Drying of air by fixed bed adsorption using molecular sieves

James Irving Nutter
Iowa State University

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DRYING OF AIR
BY FIXED BED ADSORPTION
USING MOLECULAR SIEVES

by

James Irving Nutter

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Dean of Graduate College

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1963
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ABSTRACT

The rate of drying of air in a fixed bed of Type 4A molecular sieves was investigated. Exit air water content as a function of time was measured at several values of inlet concentration, flow rate, adsorbent particle size, fixed bed height and bed temperature.

The constant mass transfer zone independent of bed height method of data analysis was found to be applicable. A pore diffusion model was developed to describe the experimental breakthrough curve for water adsorption on Type 4A molecular sieves. Recommended design procedures and equations are given for adsorbers using molecular sieves. Published mass transfer coefficient and pore diffusion models were also found to be applicable over a considerable portion of the breakthrough curve.

Experimental mass transfer zone heights were obtained from the data of 83 breakthrough curve runs. Overall, solid-phase and gas-phase mass transfer coefficients, and pore and particle diffusivities were also determined. The data reported are useful for design purposes. Inlet concentration has a small but important effect on the overall and solid-phase mass transfer coefficients and on the particle diffusivities. Adsorbent particle size and shape influence the adsorption of water on molecular sieves to a large extent. The overall and solid-phase mass transfer
coefficients and the pore and particle diffusivities were essentially independent of flow rate. The pore diffusion model appears to be the best approximation of the mass transfer mechanism for water adsorption on Type 4A molecular sieves.

The ranges for the independent variables investigated were as follows: (1) air stream flow rate - 147 to 1131 lbs. dry air/hr. ft.$^2$, (2) bed temperature - 65 to 90°F., (3) inlet air water concentration - 0.00336 to 0.01870 lbs. H$_2$O/lb. dry air, (4) adsorbent particle size - 0.0195 to 0.110 inches, (5) fixed bed height - 1.156 to 2.158 feet, (6) initial water content of molecular sieves - zero, and (7) regeneration time and temperature - 24 hours at 650°F. with a continuous dry air purge. Only the first adsorption phase of a cyclic operation was studied. The adsorption was approximately carried out under isothermal and atmospheric pressure conditions.
NOMENCLATURE

MTZ the part of the fixed bed in which the water concentration change from $C_B$ to $C_E$ is occurring ($C_B$ and $C_E$ are arbitrarily chosen as $0.05C_o$ and $0.95C_o$ respectively)

$A_m$ cross-sectional area covered by one adsorbed molecule, ft.$^2$

$a_p$ surface area of particles, ft.$^2$/lb. solid

$A_x$ bed cross-sectional area, ft.$^2$

$C$ air stream water concentration at time $t$, lbs. $H_2O$/lb. dry air

$C^*$ air stream water content in equilibrium with $X^*$, lbs. $H_2O$/lb. dry air

$C_D$ concentration in air at point of discontinuity, lbs. $H_2O$/lb. dry air

$C_i$ concentration in air at the external surface of the particle, lbs. $H_2O$/lb. dry air

$C_o$ inlet air water concentration, lbs. $H_2O$/lb. dry air

$C_r$ concentration in the fluid phase inside a particle at radius $r$, lbs. $H_2O$/lb. dry air

$d_p$ arithmetic mean particle diameter, feet

$d_{pore}$ pore diameter, feet

$D$ distribution ratio (see equation 27)

$D$ diffusivity, ft.$^2$/hr.
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<tr>
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<th>Definition</th>
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<tr>
<td>D_p</td>
<td>particle phase diffusivity, ft.²/hr.</td>
</tr>
<tr>
<td>D_pore</td>
<td>fluid phase pore diffusivity, ft.²/hr.</td>
</tr>
<tr>
<td>f</td>
<td>fractional ability of adsorbent in MTZ to still adsorb water</td>
</tr>
<tr>
<td>G</td>
<td>mass flow rate of air per unit bed cross-section, lbs. dry air/hr. ft.²</td>
</tr>
<tr>
<td>G'</td>
<td>mass flow rate of air, lbs. dry air/hr.</td>
</tr>
<tr>
<td>G''</td>
<td>lbs. dry air/min.</td>
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<tr>
<td>Δ_H</td>
<td>differential heat of adsorption, BTU/lb. mole</td>
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<tr>
<td>H.T.U.</td>
<td>height of a transfer unit, feet (see equations 26 and 33)</td>
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<tr>
<td>k_g</td>
<td>gas film mass transfer coefficient, lbs. H₂O adsorbed/hr. ft.² X-units</td>
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<tr>
<td>k_s</td>
<td>solid phase mass transfer coefficient, lbs. H₂O adsorbed/hr. ft.² X-units</td>
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<td>K,K_g,K_s</td>
<td>overall mass transfer coefficient, hrs.⁻¹ (subscripts s and g refer to solid-phase and gas phase respectively)</td>
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<td>M</td>
<td>molecular weight</td>
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<tr>
<td>m</td>
<td>amount of void space between particles, lbs. dry air/lb. dry solid</td>
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<td>N,N_g,N_s</td>
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<td>$N_R$</td>
<td>number of apparent reaction units (see equation 25)</td>
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<td>$N_{MTZ}$</td>
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<td>$p$</td>
<td>adsorbate vapor pressure, mm. Hg</td>
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<td>gas constant</td>
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<td>$r^*$</td>
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<td>$r_c$</td>
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<td>$r_p$</td>
<td>outer radius of adsorbent particle, feet</td>
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<tr>
<td>$S$</td>
<td>specific adsorption surface, ft.$^2$/lb. adsorbent</td>
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<tr>
<td>$S_o$</td>
<td>adsorbent mass flow rate, lbs. solid/hr. ft.$^2$</td>
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<tr>
<td>$T$</td>
<td>absolute temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>time, hours</td>
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<tr>
<td>$t_B$</td>
<td>time of appearance of breakthrough point, hours</td>
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<tr>
<td>$t_E$</td>
<td>time required for MTZ to establish itself and move out of the fixed bed, and the time of appearance of bed saturation point, hours</td>
</tr>
<tr>
<td>$t_{MTZ}$</td>
<td>time required for MTZ to establish itself and move its own length down the column, hours (e.g. $T_{MTZ} = t_E - t_B$)</td>
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<tr>
<td>$U$</td>
<td>area under breakthrough curve from $W_B$ to $W_E$</td>
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<tr>
<td>$V_m$</td>
<td>volume of adsorbate molecules/mole</td>
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<tr>
<td>$V_p$</td>
<td>internal pore volume of adsorbent, ft.$^3$/lb. ad-</td>
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sorbent

\( v \)  fixed bed volume, \( \text{ft.}^3 \)

\( W \)  cumulative dry air passed up to time \( t \), lbs. dry air

\( W_c \)  material balance corrected cumulative dry air passed, lbs. dry air

\( W_B \)  cumulative dry air passed up to breakthrough point, lbs. dry air

\( W_E \)  cumulative dry air passed up to bed saturation point, lbs. dry air

\( W_{MTZ} \)  total air accumulated during breakthrough curve period, lbs. dry air (e.g. \( W_{MTZ} = W_E - W_B \))

\( W_s \)  weight of adsorbent in fixed bed, lbs. dry solid

\( X \)  water content of adsorbent at time \( t \), lbs. \( \text{H}_2\text{O}/\text{lb. solid} \)

\( X^* \)  water content of adsorbent in equilibrium with \( C^* \), lbs. \( \text{H}_2\text{O}/\text{lb. solid} \)

\( X^*_o \)  water content of adsorbent in equilibrium with \( C_o \), lbs. \( \text{H}_2\text{O}/\text{lb. solid} \)

\( X^*_s \)  water content of adsorbent in equilibrium with saturated air at temperature \( T \), lbs. \( \text{H}_2\text{O}/\text{lb. solid} \)

\( X_i \)  water content of adsorbent at external surface, or interface, lbs. \( \text{H}_2\text{O}/\text{lb. solid} \)

\( X_m \)  monolayer capacity of the adsorbent, lbs. \( \text{H}_2\text{O}/\text{lb. solid} \)

\( X_p \)  Average water content of entire adsorbent particle
at time $t$, lbs. $H_2O/lb.$ solid

$X_r$ average water content of adsorbent at penetration to radius $r$ inside the particle, lbs. $H_2O/lb.$ solid

$Z$ height of fixed bed, feet

$Z_{MTZ}$ that part of fixed bed in which the water concentration change from $C_B$ to $C_E$ is occurring, feet ($C_B$ and $C_E$ are arbitrarily chosen as $0.05C_0$ and $0.95C_0$ respectively)

$Z_p$ throughput ratio (see equation 28)

$\infty$ intercept value of $X*$ for linear isotherm approximation, lbs. $H_2O/lb.$ solid

$\rho_g$ density of dry air, lbs./ft.$^3$

$\rho_L$ density of condensed vapor, lbs./ft.$^3$

$\rho_b$ bulk packed density of dry adsorbent, lbs./ft.$^3$

$\gamma_T$ surface tension of the condensed vapor

$\theta$ contact angle

$\pi$ pi

$S$ mechanism parameter (see equation 29)

$\epsilon$ bed void volume fraction, ft.$^3$ of voids/ft.$^3$ of bed

$\chi$ fractional internal porosity of the particles
INTRODUCTION

Nature of Problem

Considerable attention has been given to the study of adsorption, but recent developments in the production and in the use of adsorbents have greatly increased the necessity of finding simple and dependable design procedures. One such procedure is the mass transfer zone (MTZ) method described by Treybal (103) in which an adsorption zone of constant length and shape independent of fixed bed height is considered. It is the purpose of this work to extend application of the mass transfer zone design method by investigating fixed bed air drying with molecular sieves.

The air-water-molecular sieve system was used because there are many important uses for dry air in industry. Some typical applications are industrial air conditioning, wind tunnels, food packaging, electronics, liquid air manufacture, and metallurgical processes.

The most common method for drying air when low water contents are required is to pass the air through a fixed bed of adsorbent. Owing to the inconvenience and difficulty of handling solids, fixed beds are frequently found more economical and easier to construct and operate than moving or fluidized bed units.

The design of fixed bed processes, unfortunately, is complicated as a theoretical analysis of the operation will
show. The application of known heat and mass transfer concepts is limited or restricted by the following: (1) the dependence of process variables upon time, position in the bed, and position within the bed particles, (2) the irregular shape of the particles, and (3) the very meager knowledge of the exact mechanisms involved in adsorption.

The unit operation of adsorption is similar to the more familiar unit operations of gas adsorption and solvent extraction, but usually differs in one important respect. The latter are generally carried out in continuous countercurrent operations, whereas adsorption is most usually carried out in batch, fixed bed equipment. The unsteady state nature of the batch operation complicates the interpretation of the transfer mechanisms involved.

**Description of process and definition of terms**

As increasing amounts of constant water content air are passed through a fixed bed of regenerated adsorbent, increasing amounts of water are adsorbed by the porous solid from the air stream and an unsteady state operation prevails. The dynamic nature of the adsorption process can be shown as follows. Consider an isothermally maintained fixed bed of molecular sieves, Z feet in height, with the moist air stream entering at the top and the dry air leaving at the bottom. The dew point of the entering air stream, for example, is 60°F. Figure 1 shows some of the conditions in
Figure 1. Fixed bed adsorption conditions during operations
I — Air phase dew-point curve

II — Dew point curve of air phase in equilibrium with bed
the bed during operation.

At the start of the operation the entire bed has been regenerated to a residual water content which is in equilibrium with air of -50°F. dew point. As the inlet air with a dew point of 60°F. enters the bed, the first volume of it is quickly dried to a dew point of -50°F. in the upper part of the bed and passes down through the bed in equilibrium with it. With more and more air passing through the bed, the upper zone, which has adsorbed water until it is in equilibrium with the entering air, becomes deeper and deeper until some water has been adsorbed by the lowest layer of the bed and the exit air has a dew point just greater than -50°F. Commercial fixed beds are usually designed for 80% saturation with respect to air of 60°F. dew point at the end of the adsorption phase of the process.

At this point it is necessary to note some of the important aspects of the fixed bed adsorption process used in industry. Generally the operation of drying the air is carried out until an increase in the exit air dew point is noticed; then the operation is stopped, and the entire fixed bed regenerated to a residual water content that is in equilibrium with air of low dew point (e.g. -50°F.), before the sequence is repeated. Thus, one has the minimum dew point (-50°F.), the time of breakthrough (point where the exit air dew point just rises above -50°F.), and the average
saturation of the entire bed at breakthrough as the important considerations for operation and design of fixed beds. Note also that the "S-shaped" wave of the air phase (Figure 1) moves downward through the bed with time of operation and is still within the bed at the end of the operation.

Recapitulating, during operation the fixed bed consists of three zones, namely, (1) a zone at the inlet end of the fixed bed where the adsorbent has become saturated and is in equilibrium with the moist inlet air stream, (2) a zone at the exit air end of the fixed bed where the dry air is in equilibrium with the regenerated adsorbent, and (3) a mass transfer zone (MTZ) between the equilibrium zones in which the air stream water concentration is falling.

The time at which the exit air water content increases to some arbitrarily chosen low value is called the breakthrough point \(t_B\). Similarly, the time at which the exit air water content reaches some arbitrarily chosen value close to the value of the inlet air water content is known as the bed exhaustion point \(t_F\). The plot of exit air water content \(C\) versus time \(t\) or cumulative weight of water-free air \(W\) is generally referred to as the breakthrough curve. A breakthrough curve with the breakthrough and bed exhaustion points is shown in Figure 2.

The exit air water concentration defining the breakthrough point is very often not stated because the water
Figure 2. Representative breakthrough curve
Ratio of water content of exit to inlet air, \( \frac{C}{C_0} \)

- Time
- Cumulative dry air weight

Graph showing the ratio of water content over time, with specific points and cumulative dry air weight.
content increase at this point is rapid enough that very little error results by not specifying exactly what value applies. The length of the mass transfer zone is also not defined exactly because, although at a specified moment most of the mass transfer takes place in a relatively narrow zone, there is actually no point in the bed where absolutely no mass transfer is occurring. However, since a simple and dependable design procedure is the main objective of the MTZ method, consistent, definite positions for the breakthrough point and the bed exhaustion point are necessary.

The trend at present is to use the 5% value of the total concentration range to designate the breakthrough point, and the 95% value of the total concentration range to designate the bed exhaustion point. This enables one to define the length of the mass transfer zone as the time difference \( t_E - t_B \) or the cumulative dry air weight difference \( W_E - W_B \) between the appearance of the breakthrough point and the appearance of the bed exhaustion point. These positions are shown for the breakthrough curve in Figure 2. The ratio of the water content of exit to inlet air is the parameter generally used to present effluent water concentrations. The shape and the length of the mass transfer zone and the time of appearance of the breakthrough curve influence greatly the design and operating characteristics of a fixed bed adsorber for a particular application.
Scope of this research

In this research the adsorption of water from air on fixed beds of molecular sieves was studied. The important objectives of this research were to obtain kinetic data in the form of breakthrough curves, and to develop suitable mathematical treatments that interpreted these breakthrough curves in terms of the fundamental concepts of equilibrium and kinetic processes. The results were then utilized in the simple MTZ design procedure for fixed bed adsorption processes.

The fundamental tenets of this research were as follows: (1) to establish a suitable adsorption mechanism and rate expression for the air-water-molecular sieve system that were not only simple but also closely analogous to the actual adsorption situation; (2) to develop a mathematical model that correctly expressed the exit air water concentration as a function of time for isothermal fixed bed conditions, (this was accomplished by a breakdown of the adsorption problem into a series of steps that can be handled easily through the fundamental concepts of diffusional or kinetic processes and well-tested methods such as are employed in gas adsorption, ion exchange, dialysis, and extraction processes); (3) to establish the necessary complimentary conditions such as the limitations of the model, the variations of the constants employed in the model with the
independent variables or process operating conditions, and possibly assess the effects of scale-up, adsorbent poisoning, or loss of adsorbing power on the use of the model in design; and (4) to completely verify or establish the adsorption mechanism assumed and the mathematical model by a comprehensive correlation study with experimental breakthrough curves.

The most important independent variables were considered to be: (1) structure of adsorbent, (2) particle size and shape of adsorbent, (3) air stream flow rate, (4) inlet air water concentration, (5) water concentration in the adsorbent if the latter has not been fully regenerated, (6) bed temperature, (7) bed pressure, and (8) size and shape of the fixed bed.

Molecular sieve adsorbent was used in the experimental work to develop and extend application of the isothermal mass transfer zone (MTZ) method of fixed bed design. The adsorption of water on silica gel was studied only to the extent of duplicating past research work with the present experimental apparatus.
REVIEW OF LITERATURE

Theory and Physical Properties of Adsorbents

In this section the theory of adsorption of gases or vapors on solids is summarized. This theory covers only the micro-scale or surface chemistry approach to the adsorption problem. The development includes adsorbent structure, adsorption mechanisms, surfaces, equilibrium, material balance, kinetics, and the assumptions generally made to properly confine the investigations. Data and physical properties of adsorbents pertinent to the sub-sections are also included.

Adsorbent structure and adsorption mechanisms

Adsorption occurs as a result of the interaction between the field of force at the surface of the solid and that emanating from the molecule of the gas or vapor which is to be adsorbed. Surface properties and forces need to be identified and described for different adsorbents. Knowledge of the adsorbent structure is therefore of prime importance. Since in general a solid is in contact with a gas, a liquid, or another solid, it is more precise to use the term interface - between the solid and the other phase - instead of surface. The forces of attraction involved in the adsorption of a gas or vapor are of two kinds: physical and chemical. These give rise to physical adsorption and to chemisorption respectively. In water adsorption on the cur-
rent commercial adsorbents physical or van der Waals adsorption generally occurs as will be apparent later.

The structure of zeolites (the Linde Company's synthetic zeolites are called molecular sieves) has been intensively studied during the last 25 years. There some 40 kinds of zeolites each with its own crystal structure (10, 23). Using the zeolite studies of Barrer (10), the Linde Company researchers set out in 1948 to produce synthetic zeolites and to determine their potential in the separation of atmospheric gases. By 1952 they had produced many types of synthetic zeolites and found one of these, which they called Type A, to be most useful in the separation work. This was introduced commercially in 1954.

The "building blocks" of all zeolites are tetrahedra of four oxygen ions surrounding a silicon or aluminum ion (23). The silicon ion's four positive charges cancel half the charge on each oxygen ion. The remaining charge on each oxygen ion combines with another silicon or aluminum ion. Since aluminum ions have only three positive charges, another positive ion is required which generally attaches loosely to an oxygen at a corner of the tetrahedra. Chabazite is a common natural zeolite with adsorbing characteristics similar to Type A molecular sieves, and whose structure was determined at Pennsylvania State University (23). It has six silicon and aluminum ions, with their as-
sociated oxygens, in a tight hexagon. Two tight hexagons, face to face, form a prism. Eight of these prisms then link together partially enclosing a central cavity whose longest diameter is about 11 Å. This structure is shown in Figure 3. Each cavity connects with six adjacent cavities through apertures about 3.1 to 3.3 Å in diameter (22). The number of atoms per cc. is $3.0 \times 10^{22}$ (11).

The structure of the Linde Company's Type A molecular sieve is similarly developed as shown in Figure 4. The aluminosilicate framework is based on units containing four AlO$_4$ and four SiO$_4$ tetrahedra in a rigid group. These units link together to form a ring of eight oxygen atoms in the center of each face of the cubical unit cell, and a ring of six oxygen atoms at each corner on the 3-fold axis (22). The cubical unit cell dimension is 12.32 Å (53). 4.2 Å diam. pores, formed by the 8-oxygen rings, open into 11.4 Å diam. central cavities. In addition each large cavity is connected to eight small cavities 6.6 Å in diameter through 2.0 Å diam. pores which are formed by the 6-oxygen rings (22). Thus, there are two interconnecting pore systems, one consisting of 11.4 Å diam. cavities separated by 4.2 Å diam. openings, and the other 11.4 Å diam. cavities alternating with 6.6 Å diam. cavities and separated by 2.0 Å diam. openings.

In the dehydrated unit cell, sodium ions (for Type 4A)
Figure 3. Cell structure of the natural zeolite chabazite (33)
Figure 4. Cell structure of Type 4A molecular sieves (23)

Rough shape of aperture as shown by outlines of oxygen ions

Sodium ion
occupy positions in the center of the 6-oxygen rings. During water adsorption these ions may shift to permit passage of water molecules through the 2.0 Å diam. openings (22). Four remaining sodium ions in the unit cell are in or near the 4.2 Å diam. openings, and determine the "effective pore" diameter. These ions are partially blocking the openings, and give a free diameter of 3.5 Å and an effective diameter of 4.0 Å due to the pulsating nature of the atoms in the crystal and in the molecules passing through the openings (53). For comparison purposes the molecular diameter of water is about 3.15 Å (22). The void volume of each unit cell consists of a 775 Å³ cavity and a 157 Å³ cavity (92). Reed and Breck (92) calculated a saturation adsorption volume for water of 833 Å³ per unit cell. This suggested that the water molecules can enter both cavities.

