular sieve zeolite. Table 3.2 provides a perspective of the relative amounts used and the major gas separations performed in

Table 3.2 Applications and annual productions of major industrial sorbents.

<i>Sorbent</i>	<i>Annual U.S. Production<sup>a</sup></i>	<i>Major Uses for Gas Sorption</i>
Activated carbon	90,000 (major)	Removal of nonpolar gases and organic vapors (e.g., solvents, gasoline vapor, odors, toxic and radioactive gases); H <sub>2</sub> purification; etc.
Zeolites:		
Synthetic	30,000 <sup>b</sup> (major)	Drying; H <sub>2</sub> purification; air purification; air separation; separations based on molecular size and shape (e.g., <i>n</i> - and iso-paraffins, aromatics, etc.); gas chromatography
Natural	250,000 <sup>b</sup> (minor)	
Silica gel	150,000 (minor)	Drying; gas chromatography
Activated alumina	25,000 (major)	Drying; gas chromatography

<sup>a</sup>Late 1970s figure in metric tons. The fraction used as sorbent is indicated in parentheses.

<sup>b</sup>Worldwide total figure.

Table 3.3 Representative commercial gas-adsorption separations.

<i>Separation<sup>a</sup></i>	<i>Adsorbent</i>
I. Gas bulk separations	
Normal paraffins/iso-paraffins, aromatics	Zeolite
N <sub>2</sub> /O <sub>2</sub>	Zeolite
O <sub>2</sub> /N <sub>2</sub>	Carbon molecular-sieve
CO, CH <sub>4</sub> , CO <sub>2</sub> , N <sub>2</sub> , A, NH <sub>3</sub> /H <sub>2</sub>	Zeolite, activated carbon
Acetone/vent streams	Activated carbon
C <sub>2</sub> H <sub>4</sub> /vent streams	Activated carbon
Separation of perfume components	—
II. Gas purification	
H <sub>2</sub> O/olefin-containing cracked gas, natural gas, air, synthesis gas, etc.	Silica, alumina, zeolite
CO <sub>2</sub> /C <sub>2</sub> H <sub>4</sub> , natural gas, etc.	Zeolite
Organics/vent streams	Activated carbon, others
Sulfur compounds/natural gas, hydrogen, liquefied petroleum gas (LPG), etc.	Zeolite
Solvents/air	Activated carbon
Odors/air	Activated carbon
NO <sub>x</sub> /N <sub>2</sub>	Zeolite
SO <sub>2</sub> /vent streams	Zeolite
Hg/chlor-alkali cell gas effluent	Zeolite

<sup>a</sup>Adsorbates are listed first.

the industry. Some of the commercial adsorption separation processes are listed in Table 3.4 .

The most important characteristics of an adsorbent is its high porosity and surface area available for adsorption. For the activated carbon, silica gel, and molecular sieve materials, this high surface area is almost entirely internal, that is, within the gross structure of the adsorbent particle. This internal surface is available for adsorption through channels or pores penetrating the entire volume of the solid material. The external surface of the gross adsorbent particles makes only a very small contribution to the overall available surface area. Fig. 3.4 shows the pore size distribution of various adsorbents and also shows the "effective pore size", defined as the critical diameter of the largest molecule which can be enter the uniform pore system, of molecular sieve zeolite type 3A, 4A, 5A, 10X and 13X. The activated carbon, activated alumina, silica gel and also molecular sieve carbon have an amorphous structure with no definite pore size. The pore diameter distribution within the adsorbent particle may be fairly narrow, such as from 0 - 10 Å for a molecular sieve carbon, or may range from 20 to several thousand Angstroms for some activated carbon. The molecular sieve zeolites are crystalline and have pores of uniform size. These pores have diameters of molecular dimension and are capable of preventing molecules of greater than a certain critical diameter from entering the adsorbent and being adsorbed within the internal structure.

The selection of a proper adsorbent for a given separation is a complex problem. The predominant scientific basis for adsorbent selection is the equilibrium isotherm. The equilibrium isotherms of all constituents in the gas mixture, in the pressure and temperature range of operation, must be considered.