The structural formula for the Type A molecular sieves is: \( \text{Me}_{12/n}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \cdot n \text{H}_2\text{O} \), where \( \text{Me} \) represents exchangeable cations of charge \( n \) (22,53). The Linde Company's Type A molecular sieve is precipitated in a hydrothermal process as a fine white powder with a particle size range of 1 to 5 microns and an average size of 2 microns (22, 53). The powder is bonded with 20 percent inert clay and extruded as 1/16 and 1/8 inch diameter pellets or formed into roughly spherical beads, usually 4 to 12 mesh in size. The adsorbent is readied for use by activating with heat to
drive off the water of crystallization.

The Linde Company's molecular sieves have such a high affinity for water that they can reduce the proportion of water in a gas or liquid to a fraction of a part per million. Type A molecular sieves have been discussed extensively at this time because they are used almost exclusively in this research. The most recent physical properties can be obtained from the manufacturer's literature (77).

The Davison Chemical Division of W. R. Grace and Company has recently marketed and has given data for an identical zeolite product called microtraps (31).

Silica gel has been described and discussed by Dehler (32). The internal structure of this adsorbent has not been determined, although molecules up to 22 Å in diameter have been adsorbed.

Honig (62) classifies the forces bringing about physical adsorption as those associated with (1) permanent dipole moments in the adsorbed molecule, (2) polarization (distortion of the charge distribution within the adsorbed molecule), (3) dispersion effects, and (4) short range repulsive effects. If the adsorbent is an ionic solid, it will give rise to an electrostatic field which will be superimposed on that produced by the dispersion forces. This electric field only becomes useful through its effect on a charge or charges in the adsorbed molecule. If the molecule has a
permanent dipole moment the necessary charges are present already, whereas if the molecule is non-polar, the electrostatic field will be able to induce a weak dipole in it. For non-polar adsorbed molecules the magnitude of the adsorption potential will depend on the polarizability of the molecule. Dispersion forces are caused by the fluctuating electrical moment produced by the movement of electrons in their orbits. This moment induces a corresponding moment in an adjacent atom or ion, and thus leads to the attraction dispersion forces.

The predominant adsorption mechanism forces for non-polar molecules are the dispersion forces since polarization effects are usually small (62). For polar molecules the total adsorption potential is the sum of the electrostatic and dispersion forces, with the electrostatic contribution sometimes equal to or even exceeding that from the dispersion forces (18).

Benson et al. (17) point out that the negative ions, being the larger in an ionic adsorbent, are more polarizable. When an electrical dipole is set up within these ions, the positive charge of the dipole is repelled from that of the cation (usually a small ion) which is assumed to be negligibly polarized. This effect has been noted for the metallic oxides such as silica and alumina (110). The surfaces of these compounds consist largely of negative charges, the
positive ions being screened by the oxygen ions. Young et al. (112) found that oxygenated surface complexes are required for appreciable water adsorption. Heats of immersion experiments offer some evidence that the fields produced by different oxides are very similar in magnitude (50).

Now with a largely polar surface such as that of the zeolites one can easily see the importance of polarity in the molecules to be adsorbed. Zeolites will adsorb water in preference to any other substance (22, 23). The asymmetrical structure of the water molecule gives this electrically neutral molecule a partial positive charge on one side and a partial negative charge on the other (18, 23). Water vapor has a permanent dipole moment of $1.85 \times 10^{-18}$ esu; therefore it has the required charges to make the electrostatic field of an ionic adsorbent useful (61). Thus the highly polar water molecules are attracted to the partial charges on the inner surfaces of the zeolite cavities.

In summary the adsorbent structure of zeolites permits, first separation of molecules of different sizes, then segregation of molecules of the same size but different electrical properties. Separation occurs first by the different molecular diameters - molecules smaller than the "effective pore" diameter pass through the openings, and then preferential adsorption occurs on the internal surfaces in the order of a molecule's polarity or adsorption potential.
Arbitrarily the external surface of a solid adsorbent is taken to include the surface of all the prominences, and all the cracks which are wider than they are deep; the internal surface then comprises the walls of all cracks, pores and cavities which are deeper than they are wide (50). The term internal surface is usually confined to those cavities and channels which have openings to the exterior of the solid (e.g., sealed off pores are not included).

The properties of solids that are mainly a function of external surface are: particle size and shape, size distribution, bed porosity, and bulk density. Relationships such as those between total volume and total surface, and between porosity and particle size and shape are important.

The properties of solids that are mainly a function of internal surface are: density, pore structure, pore volume, pore size distribution, and volume to surface ratios. Density is the more important and four types may be distinguished, namely, bulk, granule, apparent solid, and true solid density, depending on amount of internal surface.

Since all the adsorbate is contained in the central cavities of the Linde Company's molecular sieves, they have dry external surfaces at saturation in gas drying, and thus can be handled in a free flowing manner. Adsorption on the outside surface areas of silica gel has also been proven negligi-
gible compared to the much greater adsorption on inside surface areas (32).

**Equilibrium and minimum dew-point**

Since an understanding of the mechanism of adsorption involves equilibria, a discussion of this phenomena is in order. The amount of gas or vapor adsorbed by a given adsorbent depends not only on the vapor pressure (p) but also on the temperature (T), the nature of the gas, and the nature of the solid. Thus one has: \( X^* = f(p, T, \text{gas}, \text{solid}) \).

An adsorption isotherm usually is a set of data representing measurement at constant temperature of the quantities of water (\( X^* \)) adsorbed by a unit of adsorbent when in equilibrium with each of a number of different concentrations (p or \( C^* \)) in a gas phase.

Graphic plots of adsorption isotherms take a wide variety of shapes. Some that have been qualitatively classified are shown in Figure 5 (26, 44, 48). Type B is characteristic of adsorbents whose pores are so small that there is space for only one molecular layer on the walls. This type usually conforms to the Langmuir (71) equilibrium concept and may represent favorable equilibrium. Glueckauf (44) refers to this isotherm as a "self-sharpening", concave-toward-the-gas-concentration-axis type. Pierce et al. (90) have recently questioned the small pore and monolayer interpretation of type B isotherms and have presented a capillary
Figure 5. Typical equilibrium adsorption isotherms
Water content of solid, \( X^* \)

Air phase water content, \( C^* \)

A Irreversible
B Self-sharpening
C Linear not through origin
D Linear
E Self-diffusing
F Multilayer
G Self-diffusing + multilayer
H Pore filling + multilayer
I Self-diffusing + pore filling
condensation concept. Type F has the top part of the isotherm modified by multilayer adsorption; the bottom part is similar to type B.

Type H is similar to type F except that it shows saturation or filling of pore spaces at high coverage. Type E isotherms are rare and occur when the initial adsorption favors a few very strong sites and interaction between adsorbed molecules is very strong (types G and I are similar). These types may represent unfavorable equilibrium and are sometimes referred to as the "self-diffusing" types (44).

Much work has been done recently in chromatography to interpret chromatogram behavior in terms of the adsorption isotherms (45, 46, 47, 50, 104). Adsorption isotherms can be calculated from chromatograms, and specific chromatogram behavior has been associated with the different isotherm types given in Figure 5 (43, 44).

Many analytical representations of these isotherms have been presented. Possibly the best known is that of Langmuir (71) for the so-called "ideal system" in which all adsorbent sites are identical and there is no interaction between molecules on adjacent sites. The Langmuir theory suggests that the equilibrium set up between the adsorbed monolayer gas and the adsorbent is a dynamic one; where the rate at which molecules condense on the bare sites of the adsorbent surface is equated to the rate at which they re-evaporate from
the occupied sites. The Langmuir isotherm (71) relationship is:

\[
\frac{X^*}{X_m} = \frac{B_p}{1 + B_p}
\]  

(1)

where:

\(X_m\) = monolayer adsorbent capacity

\(B\) = a temperature dependent constant characteristic of the adsorbate

Gas phase concentrations (\(C^*\)) can be used in place of the vapor pressure (\(p\)). The graph of this equation has the general shape of a type B isotherm. As the value of the constant \(B\) is increased (by increasing the heat of adsorption) the bend in the isotherm is sharpened and moved closer to the solid concentration axis.

Although the Langmuir relationship provides a useful standard of ideality for theoretical study, equilibria in real systems are often expressed better by the Freundlich or classical isotherm (48). This isotherm is represented by:

\[
X^* = m C^{1/n}
\]  

(2)

where:

\(m\) = a constant

\(n\) = a constant greater than unity

This classical isotherm originally was empirical, but has since been derived by a suitable site distribution treatment
that assumed no appreciable interaction between adsorbed molecules (98).

Multilayer adsorption is best represented by the Brunauer, Emmett, and Teller (27) equation (B.E.T. equation), and similar equations developed from the theories advanced by Polanyi (91) based on the concept of adsorption potential. The B.E.T. equation with certain modifications (26) can qualitatively reproduce types B, E, F, G and H isotherms (Figure 5), but oversimplification in the basic assumptions limits its general quantitative application (48). This theory retains the concept of fixed adsorption sites, but allows for the formation of an adsorbed layer more than one molecule thick; the state of "dynamic equilibrium" postulated by Langmuir for his monolayer is assumed to hold for each successive molecular layer. The B.E.T. equation takes the following form (26):

\[
\frac{p}{X^*(p_S - p)} = \frac{1}{X_m b} + \frac{(b - 1)p}{X_m b p_S}
\]

where \( b \) is a constant. The quantitative failure of this equation and the Langmuir isotherm (type B) is attributed to surface non-uniformity (i.e., variation in the site activation energies) (26, 27).

Theoretical descriptions of the minimum dew-point phenomenon have not been explicitly developed in the literature. Basic theories of equilibrium phenomenon and surface activ-
ity may be applicable.

The Linde Company's water and air data sheets (78) give the latest equilibrium and minimum dew-point data for all types and particle sizes of their molecular sieves. These data cover the temperature range of 0°C. to 350°C., water vapor pressures of 0 to 500 mm. Hg, and minimum dew-points down to -150°F. All molecular sieve isotherms show strongly favorable or extremely "self-sharpening" characteristics (type B isotherm, Figure 5). The Linde Company also supplies equilibrium data for some other adsorbates (75, 76).

The equilibrium relationships for silica gel have been quite extensively studied. An S-shaped equilibrium curve was found by all investigators. Eagleton (35) presented equilibrium data which showed "self-sharpening" type curvature from 0 to 10 and 95 to 100 percent relative humidities. Hubard (64) presented equilibrium data for silica gel covering the temperature range of 40°F. to 200°F. Dehler (32) presented data below these temperatures down to 0°F. Minimum dew-points for silica gel are available in the data of Maslan (80) and Eagleton (35).

The surface chemistry of adsorption

In order to be able to understand and predict the behavior of adsorbed substances it is necessary to be able to interpret the adsorption isotherm, to determine the surface areas of porous solids, and to gain insight as to the state
of the molecules in the adsorbed layer. For the latter, one
would like to know whether the molecules are fixed or mobile
and whether they behave similarly to, or differently from
the molecules in the bulk fluid.

Most adsorption theories are based on a description of
the adsorbed layer as monomolecular at low concentrations
and becoming multilayer as the concentration increases to­
ward saturation. The theories differ in the assumptions
made as to the condition of the adsorbate in the layer.

Theories developed using the kinetic approach of
Langmuir (71) direct attention to the process of interchange
between the gas and the adsorbed layer. These theories
usually assume fixed adsorption sites and negligible attrac­
tion forces in the adsorbate in directions parallel to the
adsorption surface. Theories developed using thermodynamic
viewpoints, call attention to the gas-solid interface, and
are concerned with the reduction in the surface free energy
of the adsorbent during adsorption (65, 67). The reduction
is usually termed the spreading pressure or surface pressure
of the adsorbing film. These thermodynamic based theories
assume that the molecules possess mobility along the adsorb­
ent surface and that the attraction forces between the ad­
sorbed molecules are of equal importance. The capillary
condensation theory describes the adsorbate as condensing to
an ordinary liquid in the pores of the solid, usually after
the walls of the pores have become lined with an adsorbed monolayer (30, 38). The last theory is the more important for molecular sieve adsorption.

Two interrelated quantities – monolayer capacity \( X_m \) of an adsorbent, and the cross-sectional area of the molecule \( A_m \) in the completed monomolecular layer – are important in a discussion of the above theories. The relation between monolayer capacity and the specific adsorption surface \( S \) of the adsorbent is given by (50):

\[
S = \frac{X_m N_A A_m}{M}
\]

where \( N_A \) is Avogadro's number. The numerical value of \( A_m \) depends on the way in which the molecules are packed on the surface in the completed monomolecular layer. The range of values determined for water is 10.8 to 14.8 Å² per molecule at 25°C. (56, 79).

The kinetic or "dynamic equilibrium" theories were discussed under equilibrium. The monomolecular capacity \( X_m \) of and adsorbent is shown to be an integral part of the adsorption isotherm interpretation. The internal physical structure of molecular sieves essentially limits water adsorption to a monolayer.

Thermodynamic principles and arguments are used throughout the last two groups of theories. A great amount of emphasis has been placed upon the entropy of adsorption
in the attempts to determine the condition of the adsorbate in the adsorbed layer. Entropy data has confirmed the validity of the B.E.T. method for determination of monolayer capacity (hence internal surface area) by adsorption of nitrogen (60). de Boer and Kruyer (19) have given localized film and mobile film models of adsorbed layer behavior, and have calculated entropies for the various mobility factors presented in each model. Gregg (50) points out that mobile films are favored when experimental and theoretical entropy values are compared. Drain and Morrison's (34) results show that adsorbed phase and liquid state entropies are very close after a three molecular layer.

Surface pressure or spreading pressure is defined as the difference between the free energy required to form a new surface in a vacuum and the free energy required to form a new surface in the presence of an adsorbed gas, if the molecules in the adsorbed film are mobile (65). An important relationship, used for evaluating the surface free energy reductions caused by adsorbed films, is the Gibbs adsorption equation. Hill (59) and Adamson (3) present and discuss this equation. The surface pressure can be evaluated from the adsorption isotherm by use of the Gibbs adsorption equation (9). At present the various surface pressures for an adsorbed film are studied to determine the conformity of adsorbed layer equations of state to experi-
mental data, or to determine the adsorption temperatures where condensation may occur (66, 67).

The capillary condensation theory was proposed originally in an attempt to explain the hysteresis loop in type H isotherms (113). Type H isotherms characterize porous solids like silica gel and activated alumina. The theory postulates that the adsorbed vapor is condensed to an ordinary liquid condition in all the pores of an adsorbent less than the capillary radius ($r_c$). This capillary radius ($r_c$) is calculated by the Kelvin equation which has the form (113):

$$\ln \frac{p}{p_s} = - \frac{2 V_m}{r_c RT} \cos \theta$$

(5)

In the derivation of the Kelvin equation the diameter of a molecule is assumed negligible in comparison to the capillary radius (77). Since the capillary radius is commonly of the order of 10 to 20 Å, some doubt has been raised as to the validity of using the standard surface tension and hemispherical meniscus concepts (77).

Evidence for the theory is found in the fact that the total volume of the adsorbed layer, calculated as a liquid for pressures near saturation, is nearly the same for a number of different vapors on a given adsorbent (50). This effect is termed the Gurvitsch rule, and is used in pore volume ($V_p$) determinations (50) by the equation:

$$V_p = \frac{X_s}{\varepsilon_L}$$

(6)
Studies of the melting point of an adsorbed film of water on silica gel gave evidence that the film is not completely identical in properties with ordinary water (82). In this work the vapor pressure curve of the adsorbed water showed no break at 0°C, and also none down to -65°C.

Pierce et al. (90) have contested the Langmuir monolayer concept of type B isotherms and have given some evidence that capillary condensation is occurring even in the steeply rising part of the isotherm. Gregg and Stock (52) recently have given similar evidence.

The behavior of a liquid on a solid is characterized by a quantity called the contact angle (θ). A contact angle of zero implies complete wetting of the solid by the liquid, a value of θ = 180° corresponds to absolute non-wetting. An expression for θ for use in the Kelvin equation may be derived in terms of interfacial tensions or in terms of interfacial surface energies (3).

If a substance possesses a fine enough microporous structure to resist gas or vapor flow, it represents a capillary system with sufficient adsorptive capacity to cause adsorbed or surface flow (68). According to Kammermeyer and Rutz (68) some condensed flow occurs for barriers containing 40 to 50 Å diameter pores and less. These researchers found in their gaseous diffusion work that the amount of condensed flow does not increase with increasing pressure although the
amount adsorbed does increase. They speculated that as more of the adsorbed material spreads to cover the surface or widen the flow channels at various locations, more of the surface flow is used up to fill a number of pools and dead-ends in the structure, and thus gives no increase in total flow. Presently, it is common practice to determine the amount of surface flow by comparison with helium flow, the latter taken as due entirely to Knudsen flow (70). The non-adsorbability of helium has recently been questioned (13). Thus a reliable method of measurement and comparison needs to be established.

By reference to the thermodynamic equation

\[ \Delta G = \Delta H - T \Delta S \]

relating free energy changes, heats of adsorption, and entropy changes, one can determine that adsorption is an exothermic process. There are two different ways of expressing the heat effect, namely, the integral (Q) or the differential (\(-\Delta H\)) heat of adsorption. The former is given in BTU per pound of adsorbent, and the latter in BTU per pound mole of adsorbate. Differential heats of adsorption are preferable since they are easily compared to latent heats of condensation.

It is possible to calculate (-\(\Delta H\)) from the adsorption isotherm at two adjacent temperatures \(T_1\) and \(T_2\), using the Clasius-Clapeyron equation. This equation is of the form (39):
where \( p_2 \) and \( p_1 \) are the equilibrium pressures at these two temperatures for a fixed adsorption.

Heats of adsorption and immersion are also experimentally measured. The Linde Company gives an approximate differential heat of adsorption value of 1800 BTU per pound of water for Type A molecular sieves (74). At ambient temperatures, the latent heat of condensation of water vapor is roughly 1000 BTU per pound.

Qualitatively, increasing differences between the differential heat of adsorption and the latent heat of condensation correspond to sharper and sharper bends in type B (Figure 5) isotherms, and stronger and stronger forces of physical adsorption (51).

**Material balance**

The conservation of mass equation described by Thomas (102) and many others for fixed bed adsorption is:

\[
\frac{\partial C}{\partial t} + \frac{m}{G'} \frac{\partial C}{\partial t} W_s \left[ \frac{\partial X}{\partial t} \right] W_s = 0 \quad (8)
\]

where \( m \) is the amount of void space between particles in lbs. dry air per lb. dry solid.

Alternatively, this equation based on the fixed bed height, \( Z \), may be used (94):
By a suitable change in the independent variables a simplified form was developed (102) that included the rate of change of air stream water content in the bed with bed distance at specified times, \( \frac{\partial C}{\partial z} \), and the local rate of water transfer from the air to the solid, \( \frac{\partial X}{\partial t} \). For example, the cumulative dry air weight \( (W) \) can be represented:

\[
W = G't - mW_s
\]

Thus one obtains:

\[
\left[ \frac{\partial C}{\partial W_s} \right]_W + \left[ \frac{\partial X}{\partial W} \right]_W = 0
\]

The local rate of water transfer, \( \frac{\partial X}{\partial W} \), may be a function of \( C \), \( X \), the adsorption isotherm, and the water distribution within the particles. The rates of change depend on the assumed mechanism of adsorption, or in turn on the form of the rate equation. The equation of continuity, expressed by equation 11, reflects the special unsteady state breakthrough behavior of fixed beds rather than the rate equations used with it.

**Rate equations and diffusion expressions**

The effective rate of adsorption is determined by one or more of several alternate diffusional steps. The se-
quence of molecular scale processes involved in adsorption can be grouped into the following as given by Vermeulen and Heister (107): (1) mass transfer from the bulk gas to the external surfaces of the adsorbent particles, (2) pore diffusion in the fluid phase within the particles, (3) reaction at the phase boundaries, (4) diffusion in the adsorbed surface layer, and (5) in cases of moderately high mass transfer with extremely slow flow rates, the breakthrough curves may be broadened by eddy dispersion or molecular diffusion in the longitudinal direction.

The rate of accumulation of a substance at a given point in a medium as a function of time is best represented by a differential form of Fick's law of diffusion. The representative equation in three rectangular dimensions and for the isotropic case is (10):

$$\frac{\partial c}{\partial t} = D \left[ \nabla^2 c \right]$$

Alternatively, one may write these in polar or other coordinate systems as desired. In adsorption an equation in spherical polar coordinates is convenient. This of the form:

$$\frac{\partial c}{\partial t} =$$
By restricting this equation to diffusion where the spherical surfaces of constant concentration are concentric, one can reduce it to:

$$\frac{D}{r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial c}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 c}{\partial \phi^2} \right]$$

By restricting this equation to diffusion where the spherical surfaces of constant concentration are concentric, one can reduce it to:

$$\frac{\partial c}{\partial t} = D \left[ \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right]$$

Various forms and some solutions to these Fick's law equations are given in Barrer (10).

It is important to know how the diffusivity in each rate expression is defined. Most of the information in the literature does not explicitly describe the respective diffusional resistances. The resistance to pore diffusion is usually considered as the drag force on gas or vapor molecules by the surface of a solid or a liquid. The diffusion coefficient for this is termed the pore diffusivity ($D_{\text{pore}}$).

Condensed flow is generally defined as the flow of a condensed vapor or an adsorbed surface layer along the internal surfaces of the pore. Vapor or gas may also be flowing adjacent to the condensed flow in the void spaces of the pores. $D_L$ is used to denote the condensed vapor diffusion coefficient. Confusion arises when this term is used for entirely liquid flow in the pores, since no distinction is made between the bulk liquid and the liquid somewhat orient-
ed or affected by interaction with the adsorbent surface. The pore diffusivity is sometimes used in this case to describe just the bulk liquid flow.

Particle diffusion as described by Vermeulen and Heister (107) denotes diffusion in the adsorbed surface layer or in the condensed phase. Others consider particle diffusion as encompassing both the pore diffusion of gases and vapors and condensed flow. The latter definition is used in this work for expressions including the particle diffusivity ($D_p$).

The rate of mass transfer for gas phase external diffusion of a component from the bulk gas to the outer surface of the solid particle may be expressed (92):

$$\frac{\partial X}{\partial t} = k_{ga_p}(C - C_i)$$

(15)

where $C_i$ is the water content of the air film at the external surface of the particle. $C_i$ is usually assumed to be a function of $X^*$, the corresponding equilibrium water content of the solid.

The rate of pore diffusion in the bulk fluid phase within a spherical particle is expressed by a modified form of equation 14 (106):

$$D_{pore} \left[ \frac{\partial^2 c_r}{\partial r^2} + \frac{2}{r} \frac{\partial c_r}{\partial r} \right] =$$

(16)
The average water content of the entire particle \(X_p\) is (106):

\[ X_p = \frac{3}{r_p^3} \int_0^{r_p} x_r r^2 dr \]  

(17)

Reaction at the adsorption surface is usually very fast compared to the rates of the other mass transfer mechanisms. Vermeulen (106) gives the rate equations for this case. Experimental phase change mass transfer coefficients are not known at present.

Barrer (10) expresses the rate of particle diffusion as:

\[ D_p \left[ \frac{\partial^2 x_r}{\partial r^2} + \frac{2}{r} \left[ \frac{\partial x_r}{\partial r} \right] \right] = \left[ \frac{\partial x_r}{\partial t} \right] \]  

(18)

Usually, the rate of particle diffusion is approximated by the linear driving force relation of Glueckauf and Coates (47). Their equation is:

\[ \left[ \frac{\partial X}{\partial t} \right]_{W_s} = k_s a_p (X_i - X) \]  

(19)

This equation assumes that all the resistances to solid dif-

\[ \mathcal{K} \left[ \frac{\partial c_r}{\partial t} \right] + \frac{\rho_b}{\rho} \left[ \frac{\partial x_r}{\partial t} \right] \]
fusion are located in a very thin shell just inside the surface of the particle. The concentration at the surface of the particle is $X_1$, and after crossing the shell resistance the concentration inside the particle falls to an average value of $X$ with no additional concentration gradients within the particle. A more rigorous approach is a quadratic approximation for the driving force. This approximation is presented and described by Vermeulen (105).

Isolation of the effects of longitudinal diffusion from the other diffusion mechanisms has been achieved and is discussed by Heister et al. (57). This work gives correlation of a large number of ion exchange breakthrough curves that indicate the mechanism effects. Acrivos (1) discusses and gives a method for estimating the combined effect of longitudinal diffusion and external mass transfer resistance.

Beek and Miller (16) discuss the turbulent heat and mass transport properties in packed beds. The variation of velocity across the bed gives a diffusive effect, the magnitude of which depends on the radial diffusivity. In the case of mass transfer, the impermeability of the walls of the fixed bed tend to flatten the radial concentration profile and decrease the importance of the radial diffusivity. Beek and Miller (16) state further that, if a reaction is exothermic, the effect of the lower velocity near the wall flattens the profile still more. Thus a flat concentration
profile is approached in adsorption, or essentially plug flow.

Rate and breakthrough curve data

The only usable rate and breakthrough data for molecular sieves is found in past research work by the writer (86). Several investigators, however, have presented data for silica gel. Maslan (80) made a few runs using silica gel, but his main work was with activated alumina. He did not measure $C/C_0$ for the entire breakthrough curve - only up to $C/C_0 = 0.3$, and did not vary bed heights nor obtain equilibrium data. Eagleton (35) obtained breakthrough curves and capacity data for silica gel in the 0 to 10 percent inlet relative humidity range.

Assumptions

In order to simplify an adsorption mechanism study the following assumptions are generally made: (1) constant inlet air composition, (2) constant inlet air flow rate, (3) initially zero water content for the adsorbent, (4) isothermal fixed bed conditions throughout, (5) no concentration, pressure, or temperature gradients across the bed perpendicular to the flow, (6) no inter-particle diffusion, (7) no longitudinal diffusion in the air stream - only diffusion to or in the adsorbent particles. While these may not be strictly valid in all cases they are used subject to modifications as the solution to the problem progresses.
Performance studies for fixed beds are concerned with breakthrough curves. Usually calculations for fixed bed adsorption processes must use one or another of a group of specialized results which take the place of a generalized solution to the problem. The specialized results are identified by a rate controlling mechanism and an equilibrium.

**Equilibrium and material balance**

The breakthrough curve can reflect the exact behavior of the equilibrium isotherm for point-wise calculations or for very favorable or very unfavorable equilibrium. In practice an effort is generally made to fit the isotherm with a separation factor or equilibrium parameter ($r^*$). This factor is defined by the equation (106):

$$
r^* = \frac{C^*/C_o (X^*/X* - 1)}{(1 - C^*/C_o)}
$$

The equilibrium parameter ($r^*$) varies from 0.15 to 0 depending on $C^*$ for water adsorption on molecular sieves. Thus breakthrough curve solutions using constant $r^*$ are not valid for this system.

It is convenient to classify solutions for breakthrough curves into the following categories depending on their separation factor range or value (107): (1) irreversible ($r^* = 0$), (2) strongly favorable ($0 \leq r^* \leq 0.3$), (3) linear ($r^* = 1$), (4) non-linear ($0.3 < r^* < 10$), and (5) strongly
unfavorable \( (r^* > 10) \). The initial slopes (or sharpness) of breakthrough curves increase with decreasing \( r^* \). Constant MTZ or constant pattern properties are generally exhibited by curves of \( r^* = 0.5 \) and less (107).

The equations of conservation for a differential section (equations 3, 9, and 11) are combined with appropriate rate expressions and equilibrium relations to give breakthrough curve models. Constants of integration are evaluated with the aid of material-balance integrals written for the entire fixed bed or for the mass transfer zone (MTZ).

**Fixed bed dynamics**

Vermeulen (106) describes in a fairly detailed manner many of the mathematical advances which have been made in calculating the kinetics of diffusion in fixed beds. The present survey intends to emphasize areas of the kinetics most useful in this research, and to indicate those areas where the separation of one mechanism from another is not yet clear.

The unfavorable equilibrium case for proportionate pattern or "self-diffusing" adsorption is treated by DeVault (104) and Walter (103). Infinite rates of adsorption or, that equilibrium is maintained everywhere in the bed, is assumed in the developments. The breakthrough curve solutions show the effluent concentration uninfluenced by the mass transfer rates in the fluid and in the particle. Important
process information for this case is largely predictable from expressions based on equilibrium concepts (41). The solutions are useful in the design of regeneration operations.

In order to obtain realistic breakthrough curves the rate can not be assumed infinite. The rate expressions are usually classed according to the following controlling mechanisms: (1) external diffusion, (2) internal pore diffusion, (3) internal solid-phase diffusion, and (4) longitudinal diffusion. For the irreversible, favorable, and linear equilibrium cases it is usually necessary to determine and state the rate controlling mechanisms for proper interpretations of performance. The pore and solid-phase diffusion mechanisms are most important in water adsorption on molecular sieves.

Linear equilibrium through the origin implies constant separation factor conditions of $r^* = 1$. The generalized solution for linear driving-force forms of the different rate determining mechanisms and for $r^* = 1$ has been given by Schumann (95). Since the general linear driving-force is only approximate for the pore diffusion and internal solid diffusion cases at $r^* = 1$, the generalized results are not precise. Exact integration of the pore diffusion and internal solid diffusion expressions, equations 16 and 18 respectively, has been given by Rosen (93) for the $r^* = 1$ case.
The constant MTZ or "self-sharpening" adsorption has perhaps been more extensively studied. The continuity expression for constant MTZ adsorption independent of fixed bed height becomes, upon integration of equation 8:

\[ \frac{C}{C_0} = \frac{X}{X^*} \]  

(21)

A semiempirical method useful for correlating fixed bed adsorption results with favorable equilibria has been introduced recently, and is discussed in the next section (MTZ method). This present survey covers developments of the more theoretical methods.

Bohart and Adams (20) first identified and discussed the constant MTZ case. For irreversible adsorption and for external diffusion rate controlling (equation 15), Selke and Bliss (96) give the following solution:

\[ \ln \frac{C}{C_0} = \left[ \frac{k_p a_p \rho_b V}{G'} \right] \left[ \left( \frac{C_0 \dot{w}}{\rho_b X^* V} \right) - 1 \right] -1 \]  

(22)

For other equilibrium, \( X^*_0 \) needs to be replaced by a function of the isotherm. A method by Eagleton and Bliss (36) for a linear not through the origin equilibrium shows this development.

The case of a constant separation factor and favorable equilibrium using equation 15 (gas film controlling) has been solved by Michaels (öl).

The fluid-phase pore diffusion rate controlling case
has been semiempirically solved for only the irreversible equilibrium ($r^* = 0$) case in unpublished work by Acrivos and Vermeulen (2). The result is given and discussed in the next section. Fluid-phase pore diffusion controlling solutions are difficult to obtain, and at present their separation from solid-phase internal diffusion is not yet clear.

The problem of determining how much fluid can be taken up by a solid before diffusion related to the solid becomes diffusion related to the fluid still remains.

The exact solution for irreversible, solid-phase internal diffusion controlled, constant MTZ adsorption is given by Boyd et al. (21). Their result is:

\[
\frac{C}{C_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{n^2}{4\pi^2D_pW} \right) \left( \frac{4\pi^2D_pW}{G_2^*d_p^2} \right) - \left( \frac{4\pi^2D_pX_0^*V}{C_0G_1^*d_p^2} \right) + 0.97 \] (23)

For the linear driving force approximation of Glueckauf and Coates (47) given by equation 19, the solution becomes:

\[
\frac{C}{C_0} = 1 - \exp \left( -\left( \frac{60D_pX_0^*V}{C_0G_1^*d_p^2} \right) \left( \frac{C_0W}{\rho_bX_0^*V} - 1 \right) + 1 \right) \] (24)

The solution for this solid diffusion case using a quadratic driving-force approximation is given in Monet and
Vermeulen (85).

Constant separation factor conditions with strongly favorable equilibrium and solid-phase diffusion controlling has also been solved by Glueckauf and Coates (47). Baddour and Gilliland (8) and Heister et al. (57) investigated the situation where diffusion in both the external and internal phases was significant and derived almost identical expressions by combining the two relationships for inter-phase diffusion. External diffusion tended to predominate at low values of breakthrough and internal diffusion had more of a retarding effect near saturation in the ion exchange work of Heister et al. (57).

Generalized solutions

In order to simplify the general analysis it is expedient to form dimensionless groups of the numerous variables. Group relationships are useful in correlating adsorption results with those of ion exchange and dialysis. Vermeulen and Heister (107) define several of these groups in their recent paper. Some of these are:

\[ N = \frac{N_R}{b} = \frac{K_p Z A_x \rho}{G'} \]  \hspace{1cm} (25)

\[ \text{H.T.U.} = \frac{Z}{N} = \frac{bZ}{N_R} \]  \hspace{1cm} (26)

where \( b \) is a correction factor accounting for linearity deviations when the diffusional resistances are added.
Stoichiometric behavior is defined by these groups (107):

\[
\bar{D} = \frac{X^* \rho_b v}{c_o} \tag{27}
\]

\[
Z_p = \frac{c_o \left[ W - mW_s \right]}{v \rho_b X^*_o} \tag{28}
\]

where \( \bar{D} \) is called the distribution ratio and \( Z_p \) the throughput ratio. A mechanism parameter \( \zeta \) (zeta) is defined as:

\[
\zeta = \frac{K_s a_p}{K_g a_p} \tag{29}
\]

where the subscripts s and g refer to solid phase and gas phase respectively. The correction factor \( b \) is a function of \( \zeta \) and \( r^* \). It is defined by this equation (57):

\[
\frac{b}{N_R} = \frac{1}{N_g} + \frac{1}{N_s} \tag{30}
\]

Klinkenberg and Sjenitzer (69) used the ion exchange data of Heister et al. (57), which isolated the effects of external and internal diffusion, to graphically present correlations which show separately the predicted effects of molecular diffusion, eddy dispersion, distribution ratio, particle-fluid diffusivity ratio and mechanism parameter.

The equation of Thomas (102) represents the most general description of breakthrough. His result in dimensionless parameters is:
\[
\frac{C}{C_0} = \frac{J(r^*N_R, Z_pN_R)}{J(r^*N_R, Z_pN_R) + \left[1 - J(N_R, r^*Z_pN_R)\right] \left[\exp(r^* - 1)N_R(Z_p^{-1})\right]}
\]

Baddour and Gilliland (8) and Heister and Vermeulen (58) show that this equation reduces to the constant MTZ, and proportionate pattern cases at the appropriate constant separation factors.

Heister and Vermeulen (58) have also graphically presented equation 31 behavior. Tabular values of the behavior are available also (88). The following tendencies are given in Heister and Vermeulen's work. For large \(N\) (> 40) and small \(r^*\) (\(\ll 0.5\)) a single curve of \(\frac{C}{C_0}\) versus \(NZ_p\) will describe all breakthrough cases at any particular \(r^*\) (and for any one controlling mechanism). At large \(N\) and large \(r^*\) (\(\gg 2\)) a single curve of \(\frac{C}{C_0}\) versus \(Z_p\) will completely describe breakthrough at any particular \(r^*\). For smaller values of \(N\) and for intermediate values of \(r^*\), an entire family of breakthrough curves is needed to describe any one \(r^*\).

In addition to the above there are other generalized correlations that are helpful in design and in interpreting fixed bed kinetics. Moison and O'Hern (83) describe these correlations for constant MTZ ion exchange; Schmelzer et al. (94) describe these for the constant MTZ and for adsorption
from liquid solutions; and Gupta and Thodos (55) describe them for packed beds.

For the constant MTZ method the number of transfer units in the MTZ \( N_{MTZ} \) is used, and is defined as (83):

\[
N_{MTZ} = \frac{K_d Z_{MTZ} A_x G}{G'}
\]

(32)

This also requires changing equation 26 to:

\[
H.T.U. = \frac{Z_{MTZ}}{N_{MTZ}}
\]

(33)

Equation 33 is thus an alternate definition for the H.T.U.

Moison and O'Hern (83) used graphical plots of Reynolds number versus H.T.U. and versus the \( j_d \)-factor of Chilton and Colburn (29) to correlate their constant MTZ ion exchange data with that of other investigators. Linear logarithmic plots were given to show the effects of bed height, particle size, inlet concentration and flow rate on the H.T.U.; similar plots were given to show the effects on the \( j_d \)-factor. Moison and O'Hern (83) believed that the slight dependence of their H.T.U. and \( Z_{MTZ} \) on the bed depth was due to longitudinal dispersion because their Reynolds numbers were low and in the range of axial mixing significance. Liquid film resistance was believed to be the rate controlling mechanism.

Schmelzer et al. (94) used logarithmic plots of mass
flow rate versus H.T.U. at various particle sizes to present toluene adsorption on silica gel. The constant MTZ method was used to determine the H.T.U. values. H.T.U. proportional to the square root of the velocity indicated to these researchers that external diffusion contributed to the rate of adsorption. \( j_d \)-factor predicted H.T.U. were only a fraction of the experimental H.T.U., and thus gave evidence of internal diffusion contributions in the rate mechanism. The interrupted run technique was used to ascertain the number of steps in the rate mechanisms at the various flow rates and to identify them.

An improved correlation for mass and heat transfer through fixed beds has been given recently by Gupta and Thodos (55). Using the modified Reynolds number introduced by Taeker and Hougen (101), Gupta and Thodos developed a correlation based on transfer area availability to account for different particle geometrical configurations other than spheres.

**External constraints on performance**

Several important considerations affecting fixed bed adsorbers have been considered as external constraints. These are: pressure, adsorbent poisoning, regeneration and loss in adsorbing power.

Maslan (80) has very extensively investigated pressurized adsorption systems in his work with activated alumina
and silica gel. Two driers were used - one small 1 inch I.D. laboratory drier for pressures up to 2000 psia and a large pilot plant size drier for pressures up to 100 psia. He found that for pressures above 100 psia all driers operate isothermally. For activated alumina his data show that the percent increase in $W_B$ capacities over pressures from 0 to 2000 psia are only 2% or less for temperatures below 110°F. Other trends or tendencies found in his results are: (1) the higher the pressure the lower the minimum dew-point, (2) the cooler the bed the lower the minimum dew-point, (3) equilibrium capacity is higher at higher pressures, (4) $k$ is inversely proportional to pressure, and (5) H.T.U. is independent of total pressure. In viewing his data it appears that the changes caused by pressure are in most cases small.

A recent generalized equation by Lapin (72) permits estimating of bed pressure drops to within ± 6%.

Adsorbent poisoning has been discussed by Wheeler (111) and Green (49). Wheeler (111) gives the steady-state rate of reaction equations in a catalyst pellet for different "poisoning conditions" (e.g. preferential poisoning of the pore mouth, homogeneous poisoning within the pores, etc.). A more recent article considers the effect of distribution of poison throughout the catalyst bed (5). Green (49) treats unsteady-state reaction rate conditions such as
initial start up periods, and decreasing activity with time. He proposed a model to describe a heterogeneous chemical reaction in a porous catalyst in which pore diffusion and poisoning are important.

An adsorbent is commonly regenerated for reuse in one of three ways: (1) exposure to a high temperature, (2) exposure to a vacuum, or (3) displacement with a more strongly adsorbed material followed by exposure to a high temperature. A problem of major concern in regeneration is the reduction in the adsorbent capacity, such as by decomposition during the adsorption step itself, since adsorbents of high specific surface can act as catalysts. Baddour and Geddes (7) discuss these effects in more detail. Design considerations for regeneration in fixed bed operations are given by Frisch and McGarvey (41).

Loss of adsorbing power with service life is described by Griesmer et al. (53). From pilot plant tests in air drying service using Type 5A molecular sieves, the adsorbent retained 58% of its original water capacity after 5,000 (16 hours each) cycles of adsorption and regeneration. This was almost a ten year service life. Of greater importance is that the cycling had no appreciable effect on the attainable minimum dew-point.
Design Methods and Equations

Most methods proposed for interpreting fixed bed data have been too cumbersome for design purposes. A recent simplified solution results from elimination of the variable, time. This was accomplished by assuming that the zone in which almost all the adsorption is taking place remains constant in length \((W_E - W_B)\) and is independent of fixed bed height. This is the same assumption used in the previous section for the constant MTZ or constant pattern case.

Discussion of this method has been given by Michaels (81) for ion exchange work, and by Treybal (103), Leavitt (73) and Barry (15) for adsorption problems.

**Isothermal mass transfer zone (MTZ) method**

deVault (104) first showed that development of the MTZ as it moves down the bed depends on the shape of the isotherm involved. This was discussed and verified by Glueckauf (44) and Barrow et al. (14). If gas and solid equilibrium is assumed at all points, and if the equilibrium isotherm is concave to the gas concentration axis, Glueckauf (44) showed that there existed a "self-sharpening" tendency, that is, the MTZ length tended to become shorter as it moved down the bed. Conversely, for an isotherm convex to the same axis, he showed that the MTZ length tended to become longer and longer as the MTZ moved down the bed, that is, a "self-diffusing" tendency existed.
The effect of non-equilibrium conditions, caused by diffusional resistances, was found to also increase the MTZ length as it moved down the bed. The assumption developed from these principles was that with a "self-sharpening" type isotherm, the tendency to shorten the MTZ length is counterbalanced by the tendencies of the diffusional resistances to increase the MTZ length. This steady state condition is assumed to be reached a short distance from the entrance to the bed, and to continue unchanged making the MTZ length constant from that point on.