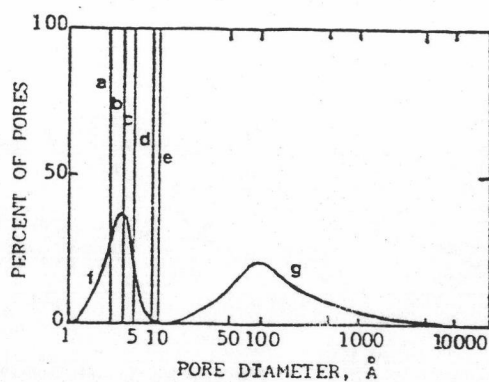


Fig. 3.2 Micropore size distribution of (a) Zeolite type 3A, (b) 4A, (c) 5A, (d) 10X, (e) 13X, (f) molecular-sieve carbon, and (g) activated carbon.

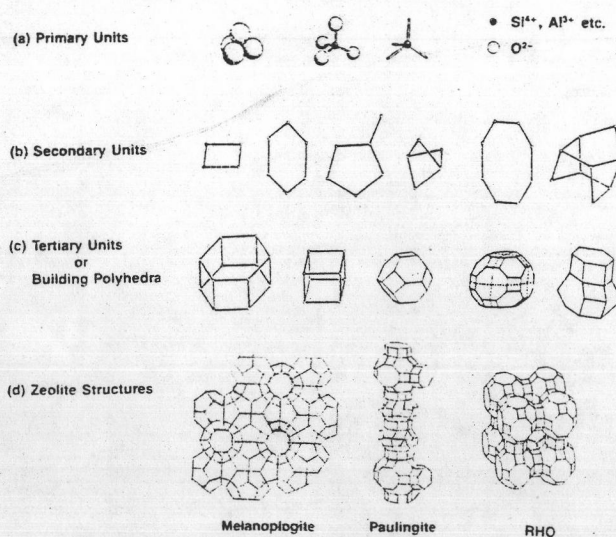


Fig. 3.3 Monomers (a) polymerize to low-molecular-weight rings and chains (b); in turn combine to form polyhedral units (c) or sheet structures. These (d) attach to growing crystal surfaces or first form clusters which subsequently agglomerate a larger crystal entities.

### 3.4 Zeolites (17)

Zeolites are porous crystalline aluminosilicates. The zeolite framework consists of an assemblage of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra, joined together in various regular arrangements through shared oxygen atoms (see Fig. 3.3), to form an open crystal lattice containing pores of molecular dimensions into which guest molecules can penetrate. Since the micropore structure is determined by the crystal lattice it is precisely uniform with no distribution of pore size. It is this feature which distinguishes the zeolites from the traditional microporous adsorbents.

As members of an unusual group of minerals, the naturally occurring crystalline zeolites have been known for many years, such as Chabazite, Erionite, Faujasite, Mordenite, Offretite, Sodalite, etc. Their chemical composition and, to a much lesser extent, their crystalline structure have been studied. They possessed the unusual ability of the dehydrated crystals to selectively adsorb molecules based on their physical size. However, all studies, and certainly any practical application of these materials, were seriously handicapped by the fact that these high-capacity and highly selective adsorbent zeolites occur only rarely in nature. Therefore, it was the extremely interesting physical properties of these zeolites, coupled with their scarcity in nature, which led several investigators to attempt to synthesize them. Barrer and his co-workers had been very active in the field of synthesizing zeolite adsorbents and studying and analyzing their physical properties.