Treybal (103) using the ion exchange development of Michaels (81) and the fixed bed adsorption data of Baglelon (55), developed a simplified MTZ approach to fixed bed adsorber design. The MTZ height equations developed for a given fixed bed condition are:

\[ Z_{MTZ} = Z \left[ \frac{t_E - t_B}{t_E - (1-f)(t_E - t_B)} \right] \]  

or

\[ Z_{MTZ} = Z \left[ \frac{W_E - W_B}{W_E - (1-f)(W_E - W_B)} \right] \]  

Using material balances around the MTZ and the entire fixed bed, the percent of equilibrium saturation at the breakthrough point for the entire fixed bed was obtained
and is given by:

$$\text{Average \% saturation in bed} = 100\% \left[ \frac{Z - f_{MTZ}}{Z} \right]$$  \hspace{1cm} (36)$$

The limitations listed by Michaels (81) on the use of this method are that (1) the adsorption be from dilute feed mixtures, (2) the isotherm be "self-sharpening", (3) the MTZ lengths be constant and independent of bed height, and (4) the height of the adsorbent bed be large relative to the height of the MTZ. Implied in the above are the assumptions listed previously in this literature review.

Eagleton (35) showed that his breakthrough curve data for silica gel in the 0 to 0.003 lbs. $H_2O$/ lb. dry air inlet humidity range was consistent with the constant MTZ length independent of bed height concept, as was predicted from the "self-sharpening" portion of the isotherm in this inlet air water content range.

**Non-isothermal mass transfer zone (MTZ) method**

In large diameter fixed beds the heat that is generated by adsorption in the bed is not easily conducted to the fixed bed wall. This radial conduction is sometimes negligible. Leavitt (73) has postulated an approach to this problem based on two distinct mass transfer zones (MTZ's). In his work the two transfer zones tend to form at the inlet end of the bed due to temperature fluctuations and move
toward the exit end at different speeds. Between these MTZ's is an expanding interzone in which the temperature, concentration, and adsorbent loading are uniform. Based on these considerations Leavitt (73) developed equations, expressing the overall mass and heat balances, that can be used to determine the local temperature conditions in the steady-state mass transfer zones. Equations were not presented that express the rates of mass transfer, or that express concentrations in the MTZ's as a function of time.

His development uses the same assumptions as for the isothermal case but with these additional ones: (1) heat loss through the bed wall is negligible (i.e. the adsorption is adiabatic), (2) axial diffusion can also be considered, (3) at any point in the MTZ, the adsorbent particles and the gas are at the same local temperature, and (4) the adsorbent is essentially in equilibrium with the local adsorbate concentration, both ahead and behind each MTZ (73). As was the case with the isothermal treatment of Michaels (81), the MTZ's need to be at steady state and independent of bed height.

The postulated two distinct transfer zones were observed for the adiabatic adsorption of CO₂ from a nitrogen stream (73). The time of breakthrough of each MTZ corresponded to the time predicted from the temperature data.
Mass transfer coefficient method

The mechanism for water adsorption is important in developing a method for checking the applicability of the MTZ method assumptions and for determining the cumulative dry air weight values of \( W_E \) and \( W_B \). A kinetic model developed by Eagleton and Bliss (36) interprets fixed bed data in terms of mass transfer coefficients by using a gas film and solid shell resistance concept. A linear not through the origin equilibrium relationship was used in their work.

The equations developed by Eagleton and Bliss (36) for both gas film and solid shell resistances contributing are:

for \( C < C_D \)

\[
\ln \left[ \frac{C_D/C_o}{C/C_o} \right] = - \left[ \frac{C_o k g a_p}{X_o G'} \right] W + \frac{k g a_p W s}{G'} + 2 - \frac{C_o}{C_D} \tag{37}
\]

for \( C > C_D \)

\[
\ln \left[ \frac{1 - C_D/C_o}{1 - C/D/C_o} \right] = - \left[ \frac{C_D/C_o}{1 - C_D/C_o} \right] \left[ \left( \frac{C_o k g a_p}{X_o G'} \right) W \right] - \frac{k g a_p W s}{G'} - 2 + \frac{C_o}{C_D} \tag{38}
\]

where \( C_D \) is given by:
For the case of solid shell resistance controlling, the equation is:

\[
C_D = \frac{\omega}{X_0^*/C_0 + k_{sp}/k_{sp}} \tag{39}
\]

Since these equations were used in calculating mass transfer coefficients for water adsorption on molecular sieves, their development, as adapted for this system, is briefly surveyed here. Isothermal operation was assumed in the developments, hence considerations were made primarily for mass transfer phenomenon.

Only one component, water, needs to be considered in the material balances; however, the air in the adsorbent phase is considered by a flow rate correction (equation 10), and counter diffusion of air is included in the diffusivities. With only one component transferred, an absolute weight basis is more convenient for adsorption and was used.

In previous work by the writer (86) the constant MTZ independent of fixed bed height concept was found to be applicable to molecular sieve adsorption. This concept permits a much needed and important simplification, which
is, that time changes and fixed bed height changes are
directly and linearly proportional. Thus the fixed bed
problem can be rearranged into a form that is easily
handled by a gas absorption procedure. In place of a fixed
bed of adsorbent with the constant MTZ wave moving through,
one assumes that a rigid mass of the adsorbent (with the
same dimensions and particle positions as that in the fixed
bed) moves countercurrent to the gas phase at a rate just
equal to the rate of descent of the MTZ. This implies that
the MTZ wave is now a stable standing wave. This is
described graphically in Figure 6. The exit gas and the
inlet adsorbent concentrations have been experimentally
shown to be very close to zero, and thus were assumed zero
in these developments.

The linear driving force equations of Hougen and Watson
(63) and Glueckauf and Coates (47) are the simplest attempt
to describe the adsorption process (equations 15 and 19
respectively). The former, based on gas film diffusion, is
a standard approach, but the latter, based on solid phase
diffusion, requires explanation. The physical dimensions of
the molecular sieve cell structure are quite amenable to the
solid phase shell resistance postulate of Glueckauf and
Coates (47) described previously. Vermeulen (105) states
that the linear solid phase driving force equation is a
simplification of Fick's law of diffusion for an adsorbent
Figure 6. Standing MTZ wave section of moving adsorbent bed
particle (equation 18).

Differential time \((dt)\) is used since it is directly and linearly related to differential bed height \((dZ)\) through the constant MTZ concept; hence a slight departure from the usual gas absorption procedures is involved. Equilibrium is assumed at the solid-fluid interface in this development. Eagleton and Bliss (36) used a linear isotherm not through the origin in their silica gel research. A linear isotherm approximation not through the origin closely duplicates the experimental isotherm for molecular sieves as is shown in Figure 7. The equation for the equilibrium line is:

\[
x^* = \alpha + \left[ \frac{x_0^* - \alpha}{c_0} \right]c^*
\]

(41)

However, this approximation makes the model discontinuous, since no experimental isotherm shows such a discontinuity. Thus two equations are needed for the breakthrough curve model.

An expression for the operating line is obtained by assuming it is linear and by writing material balances over the entire bed and over a differential section of the MTZ front boundary (see equation 21). Similar to gas absorption procedures, the mechanism parameter or relationship of driving forces is obtained by equating the rate
Figure 7. Equilibrium isotherm for water adsorption Type 4A molecular sieves at 90°F.
Water content of solid, $X$, lbs. H$_2$O/lb solid

Inlet air water content, $C^*$, lbs H$_2$O/lb dry air

Linear approximation (intercept = $\alpha$)

Molecular sieves type 4A
expressions for each phase. The equilibrium, operating and mechanism parameter lines are graphically given in Figure 8.

The interface gas concentration, $C_1$, as a function of $C$ is obtained by solving for the intersection of the mechanism parameter line with the equilibrium line. Since the equilibrium line is discontinuous, the intersection expression is also discontinuous. The operating line discontinuity point, $C_D$, is solved for by using the $(0, \infty)$ equilibrium point. Equation 39 describes this solution.

By appropriate variable eliminations and combinations, equation 15 is rearranged to a convenient form and integrated. The integrated form combined with an overall material balance yields the equations given by Eagleton and Bliss (36) (equations 37 and 38). These equations assume nothing in regard to either phase controlling.

For the special case of solid shell resistance controlling a similar development with no gas phase discontinuity is made starting with equation 19. The final form is expressed by equation 40. The gas film resistance controlling case cannot be obtained from this development because the solution becomes indeterminate.

**Pore diffusion method**

The objectives of the pore diffusion method are the same as for the past method - checking the applicability of the MTZ procedure assumptions, and determining $W_E$ and $W_B$.
Figure 8. Typical X-C diagram for molecular sieve adsorption
Water content of solid, \( x \), lbs. H\(_2\)O/lb. solid

Equilibrium line

Mechanism ratio line

Operating line

Water content of air, \( C \), lbs. H\(_2\)O/lb. dry air
values. A major effort in the development and verification of an accurate pore diffusion model is the distinguishing between the fluid phase diffusivity and the solid phase diffusivity.

Fluid phase mass transfer within the micropores occurs by diffusion through the volume of the micropores, and possibly along their surfaces. When the size of the diffusing molecules approaches the size of the capillary pores, there will be a reduction in the rate of diffusion which can be described as the drag of the capillary walls on the diffusing molecules. To account for this reduction for gases in solids, Barrer (10) postulated use of the ordinary equations for slip flow and Knudsen flow in capillaries. For liquids in solids he proposed to use the Faxen equation. Pore porosity and tortuosity (the equivalent straight length of the pores) are used in dialysis to account for fluid phase diffusion reductions. The Faxen equation given by Bacon (6), accounts for the capillary drag of the walls on liquids. This equation gives an unrealistic diffusion rate reduction when it is applied to water adsorption on molecular sieves.

The flow of gases through capillaries is characterized by the ratio of the mean free path, $\lambda$, to the micropore diameter, $d_{\text{pore}}$. The streamline (Poiseuille equation), slip, and molecular (Knudsen equation) flow regions are
defined by their \( \lambda/d_{\text{pore}} \) ratios, namely, below 0.01, 
\[ 0.01 \leq \left( \lambda/d_{\text{pore}} \right) \leq 1, \] 
and above 1, respectively (84). The flow equations are given by Brown et al. (25). The 
\( \lambda/d_{\text{pore}} \) ratio for Type 4A molecular sieves and water 
vapor is approximately 150, hence it is well into the 
molecular flow region (61).

To date, experimental measurement of flow through 
capillaries have not followed the laws of capillary flow 
(84). If the pore porosity, tortuosity, and capillary drag 
factors were considered further, it might be possible to 
obtain important information for interpretation of fluid 
phase pore diffusion.

Acrivos and Vermeulen (2) have developed expressions 
for pore diffusion in spherical particles under 
irreversible equilibrium conditions. In their work the 
fluid phase concentration in the pores was assumed 
negligible compared to the concentration in the particle. 
The spherical polar coordinate forms of Fick's law given by 
Barrer (10) (equations 13, 14 and 16) were modified to 
include the above assumption along with the others. 
Modified equation 16 was combined with an appropriate one 
particle material balance. The result was integrated to 
yield an expression for \( C/C_0 \). Acrivos and Vermeulen (2) 
empirically evaluated the integrated expression for \( C/C_0 \) 
to get this final form for their irreversible equilibrium
pore diffusion model:

\[ \frac{C}{C_0} = \]

\[ + 0.557 \left[ \left( \frac{60D_{\text{pore}} v \rho_g}{G'} \right) \left( \frac{C_0 W}{X_0 \rho_b v} - 1 \right) + 1.15 \right] \]

\[ - 0.0774 \left[ \left( \frac{60D_{\text{pore}} v \rho_g}{G'} \right) \left( \frac{C_0 W}{X_0 \rho_b v} - 1 \right) + 1.15 \right]^2 \]

Equation 42 was modified in past work by the writer to determine the relative shape of the breakthrough curve for molecular sieves (87). The equation developed is:

\[ \frac{C}{C_0} = \]

\[ + 4.63 \times 10^3 \left[ \left( \frac{k_{\text{sp}} \rho_g C_0}{G' X_0 \rho_b} \right) W - \frac{k_{\text{sp}} \rho_g v}{G'} + 1.15 \times 10^{-4} \right] \]

\[ - 5.45 \times 10^6 \left[ \left( \frac{k_{\text{sp}} \rho_g C_0}{G' X_0 \rho_b} \right) W - \frac{k_{\text{sp}} \rho_g v}{G'} + 1.15 \times 10^{-4} \right]^2 \]

In this equation particle diffusivity and pore diffusivity were assumed equal so that the mass transfer coefficients calculated from run No. 26 data could be used (87). The numerical constants were evaluated from the experimental values, \( \frac{C}{C_0} = 0.70 \) and \( \frac{C}{C_0} = 0.80 \) of run No. 26.

Equation 43 was then used to calculate the remaining portions of the breakthrough curve. Figure 9 shows the
Figure 9. Adsorption mechanism models for an air-water-molecular sieves (Type 4A) system
Ratio of water content of exit to inlet air, C/C₀

Cumulative dry air weight, W, lbs

Run conditions:  
- Inlet concentration — 0.01542 lb H₂O / lb air  
- Molecular sieves — 0.078" to 0.093" beads  
- Flow rate — 0.0328 lb dry air / min.  
- Bed height — 19.875"  
- Bed temperature — 89.9°F.
results of using this equation as compared to experimental run No. 26 data. The mass transfer coefficient models for run No. 26 data are also given in Figure 9.

Analytical Methods and Equipment

The more important methods of obtaining water concentrations and surface areas of adsorbents are briefly surveyed in this section.

Water analysis methods and equipment

Maslan (80) surveyed and evaluated most of the chemical and physical methods available at the time of his research work. He found that the chemical methods were totally unsuitable for a fast continuous analysis of gas streams. A survey of the gravimetric and volumetric physical methods gave the same conclusion. The dew-point method was found to be the best solution.

Present evaluations of available methods indicated that the dew-point and electrical resistance hygrometer methods were suitable.

Various dew-point measuring instruments have been constructed and marketed. Perhaps the oldest design that is still being used is one by the General Electric Company. The use of a General Electric designed dew-point instrument has been reported on by Maslan (80), Frank (40), Stack (100) and Eagleton (35). Since this type was purchased and used in the present research, the ideas presented in these
references have been incorporated into the present experimental procedures. This instrument operated on the principle of measuring the temperature at which moisture deposited from the air stream on a polished mirror. The operation permitted continuous, uninterrupted air stream flow. A cool inert gas stream was used to lower the mirror temperature to that of the dew-point. Eagleton (35) investigated the types of dew formed and associated phase changes observed when using the above instrument. He also gave estimated accuracies for the measurements and the subsequent calculated humidities. Eagleton's results were verified by the writer in previous work (86).

Gerthsen et al. (42) discussed the principles of automatic dew-point measuring and recording devices using thermoelectric Peltier cooling. Completely automatic and continuous dew-point measuring devices based on these principles have been marketed.

Present electrical resistance hygrometer devices are based on electrical resistance measurements of a $\text{P}_2\text{O}_5$ saturated dielectric which is hydroscopic over desired humidity ranges. This method is more accurate than dew-point for extremely low humidities.

Methods of measuring porosity and surface area

Specific external surface or interfacial area is obtained by this equation for uniform spherical particles
The air permeability method for measuring the interfacial area of irregularly shaped particles is discussed by Allen and Haigh (4). Fleming et al. (37) describes the apparatus and details the methods and procedures for measuring porosities by air displacement. Experimental porosities can then be used to calculate the external surface areas of irregularly shaped particles by the treatment given in Brown (24).

The determination of internal surface areas for adsorbents has been done chiefly by nitrogen adsorption using the B.E.T. method (26, 27) discussed previously (see equations 3 and 4). An improved method using krypton adsorption is discussed by Sing and Swallow (97).

Fixed Bed Adsorption Equipment and Economics

Yearly literature surveys on adsorption, and adsorption processes and equipment are given in the Unit Operations Reviews in Industrial and Engineering Chemistry, and also by Carter (28) and Barrer (12) in British Chemical Engineering.

A few examples of fixed bed processes and equipment using molecular sieves are given in this section. Adsorp-
tion processes that are economically better than past or existing processes are mentioned. The present availability of adsorbents including their representative costs is briefly surveyed.

**Typical fixed bed adsorption processes**

Molecular sieves are currently being used in standard fixed bed equipment (53). Typical fixed bed adsorption systems are shown in Figure 10.

A complete operating cycle normally covers these steps: (1) unsteady state adsorption until the design capacity for the adsorbent is reached, (2) removal of the component(s) adsorbed by heat or other regeneration means, and (3) cooling of the bed to a specific operating temperature.

The dual-bed system is sized to provide time for regenerating and cooling one of the adsorbers while the other is on stream. If the adsorption step is six hours or more, a dual-bed system is usually satisfactory since regeneration and cooling of one bed can be accomplished within this time limit (53). The current use of molecular sieves in simultaneously removing carbon dioxide and water from an annealing gas stream is an example of a triple-bed system (53). Design specifications met are: exit gas carbon dioxide concentration of less than 10ppm., exit gas dew-point less than -100°F., 30 minute periods for each adsorbing, heating and cooling step of the cycle, and a 6-weight %
Figure 10. Typical fixed bed adsorption processes
Purified annealing gas,

Bleed 

Purge gas

Outlet

Fuel Air

Blower

Bed 1

Bed 2

Bed 3

Heater

Bed 1

Bed 2

Bed 3

Furnace

Heat Exchanger

Cooler

Purge gas in

Purge gas out

Adsorption

Desorption

Outlet

Feed inlet

Dual bed system

Purified annealing gas

Bleed

Recycle

Purge gas in

Purge gas out

Bed 1

Bed 2

Bed 3

Blower

Cooling gas in

Purification

Triple bed system
design loading for carbon dioxide. Automatic valving provides for continuous operation. The purifying of annealing gas by molecular sieves is competitive with the present liquid scrubbing and adsorption combination.

**Economics and growth potential of adsorbents**

Present market for all adsorbents including silica gel, alumina and synthetic zeolites is estimated at more than 50 million pounds per year (109). The biggest share of this market is still held by the less expensive adsorbents like silica gel and activated alumina which sell at 25 to 35 cents per lb. Synthetic zeolites are cutting into these long developed markets despite their high cost of $1.25 to $1.75 per lb. because they are, in many cases, more efficient, require less weight for the same adsorption, have longer service life and adsorb selectively. For example, in refrigerant drying (2.5 to 5 million lbs. per year consumption) the Linde Company's molecular sieves have captured more than 50% of the market because 80% by weight less molecular sieves are required than competitive adsorbents.

The Linde Company has had the major part of the synthetic zeolite market since 1955 (109). In the last two years the Davison Chemical Division of W. R. Grace has been making and marketing synthetic zeolites, and recently the Norton Company has entered the field.
The Linde Company had two types of molecular sieves available initially; it now has six types which are marketed as 26 different products according to particle size and shape. Barry (15) has shown that in some separations the use of molecular sieves is less expensive than distillation. Griesmer et al. (53) show similar results for molecular sieve annealing gas purification when compared to liquid scrubbing.
PROPOSED MECHANISM FOR WATER ADSORPTION ON MOLECULAR SIEVES

In order to develop satisfactory mathematical models that describe the mass transfer process of water adsorption on molecular sieves, it is necessary to postulate a theoretical adsorption mechanism. Various mathematical rate expressions that approximate the mechanism are then used to develop suitable design equations and procedures. In this section the adsorption mechanism for the air-water-molecular sieves system is discussed from three viewpoints, namely, surface phenomena, molecular transport by pore diffusion and molecular transport by particle diffusion. The pore diffusion rate controlling mechanism is the one actually proposed by the writer for this system. It is considered to be a refinement of the particle diffusion mechanism.

The internal surface of each cavity is of immediate interest when fluid-solid surface phenomena are considered. This is the point where the force fields of the adsorbent and the water molecules interact. This activity concludes with the adsorption of the water molecules on the internal surface of the adsorbent. Since it is of questionable form to speak of liquid or vapor molecules in a collection of twenty to thirty molecules (e.g. the capacity of one unit cell in molecular sieves), the term fluid is used. The
literature survey information offers sufficient evidence for one to conclude that this fluid-solid activity is not rate controlling, although it needs to be an essential part of the overall adsorption mechanism (17, 22, 23, 62, 106). Water molecules almost instantaneously displace the relatively inert oxygen and nitrogen at the adsorbent surface. Thus the transport process should consider the counter diffusion of air through the pore system. The counter diffusion effect is generally included in the diffusion coefficient.

The other surface phenomena take place at a point in the adsorbent where the entering vapor condenses. It is postulated that this condensation occurs in all the cavities and pore mouths adjacent to the external surface of the adsorbent particle. Thus the condensation profile is a surface located at a radius equal to the outer radius of the particle less approximately 6 to 10 Å (a fractional part of the unit cell dimension). For all practical purposes the external surface of the particle could be used. In the gaseous diffusion work of Kammermeyer and Rutz (68) some condensed flow occurred in all pores less than 40 to 50 Å in diameter. The pores in Type 4A molecular sieves are 4.2 Å in diameter; hence the assumption of total condensation would appear valid.

The theory proposed by the writer for the formation of
the condensation profile is one similar to that of capillary condensation and vapor pressure lowering of concave surfaces. It is theorized that a concave surface is generated in each cavity adjacent to the external surface by the condensation and adsorption of the first 20 to 30 molecules of water entering. This concave surface essentially forms a pocket of molecular dimensions with openings to each of the six face-centered pores. The extreme concavity and smallness of the pocket is a result of strong forces interacting. This force activity causes a vapor pressure lowering like that in capillaries. The magnitude of the vapor pressure lowering determines the minimum dew-point. Besides the physical structure of the adsorbent the minimum dew-point is a function of the temperature and the adsorbent water loading prior to the start of the adsorption phase.

Use of the developments in the capillary condensation and vapor pressure lowering theory is limited only to the extent of defining a surface tension and a curvilinear meniscus for a collection of 20 to 30 molecules. If the standard definitions could justifiably be used, then it is thermodynamically possible to estimate the vapor pressure lowering (hence minimum dew-point) if a mathematical description of the concave surface could be obtained (30). At present it is questionable to use concepts defined for a
macro-scale system in describing a micro or molecular
scale system.

In the above theory the point of vapor pressure
lowering or driving force action is precisely located.
The theory permits explanation of some experimental
findings. The minimum dew-point is the same for each
adsorption part of a cyclic operation consisting of ad-
sorption, regeneration and cooling, even though the amount
of water adsorbed decreases with increasing number of
cycles (53). One interpretation of this is that the
position and magnitude of the vapor pressure lowering is
the same for each adsorption. It is possible to theorize
that the vapor pressure lowering is determined only by the
stable unit cell dimensions of molecular sieves provided
temperature and initial adsorbent loading are not changed.

The slight difference between Type 4A and Type 5A
molecular sieve properties could also signify physical
structure influence. Type 5A has a slightly lower minimum
dew-point than Type 4A (78). The only structural
difference between the two is that Type 5A has a calcium
ion replacing every two sodium ions. The calcium ion is
located further into the unit cell cavity and may cause the
concave surface of the vapor-liquid interface to be smaller
and more effective than that for Type 4A.

After the outermost unit cells have adsorbed the
required number of water molecules to form a condensation interface, there is likely to be a continuous stream of molecules condensing in the outermost unit cells and moving toward the center of the adsorbent particle. The condensation interface may be distorted, possibly toward increased concavity, as each molecule of vapor is attracted into the pore at the external surface, condensed to a liquid-like state and then further attracted to a point on the internal surface. The condensation interface may also be distorted as the oxygen and nitrogen molecules counter-diffuse to the external surface and the bulk gas stream. Thus, the condensation interface could be considered as only a hypothetical surface; one that indicates where some of the attraction forces are acting.

Although it is possible for water molecules to leave through the five other large pores of the unit cell, they are more likely to leave the cavity through the opening directly opposite to the one entered originally because parallel movements are also occurring in the neighboring unit cells. The condensed flow of molecules essentially passes through a long cylindrical pore until an empty or partly empty cavity is reached. This is possible because there is only sufficient space in each cavity to adsorb a monolayer; hence approximately a 4 Å diameter spherical space remains. A driving force similar to that attracting
the molecules into the first cavity acts on the water molecules in the pore.

The total resistance to molecular transport in the pores increases as the molecules penetrate further into the particle. Since the pores are of uniform size throughout the adsorbent, a series of Knudsen diffusion resistances could be postulated with a combined resistance calculated for each cavity adsorbing 20 to 30 water molecules. An average of all the individual resistances to transport to each specific cavity would be the overall pore resistance for the adsorbent particle. The average number of individual pores passed through could be approximated by dividing the overall pore diffusion resistance by the Knudsen or single-pore diffusion resistance.

Since the pore spaces in Type 4A molecular sieves are so small, the resistances to pore diffusion in this research are assumed to be the drag forces on the water molecules by the internal pore walls of the adsorbent and by the surfaces of the water molecules already adsorbed in the unit cavities. The flow of water molecules in the pore system of Type 4A molecular sieves can be considered condensed flow. Hence the resistances to condensed flow and to pore diffusion of water in molecular sieves are assumed to be the same in this research.

In studying heat of adsorption effects it is helpful
to locate a heat release interface at the condensation profile. The total heat released during water adsorption on Type A molecular sieves is approximately 1.8 times the latent heat of condensation (74). The heat released at the condensation profile would be approximately equal to or slightly greater than the heat of condensation. The remainder of the heat is perhaps released as frictional heat on the internal pore walls, and as de-activation energy at the fluid-solid interface within each cavity.

In order to isolate the resistances associated with the adsorbent particle from resistances located outside the particle such as gas film resistance, it is convenient to use a particle diffusion mechanism. A suitable method using mass transfer coefficients was described in the Literature Survey. In this approach the adsorbent particle is treated as a hollow shell so that the total solid phase resistance to diffusion can be located at the external surface of the particle. Thus, the total solid phase resistance could actually be a specific combination of the resistances described for the pore diffusion mechanism.

Recapitulating, the adsorption mechanism proposed by the writer as rate controlling for the air-water-molecular sieves system is the pore diffusion of water molecules penetrating into the adsorbent particle (e.g. molecular transport by pore diffusion). The condensation and vapor
pressure lowering activity occurring in the outermost unit cells, and the force interactions causing adsorption on the internal surfaces of the cavities of the unit cells are also essential parts of this postulated adsorption mechanism, but their transfer rates are assumed to be too fast to be controlling.
EXPERIMENTAL APPARATUS

The apparatus was designed to pass an air stream of constant water content, temperature, and flow rate into a fixed bed of adsorbent maintained in an isothermal condition. Water concentrations in the air stream going into and coming out of the fixed bed were determined by dew point measurements. Figure 11 represents a flowsheet of the experimental apparatus. Figure 12 shows the fixed bed drier design.

Air was supplied from a 90 psig line and passed through a standard air line filter (A) and pressure regulator (B). The packed column air filter (C) was a 24 inch length of 1½ inch standard steel pipe, and was filled with layers of glass wool, activated alumina, silica gel, and activated charcoal. The purpose of this filter was to trap all entrained particles and to adsorb small amounts of compressor oil in the air.

The water saturators (D) were made of 28 inch sections of 1½ inch standard steel pipe. Each saturator was filled half full of water and loosely packed with stainless steel wool to cause bubble dispersal within the liquid and de-entrainment above. The top of each saturator was fitted with a tee and a capped, straight-through line to ease filling and checking liquid level. By removing the cap from the straight-through line of the entrainment separator (E), it
Figure 11. Flowsheet of experimental apparatus

A. Standard air filter  
B. Pressure regulator  
C. Packed bed air filter  
D. Water saturator  
E. Entrainment separator  
F. Needle valve  
G. Heating coil  
H. Fixed bed drier  
I. Variable area flowmeter  
J. Dew-point potentiometer  
K. Wet and dry bulb  

psychrometric unit
1/4" Tubing (pressure tap)

1/8" Tubing (thermocouple)

3/8" Tubing (inlet air)

1/2" Brass pipe (12", 18", 24" drier section)

Coupling

Flange assembly

Wire screen

1/4" Tubing (thermocouple)

Brass tee

3/8" Tubing (exit air)

Note: Bottom pressure tap is on exit air line outside of bath

Figure 12. Details of fixed bed drier
was possible to drain both saturators by back pressuring air through this part of the system. The line between the packed column air filter and the first saturator was disconnected for this operation. The saturators could then be refilled with the required volume of distilled water. The water content of the air stream entering the fixed bed drier was controlled at a given temperature by the saturator pressure. This in turn was determined by the setting of the pressure regulator. A mercury manometer was used as a control aid for the low saturator pressures.

The entrainment separator (E), made from a 2 inch standard steel pipe 14 inches high, served to further remove entrained water drops; it also contained loosely packed steel wool. The needle valve (F), following the trap, reduced the pressure from that in the saturators to just above atmospheric pressure and controlled the air stream flow rate. All connecting piping was 3/8 inch copper tubing.

The moist air was brought to bath temperature in coil (G), constructed of 50 feet of 3/8 inch copper tubing. The 3/8 inch copper tubing line following the heating coil was fitted with a tee so that moist air could by-pass the drier. Both lines leaving the tee had shut-off valves.

Figure 12 shows details of the fixed bed drier (H). The fixed bed drier itself was ½ inch standard brass pipe (0.628 inch I.D.), and 12, 18, or 24 inches in height as required
for the run. These drier sections were coupled to the flange assembly holding the wire screen support. They gave over-all adsorbent bed heights of 13.875, 19.875, and 25.875 inches while leaving ¼ inch of free space between the adsorbent and the cross connection. Pressure tap lines were connected to the air lines above and below the fixed bed drier. Thermocouple wires also entered the apparatus above and below the fixed bed drier. The three-point series thermocouple below the drier was used to measure the difference between the exit air temperature and the bath temperature. These wires were kept dry by threading them through copper tubing and sealing the submerged ends going into the drier with cement. A Mosely Autograf X-Y Plotter (The Mosely Co., Pasadena, Calif.) was used to graphically record the temperatures.

The air from the bottom of the fixed bed drier passed through 3/8 inch copper tubing and a variable area flowmeter (I) to the dew-point instrument (J). This instrument is the portable dew-point potentiometer made by Weighing and Control Components, Inc., Hatboro, Pennsylvania. It operated on the principle of measuring the temperature at which moisture was deposited from the air stream on a polished mirror. Continuous, uninterrupted air stream flow was required. Cooling gas, necessary for varying the temperature of the polished mirror surface between -100°F. and +110°F., was
supplied by passing nitrogen gas from a pressure cylinder through a bath of liquid nitrogen, and then into the instrument where it impinged on the back of the mirror. This closely regulated cooling caused dew to form in a small spot at the center of the polished mirror. The formation of dew was observed by a 13X magnifier supplied with the instrument.

A wet and dry bulb psychrometric unit was attached to the dew-point instrument exit air line to give a continuous check on the dew-point readings. The constant temperature bath, in which items D, E, F, G, and H were submerged, consisted of a 55 gallon drum fitted with two 1000 watt immersion heaters, two thermoregulating timers, and a thermometer. Water circulation in the bath was accomplished by air jet agitation.

Regeneration of saturated adsorbent was accomplished in an electric furnace fitted with inlet and outlet pipe lines that were required for the continuous flow of a purified air purge gas.

Adsorbent particles of the required sizes were obtained either directly from the manufacturer or by fracturing the available sizes in a one quart Abbe ball mill with ½ inch steel balls.
PROCEDURE

Type 4A molecular sieve adsorbent, purchased from the Linde company, Division of Union Carbide Corp., Tonawanda, New York, was supplied in three different lots. Two lots were supplied in -8+12 Tyler mesh, roughly spherical beads, and one in 1/8 inch extruded pellets. Grade 40 silica gel, purchased from the Davison Chemical Division, W. R. Grace and Company, Baltimore, Maryland, was supplied in -6+12 Tyler mesh size, granular particles.

The spherical beads of molecular sieves and the silica gel particles were screened into various fractions by retaining them on Nos. 7, 8, 9, 10, and 12 Tyler mesh screens. The -8+9 Tyler mesh cut of the adsorbent was the main fraction used in this research. For the silica gel run (No. 8-2) and -8+10 Tyler mesh particle size runs of molecular sieves, mixtures of equal weights of the -8+9 and -9+10 screened fractions were used. Molecular sieve runs through run No. 31, were made with the -8+9, and the runs from No. 35 to No. 38 the -9+10 screened fraction of spherical particles. Runs above No. 38 were made with a new lot of spherical beads from the -8+9 and -8+10 Tyler mesh particle fractions or with granular particle fractions prepared by crushing the pellets. The limited supply of fresh molecular sieve adsorbent was the chief reason for using spherical beads from other than the -8+9 Tyler mesh size.
The pellets of molecular sieves were crushed in a one quart Abbe ball mill to obtain the -8+9, -9+10, -10+12, -14+20, and -24+32 Tyler mesh screened fractions of granular particles. The fines were separated to a large extent by the screening. The remainder were removed by passing the adsorbent down an agitated inclined tube through which a counter-current stream of air was blown.

New adsorbent was used for each run to eliminate any contamination effects or those attributable to recycling. The amount of adsorbent required was determined by filling the fixed bed drier to ¾ inch from the top. The run samples were stored in tightly capped containers. Each adsorbent sample was dried immediately before and regenerated after each run. The adsorbent sample was quickly weighed after the initial drying, and then immediately charged to the fixed bed drier for the start of the run. After the run the adsorbent was removed and weighed to ascertain the amount of water adsorbed. It was regenerated again, and the adsorbent weight after this regeneration also recorded.

Regeneration consisted of placing a crucible containing the adsorbent sample in an oven maintained at the necessary temperature for 24 hours. A temperature of 350°F. was required for silica gel and 650°F. for molecular sieves. Purified air purge gas was continuously passed through the oven to remove the water desorbed. The adsorbent sample was
stirred occasionally while being regenerated.

The following sequence was followed for a typical breakthrough run. Water was first drained from the saturators, and then replaced with 500 ml. of distilled water. The fixed bed drier was charged with adsorbent and then re-connected to the piping system in the 55 gallon drum. The drum was filled with water and the bath temperature adjusted to that required for the particular run. Air agitation of the bath was turned on. Accumulated moisture in the cooling gas lines to the dew-point instrument was removed and the Dewar flask was charged with liquid nitrogen.

The moist inlet air was by-passed around the fixed bed until the flow rate and humidity were constant for 10 minutes. The required inlet humidity as measured by the dew-point instrument, was controlled by the pressure in the saturators, or in turn by the pressure regulator setting. The run was started by passing the inlet air downward through the fixed bed. At frequent intervals the bed exit air dew-point and dry bulb temperature, and the wet and dry bulb temperatures of the air leaving the dew-point instrument were measured. Readings were taken every minute during the breakthrough curve period.

Additional data recorded during a run were: (1) saturator pressure, (2) air stream flow rate, (3) bed pressure drop, (4) system pressure drop, (5) room temperature (also
flowmeter temperature), (6) bath temperature, and (7) barometric pressure. The flow rate was kept constant by occasional adjustment of the needle valve (F, Figure 11). Similarly, the saturator pressure was maintained constant by suitable adjustment of the pressure regulator setting.

The bed, inlet air, and bed exit air temperatures were graphically recorded by the Moseley X-Y plotter. A series thermocouple was used to measure the temperature rises of the bed exit air over that of the water bath. In this manner the bed and inlet air temperatures could be checked against the zero-point of the exit air temperature curve, which actually represents the water bath temperature. The bath temperature was measured with a mercury thermometer.

Dew was deposited on the mirror by proper adjustment of the pressure and flow rate of the cooling gas. The instrument galvanometer was then adjusted to give the dew-point temperature on the indicator. The dew-point was taken as the average of the temperature at which the dew appeared covering the thermocouple wire circles, and the temperature at which the dew just disappeared.

The dew-point temperature was continually calibrated by the wet and dry bulb readings, and by using the psychrometric chart in Perry (89).

Equilibrium data for the conditions of a specific run were obtained by continuing the breakthrough run for approx-
approximately one to two hours after the exit air dew-point reached the dew-point of the inlet air. The weight of adsorbed water per weight of water-free adsorbent was the equilibrium water content of the solid for the run in question.
EXPERIMENTAL RESULTS AND DISCUSSION

Results and Data Interpretation

Interpretation of breakthrough data taken for a fixed bed operation consists of fitting the mathematical relationships thought applicable to the experimental data, thus establishing the applicability of the equations used. It was possible to postulate a theoretical adsorption mechanism for the air-water-molecular sieves (Type 4A) system by evaluating the effect of several variables on the mass transfer and by comparing mathematical models of mechanisms with the experimental data.

The pore and particle diffusion mathematical models are thought applicable to the postulated rate determining mechanism. Also, the MTZ approach of Michaels (81) and Treybal (103) appears applicable and well suited to simple design treatments. This and the next section show that the theories postulated, the mathematical models with their limitations, and the general MTZ approach are applicable to fixed bed air drying operations using molecular sieves. Run No. 26 was selected to demonstrate the type of analysis that was carried out using the experimental data.

**Breakthrough curve data**

Figure 13 shows the complete experimental data for breakthrough run No. 26. This curve is a typical representation of all the breakthrough runs made. Dew-
Figure 13. Representative breakthrough curve for air-water-molecular sieves (Type 4A) system.
point readings were taken every minute to give the high point density shown. The MTZ is described completely by this curve, but for analytical purposes the length of the MTZ is represented by $W_E - W_B$, and similarly the shape of the MTZ by the factor $(f)$. The characteristic shape factor $(f)$ is calculated by dividing the integrated area under the breakthrough curve between $W_B$ and $W_E$ (denoted by $U$, Figure 2), by the total area between $W_B$ and $W_E$ and between $C/C_0$ values from 0 to 1.0. It represents the fraction of the MTZ still able to adsorb water.

The shape factor for the breakthrough curves was found to be a constant for the runs made. The value obtained was $0.593 \pm 0.03$ for spherical beads and $0.593 \pm 0.06$ for granular particles. The larger deviation given for granular particles was probably caused by measurement inaccuracies in obtaining the sharper (steeper initial slope) breakthrough curves for small granular particles.

Material balances were made for each run. The material balance error for water adsorbed on Type 4A molecular sieves is given by the following equation:

$$\text{Percent material balance error} = 100\% \frac{\text{actual bed weight gain} - \text{calc. bed weight gain}}{\text{actual bed weight gain}}$$ (45)

The calculated bed weight gain was obtained by a graphical
integration procedure giving the area above the breakthrough curve for the entire run. This area represents the weight of water removed from the air stream or gained by the adsorbent up to complete bed saturation. The errors obtained for runs up to No. 38 are given in previous work (86). Errors of less than 10% were obtained for all runs above No. 38. The experimental breakthrough curves were corrected to 100 percent material balance before calculation of the design parameters and comparison with the mechanism models.

**Determination of diffusivities and rate coefficients**

It is apparent from equations 40, 50 and 51 that the slope of a plot of \( \ln \left(1 - \frac{C}{C_0}\right) \) versus \( W_C \) can be used to calculate the overall solid-phase rate coefficient and the apparent pore diffusivity, if a linear relationship is obtained. Figure 14 shows this plot for run No. 26. The rate coefficient and the apparent pore diffusivity are readily calculated from the slope. The pore diffusivity \( D_{pore} \) was obtained by empirically determining a material balance correction factor from the experimental breakthrough curves and dividing it into the apparent pore diffusivity. The reasons for this procedure are outlined in the pore diffusion derivation given in the Appendix. The value of \( k_s a_p \) can only be obtained as a function of \( k_s a_p \) by using this plot (see equations 37 and 38).
The slope of a plot of \( \ln \left( \frac{C}{C_0} \right) \) versus \( W_c \) can be used to calculate \( k_{g_p} \) (see equation 37). This plot for run No. 26 is given in Figure 15. Eagleton (35) determined \( k_{g_p} \) by using the slope of the best line drawn through the experimental points up to the discontinuity point \( (C_D') \). In Figure 15 it appears that this discontinuity point is below \( C/C_0 = 0.1 \) or close to zero since a non-linear relationship is obtained above this point. The adsorption is essentially solid phase controlled.

As an approximate calculation for \( k_{g_p} \) the slope of the best line (\( \ln \left( \frac{C}{C_0} \right) \) versus \( W_c \)) drawn through the experimental points from \( C/C_0 = 0 \) to \( C/C_0 = 0.1 \) was used. It was found that this method gave better accuracy than a method using an experimental value of \( C/C_0 \) close to zero. Values of \( k_{s_p}, k_{g_p}, \) and \( k_{s_p} \) obtained for the breakthrough runs are given in Tables 2 and 3. Figure 9 shows the calculated breakthrough curves for run No. 26 using these rate coefficient values.

Values of \( k_{g_p} \) and \( k_{s_p} \) can also be obtained from the slopes at each \( C/C_0 \) point along the logarithm curves. Each of these values can be used to calculate a breakthrough curve, which then can be compared to the experimental one. The point values giving the best breakthrough curve duplication were assumed to be applicable to the adsorption. Figure 16 shows the results of this procedure for run No. 26.
Figure 14. Log of the adsorption driving force versus cumulative dry air weight (run No. 26)
Run No. 26

Corrected cumulative dry air weight, $W_c$, lbs.
Figure 15. Log of the exit to inlet water content ratio versus cumulative dry air weight
It was found that $k_{gap}$ and $C_D$ correspondingly change to give nearly constant $k_{sap}$ values when parts of the experimental breakthrough curves are duplicated. Only reliable $k_{sap}$ values can be obtained by this point slope method, since the $k_{gap}$ values rapidly decrease as points of smaller driving forces than the maximum ($C_0 - C = C_0 - 0$) are used. For run No. 26 an average $k_{sap}$ value of 4.0 hrs.$^{-1}$ was obtained. This can be compared to the $k_{sap}$ value of 3.738 hrs.$^{-1}$ from Table 2. The difference may be attributed to the use of a lower driving force in calculating $k_{gap}$.