#### 3.4.1 Zeolite A

The structure of zeolite A is shown schematically in Fig. 3.4. The sodium form of type A will exclude all molecules



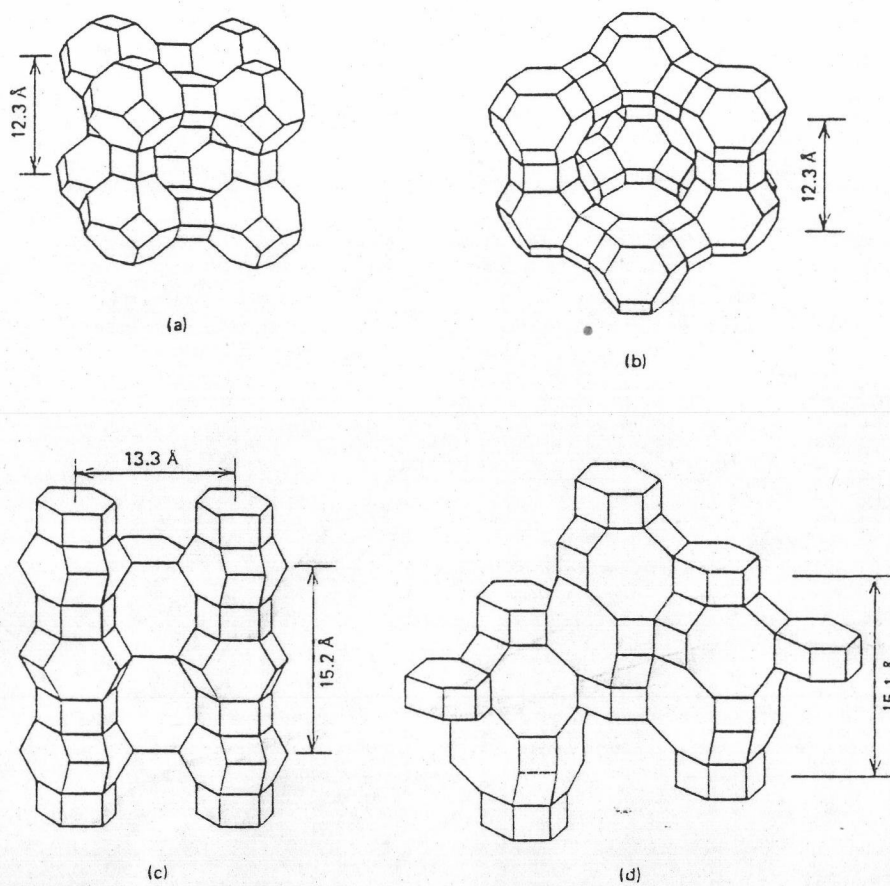


Fig. 3.4 Schematic representation showing framework structures of (a) Zeolite A, (b) Zeolite X and Y, (c) Erionite, and (d) Chabazite.

larger than about 4 Å in diameter and is, therefore, designated as molecular sieve type 4A. It will adsorb all the simple compounds, such as H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub>S, and hydrocarbon molecules containing less than three carbon atoms. By ion exchanging the sodium ions of the type 4A structure with calcium or magnesium cations, the sodium ions restricting the entrance of a molecule through the 8-membered oxygen ring are removed. As a result, only molecules larger than about 5 Å are excluded. If the sodium ions of the type 4A are replaced by potassium cations, the effective size of molecules that can be adsorbed is reduced. This is probably due to replacing the sodium ions adjacent to the 8-membered oxygen rings with larger potassium ions. The 3A sieve is widely used for drying reactive hydrocarbons such as olefins since the small pore size prevents penetrating of the lattice and thus the possibility of reaction.

#### 3.4.2 Zeolite X and Y

The synthetic zeolites X and Y and the natural zeolite Faujasite all have the same framework structure which is sketched in Fig. 3.5. The difference between the X and Y sieve lies in the Si/Al ratio which is within the range 1 - 1.5 for X and 1.5 - 3.0 for Y. The adsorptive properties of X and Y sieves may be greatly modified by ion exchange and improvements in selectivity can sometimes be obtained by using mixed cationic forms.

The sodium form of type X has been designated as type 13X and the calcium form as type 10X. The adsorption occurs through 12-membered oxygen rings which, in the case of the type 13X material, will pass molecules up to about 10 Å in diameter and, in the case of the type 10X material, will pass molecules of 9 Å diameter or less. The pores of these materials are of sufficient size so that,

in addition to those molecules adsorbed by type 5A, most of the other common chemical compounds can also be adsorbed, including isomeric paraffin, naphthenes, and aromatic hydrocarbons.