**Principal run conditions and calculated values**

Table 1 gives the principal run conditions and calculated $Z_{MTZ}$ values for the good breakthrough runs made using Type 4A molecular sieves. A few runs were not included because difficulties were encountered such as, for example, leaks in the piping system. The $Z_{MTZ}$ values were calculated by equation 35. The three bed heights used, 13.875, 19.875 and 25.875 inches, are given in terms of bed weight. The differences in weight at each of these height levels are attributed to differences in the shape of the particles, and to variation in the amount of settling of the adsorbent in the beds.
Figure 16. Calculated breakthrough curves for point evaluated mass transfer coefficients.
Ratio of water content of exit to inlet air, \( \frac{C}{C_0} \)

Corrected cumulative dry air weight, \( W_c \), lbs.
Table 1. Principal run conditions and calculated MTZ heights

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Bed weight (grams)</th>
<th>Bed temp. (°F.)</th>
<th>Particle size (Tyler Mesh)</th>
<th>Flow rate (lbs. air/hr. ft.²)</th>
<th>Inlet concentration (lbs. H₂O/1 lb. air)</th>
<th>MTZ height (inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>50.49</td>
<td>67.5</td>
<td>8+9 Ba</td>
<td>1096</td>
<td>0.01101</td>
<td>11.620</td>
</tr>
<tr>
<td>3</td>
<td>50.65</td>
<td>71.1</td>
<td>8+9 B</td>
<td>1118</td>
<td>0.01137</td>
<td>11.180</td>
</tr>
<tr>
<td>4</td>
<td>50.74</td>
<td>65.8</td>
<td>8+9 B</td>
<td>1131</td>
<td>0.00988</td>
<td>10.720</td>
</tr>
<tr>
<td>5</td>
<td>49.38</td>
<td>67.3</td>
<td>8+9 B</td>
<td>1131</td>
<td>0.01042</td>
<td>12.620</td>
</tr>
<tr>
<td>6</td>
<td>71.18</td>
<td>65.9</td>
<td>8+9 B</td>
<td>1097</td>
<td>0.00938</td>
<td>10.050</td>
</tr>
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<td>7</td>
<td>92.61</td>
<td>68.8</td>
<td>8+9 B</td>
<td>1107</td>
<td>0.01065</td>
<td>11.290</td>
</tr>
<tr>
<td>8</td>
<td>90.66</td>
<td>65.5</td>
<td>8+9 B</td>
<td>469</td>
<td>0.00998</td>
<td>5.110</td>
</tr>
<tr>
<td>9</td>
<td>70.81</td>
<td>66.8</td>
<td>8+9 B</td>
<td>469</td>
<td>0.01065</td>
<td>5.240</td>
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<td>10</td>
<td>50.59</td>
<td>80.9</td>
<td>8+9 B</td>
<td>1139</td>
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<td>11.670</td>
</tr>
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<td>11</td>
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**Note:** B denotes spherical beads used.
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bG denotes granular particles used
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Tables 2 and 3 give the calculated mass transfer rate coefficients for each breakthrough run. Particle and pore diffusivities for each run are given in Table 4. Some graphical plots of these data are given in the design correlations section.

Calculations of $K_a$ and $D_p$ were made as described in the previous section. The calculations of $k_s a_p$ and $k_g a_p$ were made using equations 37 and 38 and the method utilizing the best line drawn through the $C/C_0 = 0$ to $C/C_0 = 0.10$ range of data points. Particle diffusivities were calculated using this equation from the work of
Glueckauf and Coates (47):

\[
k_s A_p = \frac{60 D_p}{d_p^2}
\]  \hspace{1cm} (46)

For comparison purposes the Knudsen diffusivities calculated for Type 4A molecular sieves and water vapor are 3.09 \((10^{-3})\), 3.06 \((10^{-3})\), 3.04 \((10^{-3})\) and 3.02 \((10^{-3})\) for the 90, 80, 70 and 66.5°F. adsorbent bed temperatures, respectively. The equation given in Smith (99) was used. Comparison of these with the particle diffusivities given in Table 4 indicate a thousand-fold reduction, or possibly molecular transport through a thousand internal pores.

Experimental porosities were obtained by liquid displacement measurements for the particle sizes used in this research. Porosities for granular particles were also calculated based on an average bed weight for each particle size filling the 19.375 inch drier, and a particle specific gravity of 1.1 (74). Porosities for spherical beads were calculated using an arithmetic mean particle diameter and the volume of a sphere equation. These porosities and the calculated external surface areas for the particles are given in Table 5. The sphericity versus porosity experimental relationship given in Brown (24) was used to calculate the external surface areas of the particles. The air displacement method for measuring porosities might have given improved accuracy, but the possible increase in
Table 2. Calculated mass transfer rate coefficients versus inlet concentration

<table>
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<th>Run No.</th>
<th>Inlet concentration, C₀ (lb. H₂O/lb. air)</th>
<th>Overall rate coefficient, kₛₚ (lb. air/(hr. lb. solid))</th>
<th>Gas phase rate coefficient, kₐₚ (hours⁻¹)</th>
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Table 4. Calculated particle and pore diffusivities versus inlet concentration and flow rate

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<td>663</td>
<td>15.600</td>
<td>10.19000</td>
</tr>
<tr>
<td>72</td>
<td>0.01542</td>
<td>812</td>
<td>3.837</td>
<td>2.03000</td>
</tr>
<tr>
<td>73</td>
<td>0.00784</td>
<td>971</td>
<td>6.830</td>
<td>3.68000</td>
</tr>
<tr>
<td>74</td>
<td>0.00784</td>
<td>665</td>
<td>6.230</td>
<td>3.47000</td>
</tr>
<tr>
<td>75</td>
<td>0.01572</td>
<td>443</td>
<td>10.820</td>
<td>6.90000</td>
</tr>
<tr>
<td>76</td>
<td>0.01485</td>
<td>295</td>
<td>6.120</td>
<td>0.56600</td>
</tr>
<tr>
<td>77</td>
<td>0.01542</td>
<td>442</td>
<td>7.990</td>
<td>0.93300</td>
</tr>
<tr>
<td>78</td>
<td>0.00681</td>
<td>972</td>
<td>2.267</td>
<td>1.59800</td>
</tr>
<tr>
<td>79</td>
<td>0.00460</td>
<td>972</td>
<td>1.331</td>
<td>1.14700</td>
</tr>
<tr>
<td>80</td>
<td>0.00336</td>
<td>971</td>
<td>0.835</td>
<td>0.40700</td>
</tr>
</tbody>
</table>
accuracy was judged as not sufficient to justify using the method in this research.

The experimental water capacities for Type 4A molecular sieves are given in Figure 17. The linear not through the origin isotherm approximations are shown for each bed temperature and the intercept values (°C) as well.

**Independent variable effects**

Several of the independent variables listed in the introduction do not appear to limit or control the design and operation of fixed bed adsorbers. However, the operating values of these independent variables should remain within a given wide range of optimum values.

Effective transfer of the heat of adsorption to the constant temperature bath essentially determines the fixed

---

Table 4. (Continued)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Inlet concentration, $C_0$ (lb. $H_2O$/lb. air)</th>
<th>Flow rate, $G$ (lbs. air/hr.)</th>
<th>Particle diffusion, $D_p$($10^6$) (ft.$^2$/hr.)</th>
<th>Pore diffusion, $D_{pore}$($10^6$) (ft.$^2$/hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>81</td>
<td>0.01542</td>
<td>443</td>
<td>10.970</td>
<td>6.73000</td>
</tr>
<tr>
<td>82</td>
<td>0.01542</td>
<td>442</td>
<td>5.360</td>
<td>0.63900</td>
</tr>
<tr>
<td>83</td>
<td>0.00988</td>
<td>972</td>
<td>3.920</td>
<td>2.66000</td>
</tr>
<tr>
<td>Particle size (Tyler mesh)</td>
<td>Arithmetic mean particle diameter (inches)</td>
<td>Calculated porosity (ft.³ bed)</td>
<td>Experimental porosity (ft.³ bed)</td>
<td>External surface area (ft.²/ lb. solid)</td>
</tr>
<tr>
<td>---------------------------</td>
<td>------------------------------------------</td>
<td>-------------------------------</td>
<td>---------------------------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>8+9 B²</td>
<td>0.0855</td>
<td>0.453c</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8+10B</td>
<td>0.0790</td>
<td>0.434</td>
<td>0.445</td>
<td>10.87</td>
</tr>
<tr>
<td>7+8 Gb</td>
<td>0.1015</td>
<td>0.398</td>
<td>0.416</td>
<td>10.59</td>
</tr>
<tr>
<td>8+9 G</td>
<td>0.0855</td>
<td>0.418</td>
<td>0.423</td>
<td>13.22</td>
</tr>
<tr>
<td>8+10G</td>
<td>0.0790</td>
<td>0.418</td>
<td>0.431</td>
<td>14.70</td>
</tr>
<tr>
<td>-10+12G</td>
<td>0.0600</td>
<td>0.424</td>
<td>0.443</td>
<td>19.06</td>
</tr>
<tr>
<td>-12+14G</td>
<td>0.0505</td>
<td>0.431</td>
<td>0.443</td>
<td>22.90</td>
</tr>
<tr>
<td>-14+20G</td>
<td>0.0394</td>
<td>0.436</td>
<td>0.448</td>
<td>30.60</td>
</tr>
<tr>
<td>-24+32G</td>
<td>0.0236</td>
<td>0.448</td>
<td>0.456</td>
<td>-</td>
</tr>
</tbody>
</table>

²B denotes spherical beads used
³G denotes granular particles used
⁴c calculated using adsorbent bed weight for run No. 44
⁵d calculated using an average of 29 adsorbent weights
⁶e calculated using adsorbent bed weight for run No. 68

Bed temperature and whether isothermal operation has been attained. The exit air stream temperature profile is one method of evaluating the heat effects. For water adsorption on Type 4A molecular sieves the exit air temperature rises to a maximum value at the point of maximum water transfer, namely, the breakthrough point. It then decreases during the MTZ period to the same temperature as
Figure 17. Experimental equilibrium isotherms for Type 4A molecular sieves at 66.5°F, 70°F, 80°F, and 90°F.
Water content of solid, $X^*_o$ 

$\frac{\text{lbs H}_2\text{O}}{\text{lb solid}}$
that of the fixed bed originally (e.g., that of the constant temperature bath). No measurable difference in temperature was observed after the exit air water content reached that of the inlet. Thus one can assume negligible accumulation of heat in the adsorbent bed. Order of magnitude calculations showed that approximately 90% of the heat of adsorption is transferred to the constant temperature bath, while the remainder is removed by the exit air stream.

Figures 18, 19 and 20 show the maximum exit air temperature rises for various water transfer rates at 90, 80 and 70°F. bed temperatures. Changes or upsets in the amount of heat transferred to the constant temperature bath were greatly magnified in the exit air stream temperature effects. Hence deviations in the temperature rise data were mainly due to external conditions such as the degree of agitation in the bath. It appears that for spherical beads and the larger granular particles one can generally assume isothermal operation provided that similar apparatus is used.

Bed height does not appear to affect the MTZ or the adsorption of water on Type 4A molecular sieves. This is the major requirement for the use of the simple MTZ design procedure, and was extensively investigated in previous work (86). Figures 21 and 22 show that the MTZ length is constant and independent of fixed bed height. These
Figure 18. Exit air stream temperature rise over 90°F. bed temperature

Figure 19. Exit air stream temperature rise over 80°F. bed temperature

Figure 20. Exit air stream temperature rise over 70°F. bed temperature
Figure 21. Effect of bed height (weight) on MTZ length at a flow rate of 914 lbs. dry air/hr. ft. and a bed temperature of 90°F.
Figure 22. Effect of bed height (weight) on MTZ length at a bed temperature of 66.5°F, and an average inlet concentration of 0.01045 lbs. H₂O/lb. dry air
graphs cover a representative sample of past molecular sieve experimental data (86).

Bed diameter is usually fixed by capacity requirements and adsorbent particle size. The Linde Company recommends a bed to particle diameter ratio of 20 regardless of whether the operation is isothermal or adiabatic (53). This was judged as too high for satisfactory isothermal operation. Although the bed to particle diameter ratio is not considered critical above 1.8 when considering gas flow distribution, it was decided that a larger ratio should be used to completely avoid any channelling effects, but not so large as to inhibit radial heat transport (80). A 7.5 ratio was believed to be satisfactory and was used in the design of the driers. The experimental driers were originally designed for the -8+9 Tyler mesh particles, and gave satisfactory isothermal operation. Hence it was decided to use smaller particles in the particle size evaluations.

Bed pressure drops and system pressure drops (below the fixed bed) were measured and are given in Table 6. The adsorption essentially occurred at atmospheric pressure since these pressure drops were not large. Pressure has a negligible effect on water adsorption as Maslan (80) reports in his work with silica gel. A pressure of 760 mm Hg was used in the absolute humidity calculations, since
Table 6. Bed and system pressure drops and average adsorbent bed densities

<table>
<thead>
<tr>
<th>Particle size (Tyler Mesh)</th>
<th>Maximum flow rate (lbs. air/ft.(^2))</th>
<th>Average bed density (lbs. solid/ft.(^3))</th>
<th>Bed pressure drop (mm Hg)</th>
<th>System pressure drop (below fixed bed) (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8+9 B</td>
<td>972</td>
<td>43.8</td>
<td>44</td>
<td>47</td>
</tr>
<tr>
<td>- 8&quot;10B</td>
<td>972</td>
<td>43.4</td>
<td>50</td>
<td>49</td>
</tr>
<tr>
<td>- 7+8 G</td>
<td>972</td>
<td>40.7</td>
<td>64</td>
<td>48</td>
</tr>
<tr>
<td>- 8+9 G</td>
<td>972</td>
<td>39.7</td>
<td>70</td>
<td>47</td>
</tr>
<tr>
<td>- 8+10G</td>
<td>664</td>
<td>39.7</td>
<td>60</td>
<td>37</td>
</tr>
<tr>
<td>-10+12G</td>
<td>442</td>
<td>39.3</td>
<td>56</td>
<td>17</td>
</tr>
<tr>
<td>-12+14G</td>
<td>443</td>
<td>38.8</td>
<td>66</td>
<td>17</td>
</tr>
<tr>
<td>-14+20G</td>
<td>452</td>
<td>38.2</td>
<td>96</td>
<td>19</td>
</tr>
<tr>
<td>-24+32G</td>
<td>443</td>
<td>37.6</td>
<td>239</td>
<td>17</td>
</tr>
</tbody>
</table>

\(^{a}\)B denotes spherical beads used  
\(^{b}\)G denotes granular particles used  

Very little inaccuracy results from barometric fluctuations.

Adsorbent capacity loss with time may be due to the length of time the adsorbent is exposed to a material at a high temperature, or it may simply be due to the number of times it is cycled, or a combination of the two. As one check on the first cause two run adsorbent samples (Nos. 81 and 32) were subjected to regeneration conditions of 650°F. and an air stream purge gas for over four months without interruption. Comparison with identical condition
runs (Nos. 75 and 81, and Nos. 77 and 82) show no loss in adsorbent capacity, and in fact, no difference in adsorption characteristics. As a preliminary evaluation, the above could indicate that the capacity loss with time may be primarily due to a change in the adsorbent itself provided that adsorbent poisoning is negligible.

Adsorbent bed densities are also given in Table 6. They are averages that were obtained from the initial adsorbent weights charged to the fixed bed. The adsorbent bed was slowly filled to a specific bed height. The bed was tapped lightly during filling. The weight of adsorbent required for this procedure was recorded as the initial weight. Adsorbent beds generally tend to become more dense and to exhibit a decrease in voidage during operation. In this research the bed heights were essentially the same after a run as before.

**Design correlations for molecular sieves**

The design correlations obtained for molecular sieves describe MTZ bed heights mass transfer rate coefficients and diffusivities as functions of the important independent variables. Inlet concentration ($C_0$), flow rate ($G$), particle size ($d_p$), bed temperature and particle shape appear to be the independent variables most affecting the design parameters. A statistically designed program of runs was used to obtain the relationships shown in the figures.
Mass transfer zone heights

Figures 23 and 24 show the effects of inlet concentration on the MTZ height - the former versus bed temperature and the latter versus particle shape. The temperature dependent curves in Figure 23 are displaced similarly to the respective equilibrium isotherms.

The particle shape effect is more pronounced than it appears in Figure 24 when packed bed density is considered. As the packed bed density is decreased (which is generally the case when granular particles replace spherical beads) the $Z_{MTZ}$ should increase. Since the data show a one-third reduction in $Z_{MTZ}$ values, one is led to believe that the greater surface area of granular particles is responsible. In the postulated pore diffusion mechanism the particle's external surface is essentially the condensing surface for water molecules entering the pore system. If the average rate of transport of water molecules through a pore is constant, the reduction in $Z_{MTZ}$ values for granular particles indicates a faster approach to equilibrium and a larger number of water molecules condensing at the greater external surface.

The effects of flow rate on the MTZ heights are given in Figures 25, 26 and 27. In Figure 25 isotherms are shown indicating the relative magnitude and direction of temperature effects on MTZ heights, but the average de-
Figure 23. MTZ height versus inlet air water content for Type 4A molecular sieves

Figure 24. Effect of particle shape on MTZ height
Air flow rate: 914 lbs/hr ft²
Adsorbent particle size: 0.065–0.093 inches
(-8+9 mesh spherical beads)

MTZ height, ZMTZ, inches

Inlet air water content, C₀, (lb H₂O/lb dry air) x 10³

Bed temperature: 80°F
Bed height: 19.875 inches

MTZ height, ZMTZ, inches

Particle sizes
- X -8+9 Tyler mesh fraction
- O -8+10 Tyler mesh fraction

Granular particles
(-8+9 mesh)

Spherical beads
(-8+9 mesh)

Air flow rates:
- X 972 lbs/hr ft²
- ▲ 443 lbs/hr ft²
- ◆ 914 lbs/hr ft²
- ■ 663 lbs/hr ft²

Inlet air water content, C₀, (lb H₂O/lb dry air) x 10³
Figure 25. MTZ height versus flow rate for Type 4A molecular sieve (spherical beads)
Particle size: -8+9 mesh spherical beads
Inlet concentrations:

- ▽ 0.01101 lbs H₂O/lb dry air
- ▲ 0.01542 lbs H₂O/lb dry air

Bed heights:

- ▽ 13.875 inches
- ▲ 19.875 inches
- ▼ 25.875 inches

T=90°F, ΔT=66.5°F

Air flow rate, G, lbs dry air/hr ft²
Bed temperature: 70°F
Bed height: 19.875 inches
Inlet concentration: 0.00988 lbs
\( \text{H}_2\text{O}/\text{lb air} \)

- 8+10 mesh fraction spherical beads
- 7+8 mesh fraction granular particles
- 12+14 mesh fraction granular particles

Figure 26. Flow rate and particle size effects on MTZ height at 70°F bed temperature
Bed temperature: 90°F
Bed height: 19.875 inches
Inlet concentration: 0.01542 lbs H₂O/lb air

Particle sizes:
- o - 8+9 mesh fraction
- x - 7+8 mesh fraction
- ▼ - 10+12 mesh fraction
- ▲ - 14+20 mesh fraction
- ▼ - 24+32 mesh fraction

Figure 27. Flow rate and particle size effects on MTZ height at 90°F bed temperature.
viation from each line is greater than the difference between the isotherms. Hence the data primarily indicate the influence of flow rate on the $Z_{MTZ}$ for design purposes.

Figures 26 and 27 indicate the relative speeds of mass transfer as smaller and smaller particles are used. Mass transfer was so much faster for small particles that slower flow rates had to be used to measure the water content changes in the MTZ. Figure 28 is a cross plot of the data given in Figure 27. These figures are not particularly suitable for design values because only a few data points were available to describe the effects. Dotted lines are used to denote order of magnitude relationships.

Again the effect of particle size and shape appears to indicate the importance of external surface in molecular sieve water adsorption. Decreasing the particle size decreases the $Z_{MTZ}$. Substitution of granular particles for spherical beads decreases the $Z_{MTZ}$. Flow rate appears to be directly and linearly proportional to $Z_{MTZ}$. Apparently the function of flow is only to transport the required number of water molecules to the vicinity of the adsorbent particle's external surface, provided longitudinal diffusion and gas film resistance are negligible. The flow rates used in this research do not appear to be in the range where the latter two effects are significant.

Combination of the $Z_{MTZ}$ equation (equation 35) with
Figure 28. MTZ height versus mean particle diameter for 90°F. bed temperature
Bed temperature: 90°F
Bed height: 19.875 inches
Inlet concentration: 0.01542 lbs H₂O/lb air

Air flow rates:
× 972 lbs/hr ft²
● 663 lbs/hr ft²
▼ 443 lbs/hr ft²
▲ 294 lbs/hr ft²
▼ 147 lbs/hr ft²

Granular particles

Arithmetic mean particle diameter, \( d_p \), inches

MTZ height, \( Z_{MTZ} \), inches
the various breakthrough curve models (equations 37, 38, 40 or 51) give analytical expressions that describe the effect of the independent variables on the design parameters.

Using equation 40 - the overall solid phase resistance model - for calculating \( W_B \), and an empirical expression obtained from run No. 26 data for \( W_B \), one finds:

\[
Z_{MTZ} = \frac{2.148 \ C_0 G'Z}{0.279 \ C_0 G' + W_s K_s a_p} \tag{47}
\]

where:

\[
W = \frac{X^* W_s}{C_0} + \frac{1.2 X^* G'}{K_s a_p} \tag{48}
\]

Equation 47 represents the relative effect of \( C_0 \) on \( Z_{MTZ} \) as shown in Figure 23. It also represents the relative effect of \( G \) on \( Z_{MTZ} \) as given in Figure 25. It appears that the slope of the \( Z_{MTZ} \) versus \( C_0 \) line reflects the non-constant character of the equilibrium parameter (\( r^* \)).

Further work is necessary to determine how these relationships function as zero inlet concentration and zero flow rate are approached. Similarly, one can develop other expressions using the different mechanism models.

**Mass transfer rate coefficients**

Figures 29, 30 and 31 show the \( K_s a_p \), \( k_s a_p \) and \( k_g a_p \) values, respectively, for the data points shown in Figure 23. The graphs of \( K_s a_p \) and \( k_s a_p \) versus \( C_0 \) are very similar to \( Z_{MTZ} \) graphs
Figure 29. Overall rate coefficient versus inlet air water content for Type 4A molecular sieve beads

Figure 30. Solid phase rate coefficient versus inlet air water content for Type 4A molecular sieve beads

Figure 31. Gas phase rate coefficient versus inlet air water content for Type 4A molecular sieve beads
Overall rate coefficient, $K_a$, hours$^{-1}$

Air flow rate: 914 lbs./hr ft$^2$
Adsorbent particle size: 0.065 - 0.093 inches (Spherical beads)

Inlet air water content, $C_o$, (lb. H$_2$O/lb. dry air) x 10$^3$

Solid phase rate coefficient, $k_s$, hours$^{-1}$

Air flow rate: 914 lbs./hr ft$^2$
Adsorbent particle size: 0.065 - 0.093 inches (Spherical beads)

Inlet air water content, $C_o$, (lb. H$_2$O/lb. dry air) x 10$^3$

Gas phase rate coefficient, $k_g$, lbs. H$_2$O

Air flow rate: 914 lbs./hr ft$^2$
Adsorbent particle size: 0.065 - 0.093 inches (Spherical beads)

Inlet air water content, $C_o$, (lb. H$_2$O/lb. dry air) x 10$^3$
and are utilized for adsorber design in the same way. The
inlet concentration effect shown in Figures 29 and 30 in­
dicates the possibility of a fluid-phase mechanism, such
as pore diffusion, in the predominately solid-phase rate
controlled expression. The solid-phase rate controlled
model gives an asymptotic breakthrough curve near \( C/C_0 \approx 1 \).
This result is not in agreement with the experimental data.
The pore diffusion rate controlled model duplicates both
the solid-phase model and the experimental data in the
lower portion of the breakthrough curve. It also has a
finite limit near \( C/C_0 = 1 \), and agrees with experimental
data in the upper portion of the breakthrough curve. Thus
the pore diffusion mechanism model is a refinement of the
solid-phase mass transfer coefficient model, and appears
to give a more accurate description of water adsorption
on molecular sieves. The equations describing the pore
diffusion model are given in the next section. Appropriate
comparisons of the calculated breakthrough curves with
experimental curves are also given.

Since there is very little difference in value between
\( k_{s_a} \) and \( k_{s_p} \), a slight change in a \( k_{s_a} \) value is observed
for a considerably larger change in the corresponding
\( k_{s_p} \) value. Because of this and since the \( k_{s_p} \) values can
only be determined from the most inaccurate part of the
breakthrough curve, no generalizations can safely be made
in this research for $k_{g a p}$. However, the $k_{g a p}$ data are still of some use in correcting for gas film resistances in the minimum dew-point portion of the breakthrough curve. This influence extends only up to the 0.1 $C/C_0$ point of the curve.

Figure 32 shows the effect of particle shape on $K_{sa p}$ for various inlet concentrations. Figures 33, 34 and 35 graphically describe the flow rate effects on $K_{sa p}$, $K_{sa p}$ and $k_{g a p}$, respectively. It appears that $K_{sa p}$ and $k_{sa p}$ are independent of flow rate. Theoretically, $k_{g a p}$ should correspondingly increase with flow rate, but it is difficult to determine this effect from the experimental $k_{g a p}$ data.

Figure 36 shows the effect of mean particle diameter on the $K_{sa p}$ values computed for the data points given in Figure 28.

Particle and pore diffusivities

Particle diffusivities exhibit the same relationships to $C_0$ and $G$ as do the $K_{sa p}$ values since they differ only by the particle diameter (see equation 46). A sample particle diffusivity plot is given in Figure 37 for comparison with Figure 30.

Figure 38 indicates that the experimental pore diffusivities are almost independent of inlet concentration. Smaller spherical beads were used for the 70°F. runs. The increase in $D_{pore}$ over the entire $C_0$ range is less than the maximum deviation of points from the line. Internal re-
Figure 32. Effect of particle shape on overall rate coefficients at various inlet air water contents for Type 4A molecular sieves
Overall rate coefficient, $K_{\text{overall}}$, hours$^{-1}$

Bed temperature: $80^\circ F$

Particle size:
- ox-8+9 Tyler mesh fraction $\times$
- $\bullet$-8+10 Tyler mesh fraction $\bullet$

Granular particles

Spherical beads

Air flow rates:
- $\times$ 972 lbs./hr. ft$^2$
- $\bullet$ 663 lbs./hr. ft$^2$
- $\nabla$ 443 lbs./hr. ft$^2$

Inlet air water content, $C_0$, (lb. H$_2$O/lb. dry air) $\times 10^3$
Figure 33. Overall rate coefficient versus flow rate for Type 4A molecular sieve beads

Figure 34. Solid phase rate coefficient versus flow rate for Type 4A molecular sieve beads

Figure 35. Gas phase rate coefficient versus flow rate for Type 4A molecular sieve beads
Overall rate coefficient, $K_s$, hours$^{-1}$

- Particle size: -8+9 mesh spherical beads
- Inlet concentration:
  - $0.01101$ lbs H$_2$O/lb dry air
  - $0.01542$ lbs H$_2$O/lb dry air

Bed heights:
- 13.875 inches
- 19.875 inches
- 25.875 inches

Air flow rate, $G$, lbs. dry air/hr. ft$^2$

---

Solid phase rate coefficient, $k_s$, hours$^{-1}$

- Particle size: -8+9 mesh spherical beads
- Inlet concentration:
  - $0.01101$ lbs H$_2$O/lb dry air
  - $0.01542$ lbs H$_2$O/lb dry air

Bed heights:
- 13.875 inches
- 19.875 inches
- 25.875 inches

Air flow rate, $G$, lbs. dry air/hr. ft$^2$

---

Gas phase rate coefficient, $k_g$, lbs. air/(hr. lb. solid)

- T = 90°F
- T = 66.5°F

Air flow rate, $G$, lbs. dry air/hr. ft$^2$
Figure 36. Effect of mean particle diameter on the overall rate coefficient at 90°F. bed temperature
Overall rate coefficient, \( K_s a_p \), hours\(^{-1}\)

Air flow rates:
- \( X \) 972 lbs/hr ft\(^2\)
- \( \bullet \) 663 lbs/hr ft\(^2\)
- \( \nabla \) 443 lbs/hr ft\(^2\)
- \( O \) 294 lbs/hr ft\(^2\)
- \( \nabla \) 147 lbs/hr ft\(^2\)

Bed temperature: 90°F
Bed height: 19.875 inches
Inlet concentration: 0.01542 lbs H\(_2\)O/lb air

Arithmetic mean particle diameter, \( d_p \), inches
Figure 37. Particle diffusivities versus inlet air water content for Type 4A molecular sieve beads
Particle diffusivity, $D_p$, $(\text{ft}^2/\text{hr.}) \times 10^6$

Air flow rate: 914 lbs./hr. ft$^2$

Adsorbent particle size: 0.065 - 0.093 inches
(Spherical beads)

Inlet air water content, $C_0$, (lb. H$_2$O/lb. dry air) $\times 10^3$
Figure 38. Pore diffusivities versus inlet air water content for Type 4A molecular sieve beads

Figure 39. Particle and pore diffusivity comparisons at various inlet air water contents for Type 4A molecular sieve beads

Figure 40. Effect of particle shape on pore diffusivities at various inlet air water contents for Type 4A molecular sieves
sistances are isolated from the resistances at the external surface of the particles when $D_{\text{pore}}$ is independent of the operating variables (e.g., $C_o$ and $G$). Figure 39 indicates that pore diffusivities approximate this condition better than particle diffusivities.

The effect of particle shape and possibly, particle volume, on $D_{\text{pore}}$ is given in Figure 40. The difference between -8+9 Tyler mesh beads and granular particles, as indicated by the lines, may be due to the increased volume or the increased external surface area of the granular particles; or it may be due to a combination of both. Pore diffusivities for the -8+10 mesh granular particle runs are slightly higher than those for the -8+9 mesh beads but there is not sufficient data to generalize further.

Figure 41 describes the effect of another material balance variable, $W_s$, on $D_{\text{pore}}$. In the breakthrough curve model for the pore diffusion mechanism it was found that a parameter including $C_o$ and $W_s$ was needed to satisfy the material balance and to locate the upper boundary condition. This parameter was used to modify $D_{\text{pore}}$ in the mathematical model. Fundamental surface chemistry work is needed to resolve the differences between macro and molecular scale transport processes. Relationships of some variables to $D_{\text{pore}}$ are difficult if not impossible to explain without this understanding. At present $D_{\text{pore}}$ is
Figure 4.1. Pore diffusivity versus adsorbent bed weight for Type 4A molecular sieve beads
Pore diffusivity, $D_{pore}$, $(\text{ft}^2/\text{hr.}) \times 10^6$

Air flow rate: 914 lbs./hr. ft$^2$
Inlet concentration: 0.00772 to 0.01870 lbs. H$_2$O/lb. dry air

Bed temperature:
- O 80°F.
- x 90°F.

Adsorbent weight, $W_s$, lbs.
used as a convenient estimating function since it is a macro-scale defined term used in this molecular scale system of water adsorption on molecular sieves.

In Figure 42 $D_{pore}$ appears to be independent of air flow rate. The effect of bed height (or adsorbent bed weight) is aptly described in this figure also.

Use and limitations of the developments and apparatus

The design values were obtained only for the first adsorption cycle using Type 4A molecular sieves. Hence the developments describe molecular sieve water adsorption for only this first adsorption cycle, and essentially for isothermally maintained, uncontaminated fixed beds of the adsorbent. The air stream was also purified before water saturation.

The eight independent variables listed in the introduction have been thoroughly scrutinized as to their importance in molecular sieve water adsorption. By considering fully the research reported in the literature and the observations of molecular sieve air drying performance, the writer determined that primary emphasis should be placed on variables 1, 2, 3, 4 and 6. Study of the other variables was limited to an assessment of their effect on the parameters in the developments for molecular sieves, and to the finding of optimum conditions for the experimental apparatus and procedure (e.g., effect of pressure
Figure 42. Pore diffusivities versus flow rate for Type 4A molecular sieve beads
Particle size: 0.078 – 0.093 inches (beads)

Inlet concentration:

- ▲ △ ○ 0.0110 lbs. H₂O/lb. dry air
- ○ 0.0154 lbs. H₂O/lb. dry air

Pore diffusivity, $D_{pore}$, (ft²/hr.) x 10⁶

Bed heights (z):
- ▲ 13.875" inches
- ○ △ 19.875" inches
- ▼ 25.875" inches

Air flow rate, $G$, lbs. dry air/hr. ft²
on $W_B$). The assessment was based primarily on published research and information on adsorption and adsorbents.

The adsorption of water on silica gel was studied only to the extent of duplicating past research work with the present experimental apparatus. This duplication was reported previously by the writer (36), but it is presented again in Figure 4-3. The good duplication of run No. S-8 of Eagleton (35) is shown in this figure. Reproducibility checks made in the past molecular sieve research consisted of comparing the breakthrough curves for the different bed heights, and verifying run No. 36 results by operating under exactly the same conditions for another run (No. 38) (36). Run Nos. 75 and 81 and Nos. 77 and 82 represent reproducibility checks made in the present research. These runs were made to evaluate heating effects of the regeneration operation. Each pair of runs were made under identical experimental conditions.

The apparatus was basically designed to allow a wide variety of experimental conditions. Most of the experimental limitations were described and discussed in previous work (36). The range of the attainable inlet humidities was the major limitation. Inlet air pressure over the bed controlled the maximum humidity attainable, and the saturator pressure requirement limited the low humidity value. Actual experimental conditions in this research limited the
Figure 43. Reproducibility of past research for silica gel
Run No. S-3 Eagleton (35)
Bath temperature - 79.95°F.
Flow rate - 0.00364 lbs. dry air/min.
Inlet humidity - 0.00934 lbs. $\text{H}_2\text{O}/\text{lb.} \text{ dry air}$
Water content of solid - 0.290 lbs. $\text{H}_2\text{O}/\text{lb.} \text{ solid}$
Material balance error - 5.07%
Run No. S-2 past research by the writer (86)
Bath temperature - 80.0°F.
Flow rate - 0.00390 lbs. dry air/min.
Inlet humidity - 0.01027 lbs. $\text{H}_2\text{O}/\text{lb.} \text{ dry air}$
Water content of solid - 0.5195 lbs. $\text{H}_2\text{O}/\text{lb.} \text{ solid}$
Material balance error - 2.12%
Ratio of water content of exit to inlet air, $\frac{C}{C_o}$

- ○ Run no. S-8 Eagleton
- ● Run no. S-2 this research

Cumulative dry air weight, $W$, lbs.
range to 25 - 30% relative humidities.

Upsetting variables and external constraints

In adsorption operations there are several variables which can upset any mathematical model and equations that may be used. These are briefly covered here.

Variation in adsorbent capacity from batch to batch usually can be neglected. MTZ heights may have to be adjusted for varying particle size distributions. MTZ heights were found to increase with increasing average particle diameter. Also adjustments normally are necessary for the increase in bed density as the bed is cycled. MTZ heights would probably decrease as the density increases. Slight variations in stream temperature, inlet concentration and heat effects can usually be neglected.

The decrease in adsorbent capacity with the number of cycles of use is probably more difficult to integrate into the developments. Barry (15) suggests that a linear relationship of log capacity versus log number of cycles be included in the design developments for molecular sieves.

Contamination problems are always present and are sometimes extremely troublesome in adsorption. Since the pores are very small and especially vulnerable to contamination at the external surface, care should be exercised in purifying entering streams and in ensuring adequate regeneration.
RECOMMENDED DESIGN PROCEDURES AND EQUATIONS FOR ADSORBERS USING MOLECULAR SIEVES

The information required for design purposes and for determining or understanding the molecular sieve adsorption mechanism is the exit air stream concentration as a function of the cumulative variables (e.g., time, dry air passed, or bed position). The main objective of this research was to obtain this information both experimentally and analytically.

If one knows or can calculate the value of $Z_{MTZ}$, the height of the mass transfer zone, for a given set of operating conditions, and $f$, the fractional ability of the absorbent in the MTZ to still adsorb water, it is possible to predict the average percent saturation of a given absorbent bed at the breakthrough point (equation 36). In design calculations it then becomes possible, for example, to determine the pounds of air a given bed can dry before moisture will appear in the exit air stream, or if one knows the amount of air to be dried, to calculate the bed height ($Z$) required.

The $Z_{MTZ}$ is calculated by using equation 34 or 35. Derivations of equations 34 through 36 are given in previous work by the writer (66). The required values of $W_E$ and $W_B$ are calculated through the use of breakthrough curve mechanism models, or are determined experimentally. Both the models and the experimental values are presented in this
research.

The design procedures and the models developed for water adsorption on molecular sieves involve two approaches. One method utilizes mass transfer coefficients; the other considers diffusivities in order to approximate the postulated adsorption mechanism. Both methods are used to calculate values of $W_E$ and $W_B$ in the MTZ approach after experimental mass transfer coefficients and diffusivities have been determined.

Appropriate mass transfer coefficients are selected based on the desired operating conditions of inlet concentration flow rate, particle size and bed temperature. Insertion of these mass transfer coefficients and operating condition values into equations 37 and 38, or equation 40 enables one to calculate $W_E$ and $W_B$.

The mass transfer coefficient models as shown in Figure 9 exhibit an asymptotic solution above $C/C_0 = 0.80$. This occurs because these models do not have a finite boundary condition at the limiting capacity point, $C/C_0 = 1.0$. In the design procedure it appears best to use a multiplying factor to a smaller portion of the breakthrough curve than the MTZ length. The multiplying factor was empirically determined from experimental MTZ data. The following equation is applicable for $W$ calculated by equa-
tions 37, 38 or 40.

\[ 1.876 \left[ \frac{W}{C_o} = 0.75 \right] - W_B = W_E - W_B \]  \hspace{1cm} (49)

Since the mass transfer coefficient development does not rigorously describe the rate controlling step of the postulated adsorption mechanism for molecular sieves, a diffusivity model based on a pore diffusion mechanism and linear not through the origin equilibrium was developed. Two equations were developed that calculate \( w_{MTZ} \) exactly. These equations are:

\[
W = \frac{X^* W_s}{C_o} \hspace{1cm} (50)
\]

\[
W = \frac{\omega W_s}{C_o} + \left[ (X_0^* - \infty) \frac{W_s \pi d_p^5 G'}{72 \rho_g (1 - \varepsilon) \nu^2 C_o d_{pore}} \right] \left[ \ln \left(1 - \frac{\omega}{C_o} \right)^{-1} - (1 - \frac{\omega}{C_o}) \right] \hspace{1cm} (51)
\]
Equation 51 exactly duplicates the experimental breakthrough curve data. The material balance displacement on the W axis by using equation 51 instead of equation 46 was found empirically. Figure 44 shows the results of using these equations for run No. 26 and run No. 21. Derivations of equations 50 and 51 are given in the Appendix.

In design \( W_{MTZ} \) can be calculated using either equation 50 or equation 51. Both of these equations reduce to:

\[
W_E - W_B = 3.842 \left[ (X_o - \infty) \frac{W_s \Pi d_p^2 G'}{72 \rho_g (1 - \varepsilon) \sqrt{C_o D_{pore}}} \right]
\]

The \( W_E \) required in equation 35 should be calculated using equation 51 since this more closely duplicates the experimental value. \( D_{pore} \) values are selected based on desired operating conditions of inlet concentration, flow rate, particle size and bed temperature.
Figure 44. Pore diffusion mechanism models for air - water - molecular sieves (Type 4A) system
Ratio of water content of exit to inlet air, $\frac{C}{C_0}$

Run conditions:
- Inlet concentration (lb. H$_2$O/lb. air)
  - Run 26: 0.01542
  - Run 21: 0.00799
- Molecular sieves (beads)
  - Run 26: 0.078" to 0.093"
  - Run 21: 0.078" to 0.093"
- Flow rate (lb. dry air/hr)
  - Run 26: 1.969
  - Run 21: 1.963
- Bed height (inches)
  - Run 26: 19.875
  - Run 21: 19.875
- Bed temperature (°F)
  - Run 26: 89.9
  - Run 21: 80.2
CONCLUSIONS AND RECOMMENDATIONS

The conclusions reported previously by the writer for water adsorption on Type 4A molecular sieves apply to the present research (66). These results primarily showed that the MTZ design method was applicable to molecular sieve adsorption and provided a simple way of designing fixed bed adsorbers which will contain this adsorbent. The important conclusions of the past work are included below with those of the present research.

1. The experimental equilibrium isotherms for Type 4A molecular sieves correlated very well with published data.

2. Isothermal operation was essentially attained for all runs. The heat of adsorption was not as effectively transferred to the constant temperature bath for small particles as it was for large particles.

3. The breakthrough curve runs for 15.875, 19.375 and 25.875 inch bed heights, with all other run conditions the same, showed that the MTZ length is independent of bed height for Type 4A molecular sieves in water adsorption.

4. The breakthrough shape factor (f) was found to be a constant and equal to 0.593. Deviations were ± 0.03 for spherical beads and ± 0.06 for granular particles.

5. Linear relationships with small positive slopes were obtained for MTZ heights versus inlet air water concentrations at constant bed temperature and flow rate con-
ditions. These relationships were nearly parallel lines for the 70, 80 and 90°F. bed temperatures. These linear relationships were nearly parallel lines for the 70, 80 and 90°F. bed temperatures. These linear relationships for MTZ heights versus inlet air water concentrations showed only slight increases in $Z_{MTZ}$ values for 10°F. increases in bed temperature.

6. Particle shape appears to have a very large effect on MTZ heights. Increases in the external surface area for the same particle volume give large decreases in the MTZ heights.

7. Flow rate appears to be directly and linearly proportional to the MTZ heights.

8. Decreases in the mean particle diameter give corresponding decreases in the MTZ heights. The increase in external surface area with decreasing particle size causes faster water transfers to molecular sieves adsorbent. $K_{S_{p}}$, $k_{S_{p}}$ and $D_{p}$ values increase with increasing external surface area.

9. The relative magnitudes of the $Z_{MTZ}$ experimental relationships for inlet air water concentrations and flow rate correlate very well with those predicted analytically.

10. Linear relationships with small positive slopes were obtained for $K_{S_{p}}$, $k_{S_{p}}$ and $D_{p}$ values versus inlet air water concentrations at constant bed temperature and flow.
rate conditions. These relationships were similar to those obtained for $Z_{\text{MTZ}}$ versus $C_0$. The effect of $C_0$ on $K_{\text{s}a_p}$, $K_{\text{s}a_p}$ and $D_p$ appears to indicate a fluid-phase mechanism effect in the predominately solid-phase controlled rate expression.

11. Due to the relative magnitudes of the phase resistances no generalizations could be made for gas phase rate coefficients ($k_{\text{g}a_p}$) except to draw statistically evaluated lines through the data. These resistances do not control the rate of water adsorption on Type 4A molecular sieves for the flow rates used in this research.

12. $K_{\text{s}a_p}$, $K_{\text{s}a_p}$ and $D_p$ appear to be independent of flow rates.

13. Particle diffusivities give the same relationships as for $k_{\text{s}a_p}$ since they differ from the latter only by a constant times the particle diameter.

14. Experimental pore diffusivities are almost independent of inlet concentration. A very small positive slope was obtained.

15. Pore diffusivity appears to be independent of air flow rate.

16. Particle size has a very large effect on the pore diffusivity.

17. The mass transfer rate coefficient mechanism models correlate very well with the experimental data over
the 0 to 0.75 \( C/C_0 \) range of inlet air water concentrations.

18. The pore diffusion mechanism models either for an irreversible equilibrium or for a linear not through the origin equilibrium correlate very well with the experimental data over the entire \( C/C_0 \) range of the breakthrough curves.

19. It appears that the pore diffusion mechanism more closely duplicates the water adsorption behavior on Type 4A molecular sieves than the mass transfer rate coefficient models. Independent variable effects and model comparisons with the experimental data support the applicability of the pore diffusion mechanism to molecular sieve water adsorption. This mechanism appears to be a good approximation to the author's postulated theory of water adsorption on Type 4A molecular sieves.

20. It is recommended that more breakthrough curve data be taken to determine how the \( Z_{HTZ} \) and rate coefficient relationships function as zero inlet concentration and flow rate are approached.

21. It is also recommended that work be done to further evaluate the effects of bed temperature and flow rate.

22. It is recommended that work be undertaken to evaluate external surface effects on the experimental diffusivities.

23. It is recommended that scaled-up versions of the apparatus be developed and tested using the larger particle
sizes and pellets of molecular sieves available.

24. It is recommended that a pore diffusion model be developed for use with the random length cylindrical pellets of molecular sieves.

25. It is recommended that parallel investigations be undertaken to evaluate the use of the methods, models and procedures in this research in adiabatic or non-isothermal air drying.
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APPENDIX

Pore Diffusion Model Derivation

The following development briefly outlines the pore diffusion model proposed for water adsorption on molecular sieves.

The rate equation expressing Fick's law of diffusion for one particle and the isotropic case in spherical coordinates is:

\[
\chi \left[ \frac{\partial C_r}{\partial t} \right] + \frac{\rho_b}{\rho_g} \left[ \frac{\partial X_r}{\partial t} \right] = \frac{D_{pore}}{r^2} \left[ \frac{\partial \left( r^2 \frac{\partial C}{\partial r} \right)}{\partial r} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial C}{\partial \theta} \right) \right] + \frac{1}{\sin^2 \theta} \left( \frac{\partial^2 C}{\partial \theta^2} \right)
\]

By assuming constant concentric concentration profiles in the spherical particle, and that the fluid-phase concentration in the pores is negligible compared to the solid-phase concentration, one can reduce equation 53 to:

\[
\frac{\rho_b}{\rho_g} \left[ \frac{\partial X_r}{\partial t} \right] = \frac{D_{pore}}{r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_r}{\partial r} \right) \right]
\]
since

\[ \left( \frac{\partial c_r}{\partial t} \right) = 0 \quad \left( \frac{\partial^2 c_r}{\partial \theta^2} \right) = 0 \quad \left( \frac{\partial c_r}{\partial \theta} \right) = 0 \]

The average water content in the entire particle is given by:

\[ X_p = \frac{3}{r_p^2} \int_0^{r_p} x_r r^2 \, dr \quad (55) \]

Equation 55 is differentiated and substituted into equation 54. The resulting expression is partially integrated over \( r \) from 0 to \( r_p \) to yield the following:

\[ \frac{\partial X_p}{\partial t} = \frac{\rho_p \rho_p^{\text{pore}} r^2}{\rho_b r_p^3} \left[ \frac{\partial c_r}{\partial r} \right] \quad (56) \]

An operating line material balance over one particle is represented by:

\[ \left( \frac{C_r}{C_i} \right) = \left( \frac{X_r}{X_i} \right) \quad (57) \]

By equating the above material balance ratios to the volume fractions involved (assuming saturation from \( r_p \) to \( r \)), one obtains:

\[ \left( \frac{C_r}{C_i} \right) = \left( \frac{X_r}{X_i} \right) = 1 - (r/r_p)^3 \quad (58) \]

When the linear not through the origin equilibrium isotherm approximation (equation 41) is used and substituted for \( X_i \) in equation 58, one obtains:
\[
\frac{X_r}{\alpha + \left[ \frac{X^* - \alpha}{C_0} \right] C_i} = 1 - \left( \frac{r}{r_p} \right)^3.
\] (59)

Equation 59 is differentiated keeping \( C_i \) constant. Through the chain rule the differentiated result is multiplied by \( \frac{\partial r}{\partial t} \) giving the following:

\[
\frac{\partial X_r}{\partial t} = -\left[ \frac{\alpha 3r^2}{r_p^3} \right] \frac{\partial r}{\partial t} - \left[ \frac{C_i 3r^2}{r_p^3} \right] \frac{X^* - \alpha}{C_0} \frac{\partial r}{\partial t}.
\] (60)

To get the combined material balance and rate expression one equates equation 60 and equation 56. After reduction the result is:

\[
\frac{\rho_{\text{pore}} D}{\rho_b} \left[ \frac{\partial C_r}{\partial r} \right] = -\alpha \left[ \frac{\partial r}{\partial t} \right] - C_i \left[ \frac{X^* - \alpha}{C_0} \right] \frac{\partial r}{\partial t}.
\] (61)

Equation 58 is differentiated and substituted for \( \frac{\partial C_r}{\partial r} \) in equation 61. The result is:

\[
\frac{\rho_{\text{pore}} C_i 3r^2}{\rho_b r_p^3} = \left( \alpha + C_i \left[ \frac{X^* - \alpha}{C_0} \right] \right) \frac{dr}{dt}.
\] (62)

Equation 62 can be integrated directly by assuming \( C_i \) constant over the time to saturate one particle, or one can substitute for \( dt \) using the differential of equation 10.
After this substitution the expression is integrated over $r$ from 0 to $r_p$, and over $W$ from $W$ to 0. The result after reduction and rearrangement is:

\[
1 = \left[ \frac{C_i}{C_o} \right] \left[ \frac{3 (\rho g_D \text{pore} C_o)}{\rho_b \alpha G' r_p^2} \right] W - \left[ \frac{X_o^* - \alpha}{\alpha} \right] \left[ \frac{C_i}{C_o} \right] \tag{63}
\]

An equation for the entire fixed bed is obtained by multiplying the one particle $W$ in equation 63 by the number of particles in the bed (particles assumed to be spheres), and changing $C_i$, which refers to the one particle, to $C$, which refers to the entire fixed bed. Equation 63 thus becomes (letting $r_p^2 = d_p^2/4$):

\[
1 = \left[ \frac{C}{C_o} \right] \frac{72(1 - \varepsilon) \nu (\rho g_D \text{pore} C_o)}{\rho_b \alpha G' \pi a_p^5} W - \left[ \frac{X_o^* - \alpha}{\alpha} \right] \left[ \frac{C}{C_o} \right] \tag{64}
\]

The differential of equation 64 is a differential equation relating $C/C_o$ to $f(W)$ for the entire fixed bed. Upon rearrangement the differential expression is of the form:

\[
\left[ - \frac{X_o^* - \alpha}{\alpha} \right] \frac{d(C/C_o)}{C/C_o} = B \ dW \tag{65}
\]

where:
Equation 65 is non-separable, hence one has three alternatives for a simple result: (1) neglect the (-WB) term, (2) consider the (-WB) term a constant, or (3) leave the (-WB) term as a function of $C/C_0$ but evaluate it empirically. The first two alternatives do not give exact breakthrough curve duplication. The third alternative can be approached by comparing the overall mass transfer rate coefficient model (equation 40) to this case, and by determining the boundary conditions at $C/C_0 = 0$, and at $C/C_0 = 1$ or some other convenient point of the curve.

An overall material balance for the fixed bed when $C/C_0$ is just reached is: amount of $H_2O$ in with air up to $C/C_0$ point equals amount of $H_2O$ adsorbed by solid when bed saturated plus amount of $H_2O$ exiting with air minus amount of $H_2O$ that still can be adsorbed by solid. This is represented mathematically by:

$$C_0 \bar{w} = \bar{w}_s X_0^* - \int_C^{C_0} (C_0 - C) \, dW + \int_0^C C \, dW$$  \hspace{1cm} (66)

Equation 66 is modified by dividing by $C_0$. The (-WB) term in equation 65 is accounted for by adding a $f(C/C_0)$ term to equation 66. Equation 65 without the (-WB) term
can then be used to evaluate the integrals in equation 66. The integral over \( \frac{C}{C_0} \) from \( \frac{C}{C_0} \) to 1.0 has an undefined limit at \( \frac{C}{C_0} = 0 \). Therefore, the lower limit is changed to \( (1 - \frac{C}{C_0}) \). The boundary value difference caused by this limit change is also accounted for in the \( f(\frac{C}{C_0}) \) term added to the material balance. The integral expression has the form:

\[
C_0w = W_sX_0^* + \left[ \frac{C_0}{B} \right] \left[ \frac{X_0^* - \alpha}{\alpha} \right] f(\frac{C}{C_0}) \\
- \left[ \frac{C_0}{B} \right] \left[ \frac{X_0^* - \alpha}{\alpha} \right] \int_{1.0}^{(1 - \frac{C}{C_0})} \frac{(1 - \frac{C}{C_0})}{(1 - \frac{C}{C_0}) (\frac{C}{C_0})} \, d(\frac{C}{C_0}) \\
+ \left[ \frac{C_0}{B} \right] \left[ \frac{X_0^* - \alpha}{\alpha} \right] \int_{0}^{\left(\frac{C}{C_0}\right)} \frac{(\frac{C}{C_0})}{(\frac{C}{C_0})} \, d(\frac{C}{C_0})
\]

Integration of equation 67 and subsequent reduction yields:

\[
W = \frac{W_sX_0^*}{C_0} - \left[ \frac{1}{B} \right] \left[ \frac{X_0^* - \alpha}{\alpha} \right] \ln(1 - \frac{C}{C_0})^{-1} + f(\frac{C}{C_0}) \]  

Subtraction of equation 68 evaluated at \( \frac{C}{C_0} = 0 \) from the overall mass transfer rate coefficient expression (equation 40) evaluated at \( \frac{C}{C_0} = 0 \) yields the following
The relationship of $K_{sp}$ to $D_{pore}$:

$$K_{sp} = \frac{G'X_0^*}{(X_0^* - \kappa)} \frac{1}{\text{constant}} \left[ \frac{72(1 - \varepsilon)\nu \rho g \sigma_{D_{pore}}}{\rho_b \pi \kappa G'(d_p^5)} \right]$$  \hspace{1em} (69)

The right side of equation 69 can be substituted for $K_{sp}$ in the overall rate coefficient expression (equation 40). The result after material balance modification is:

$$W = \frac{X_0^* W_s}{C_0}$$ \hspace{1em} (70)

$$\ln(1 - C/C_0)^{-1} + g(C/C_0)$$

Equation 70 includes only the lower boundary condition (e.g., $W$ at $C/C_0 = 0$). Since it was difficult to establish another boundary condition of known $W$ and $C/C_0$, the $g(C/C_0)$ term in equation 70 was evaluated empirically. The solid-phase driving force $(1 - C/C_0)$ was found suitable for $g(C/C_0)$. The value of the constant was empirically determined from the MTZ data of each breakthrough curve. This constant was divided into each apparent pore diffusivity in order to simplify the independent variable analysis. Thus, the pore diffusivity is given by:

$$D_{pore} = \frac{(D_{pore})_{apparent}}{\text{constant}}$$ \hspace{1em} (71)

The apparent pore diffusivity was calculated from the
slope of $\ln(1 - C/C_0)^{-1}$ versus $W_c$ using this equation:

$$(D_{pore})_{\text{apparent}} = \left[ \frac{W_s \int \alpha \frac{dG'}{dp}}{72 \rho_g (1 - \varepsilon) v^2 C_0 m_2} \right] \left[ \frac{X_o^* - \alpha}{\alpha} \right]$$

where $m_2$ is the slope.

Equations 50 and 51 include the above modifications of equation 70, and exactly describe the breakthrough curve mass transfer zone. The material balance displacement on the horizontal axis by using $\alpha$ (equation 51) instead of $X_o^*$ (equation 50) was found empirically.

Sample Calculations

The following calculation methods used in this research are given here using the data of breakthrough run No. 26 as an example.

The volumetric flow rate as obtained from the flowmeter reading and the calibration curve, was corrected to the temperature and barometric pressure existing during the run. Using the inlet air dew-point and the value of the water vapor pressure for this dew-point (61), the volumetric flow rate of dry air was calculated. From dry air density data (61), the mass flow rate was obtained. This value was used with the experimental breakthrough curve time data to compute $W$ (equation 10).

The values of absolute humidity ($C$) in lbs. $H_2O/lb$. dry
air were calculated from the vapor pressure data in Perry (89) for liquid water over the temperature range of \(-100^\circ F\) to \(+80^\circ F\). A table was prepared of dew-point versus absolute humidity for ease of computation (not reproduced in thesis). The ratio of water content of exit to inlet air \((C/C_0)\) was calculated from the absolute humidity data.

Selected breakthrough curve values of \(t\), \(W\), exit air dew-point and \(C/C_0\) for run No. 26 are given in previous work (86).

The height of the MTZ is calculated from the following experimental data using equation 35.

\[
\begin{align*}
W_b &= 1.51 \text{ lbs. dry air} \\
W_E &= 2.74 \text{ lbs dry air} \\
Z &= 19.875 \text{ inches} \\
f &= 0.593 \\
C_0 &= 0.01542 \text{ lbs. } H_2O/\text{lb. dry air} \\
X_0^* &= 0.2250 \text{ lbs. } H_2O/\text{lb. solid} \\
G' &= 1.9686 \text{ lbs. dry air/hr.} \\
\alpha &= 0.2000 \text{ lbs } H_2O/\text{lb. solid} \\
m_1 &= \text{ slope of } -\ln(C/C_0) \text{ vs. } W_c = 14.93 \\
m_2 &= \text{ slope of } -\ln(1 - C/C_0) \text{ vs. } W_c = -1.670
\end{align*}
\]

\[
Z_{MTZ} = Z \left[ \frac{W_E - W_B}{W_E - (1 - f)(W_E - W_B)} \right]
\]
\[201 = 19.875 \frac{(2.74 - 1.51)}{(2.74) - (1 - 0.593)(2.74 - 1.51)}\]
\[= 10.91 \text{ inches}\]

The average percent saturation in the bed was obtained from the experimental data and also calculated by equation 36. From experimental data:

\[
\text{Average percent saturation in bed} = 100\% \frac{(W_B)(C_o)(454)}{\text{Total water adsorbed by adsorbent, grams}}
\]

\[= 100\% \frac{(1.51)(0.01542)(454)}{(15.9463)}\]
\[= 66.8\%\]

By equation 36:

\[
\text{Average percent saturation in bed} = 100\% \left[ \frac{Z - fZ_{MTZ}}{Z} \right]
\]
\[= 100\% \left[ \frac{(19.875) - (0.593)(10.91)}{19.875} \right]\]
\[= 67.4\%\]

The required values of \(W_B\) and \(W_Z\) are calculated by using the mechanism models. The design parameters (e.g., \(K_s a_p, k_s a_p\), etc.) needed in each of these mechanism models were calculated by a reverse procedure.
The overall rate coefficient (assumed constant over the 0.2 to 0.8 C/C₀ range) was calculated using the slope of \(-\ln(1 - C/C₀)\) versus \(W_c\).

\[
K_{s a p} = \frac{(m_2)(X^*)(G')}{(\infty)} \quad (74)
\]

\[
= \frac{(1.670)(0.2250)(1.9686)}{(0.2000)}
\]

\[
= 3.695 \text{ hours}^{-1}
\]

The gas-phase and solid-phase rate coefficients were calculated as follows:

\[
k_{g a p} = \frac{(m_1)(X^*)(G')}{(C_0)} \quad (75)
\]

\[
= \frac{(14.93)(0.2250)(1.9686)}{(0.01542)}
\]

\[
= 428 \frac{\text{lbs. H}_2\text{O transferred}}{(\text{hr.})(\text{lb. solid})(\text{C-units})}
\]

\[
R = \frac{1}{1 - (m_1/m_2)} \quad (76)
\]

\[
= \frac{1}{1 + (14.93/1.670)}
\]

\[
= 0.1006
\]

\[
\zeta = \frac{\alpha - X^*_0 R}{RC_0} \quad (77)
\]
\[
(0.2000) - (0.2250)(0.1006) \\
\quad = (0.1006)(0.01542) \\
\quad = 114.5
\]

\[
k_{sp} = \frac{k_{sp}}{\phi} \\
= \frac{428}{114.5} = 3.738 \text{ hours}^{-1}
\]

Particle and pore diffusivities were calculated as follows using these additional experimental data:

- \( W_s = 0.1561 \text{ lbs. solid} \)
- \( d_p = 0.007125 \text{ feet (-8+9 Tyler mesh)} \)
- \( \rho_g = 0.0698 \text{ lbs./ft.}^3 \)
- \( \epsilon = 0.453 \text{ ft.}^3 \text{ of voids/ft.}^3 \text{ of bed} \)
- \( v = 0.00355 \text{ ft.}^3 \)
- \( (X_0^*)_{\text{average}} = 0.2200 \text{ lbs. H}_2\text{O/lb. solid} \)

The particle diffusivity was calculated using equation 46.

\[
D_p = \frac{k_{sp} d_p^2}{60} \\
\quad = \frac{(3.738)(0.007125)^2}{60} \\
\quad = 3.163(10^{-6}) \text{ ft.}^2/\text{hr.}
\]

The apparent pore diffusivity was calculated using an average \( X_0^* \) from the linear approximation isotherm (Figure
17), and this equation:

\[(D_{\text{pore}})_{\text{apparent}} = \text{Equation 71}\]

\[
\frac{W_s \pi \alpha G_p^5}{72(1 - \varepsilon)m_2 \rho g v^2 c_o} \left[ \frac{X_0^* - \alpha}{\alpha} \right]
\]

\[
= \left[ \frac{(0.1561)(3.14)(0.200)(0.007125)^5(1.9686)}{(72)(1-0.453)(1.670)(0.0698)(0.00355)^2(0.01542)} \right]
\]

\[
\cdot \left[ \frac{0.2200 - 0.2000}{0.2000} \right]
\]

\[
= 0.396(10^{-6}) \text{ ft.}^2/\text{hr.}
\]

\[R' = \frac{W_E - W_B}{(3.842)m_2}\]

\[
= \frac{2.74 - 151}{(3.842)(1.670)}
\]

\[
= 0.1915
\]

Pore diffusivities were then obtained by modifying the apparent pore diffusivity with the empirical factor \(R'\).

Equation 71 is applicable:

\[D_{\text{pore}} = \frac{(D_{\text{pore}})_{\text{apparent}}}{R'}\]

\[
= \frac{0.396(10^{-6})}{0.195} = 2.07(10^{-6}) \text{ ft.}^2/\text{hr.}
\]