CHAPTER I

General Introduction
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Cation sites in Zeolite Framework
Synthesis of Zeolites
Ion Exchange and Adsorption, Phenomenon in Zeolites
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INTRODUCTION

The term 'Zeolite' was created by Cronstedt\(^1\) from the Greek γελόω = "to boil" and λίθος = 'stone', for minerals which expel water when heated and hence seem to boil. They are very common and well known as fine crystals of hydrothermal genesis in geodes and fissures of eruptive rocks, or as microcrystalline masses of sedimentary origin.

A zeolite is a framework aluminosilicate whose structure contains channels filled with water and exchangeable cations. Ion exchange is possible at low temperature (100°C at the most) and water is lost at about 250°C and reversibly re-adsorbed at room temperature. As is well known, the primary building units of the structures of silicates are the TO\(_4\) tetrahedra, where T is mainly silicon. In framework silicates these primary building unit (PBU) are linked so as to form a 3-dimensional framework and (nearly) all oxygen are shared by the tetrahedra. The sharing coefficient (Zeltai, 1960) is hence 2 or a little less. If all tetrahedra were centred by silicon and the sharing coefficient is 2, the chemical formula of the framework would be Si\(_2\)O\(_2\)\(_n\), if there is some Al in the tetrahedra the formula is [Al\(_{2n-1}\)Si\(_n\)-O\(_2\)]\(^m\)
The negative charges being balanced by the extraframework cations, usually \( \text{K}, \text{Na}, \text{Ca} \) and less frequently \( \text{Li}, \text{Mg}, \text{Sr}, \text{Ba} \). In synthetic zeolites the composition may vary more widely, including \( \text{Ca}, \text{Ce}, \text{Ba}, \text{P} \), as tetrathiadral cations, and all alkali, alkaline earth and rare earth elements and also organic complexes (for instance tetramethyl ammonium) as extraframework cations.

The general formula for zeolites is hence -

\[
\left[ \frac{M_2}{xN_2} \times Al_2O_3 \cdot YSiO_2 \right] \cdot nH_2O
\]

where \( M \) is the cation of valence \( n \), \( W \) is the number of water molecules and the ratio \( Y/X \) usually has values from 1 to 5 depending upon the structure.

The ability to lose water at high temperature (150 to 400°C) and re-adsorb it from the atmosphere at room temperature is one of the properties which qualifies a framework silicate mineral as a zeolite.

A zeolite phase, once dehydrated (or "activated") may re-adsorb not only water, but also gases, vapours and fluids, especially if their molecules are polar. This capacity to adsorb a variety of molecules is in turn related to the catalytic properties of zeolites.

To conclude this introduction some historical remarks
on the research on zeolite may be useful. As already mentioned this history began as early as 1756 with a publication by Cronstedt. One hundred years later, Defrency\textsuperscript{2} listed 17 zeolites but Dana\textsuperscript{3} recorded 19 zeolites, plus another 2 which were described later.

**STRUCTURE**

Following Moll\textsuperscript{4,5}, the topology of a tetrahedral framework may be represented by its tetrahedral centres (nodes) and by oxygen bridges (link ages) on and, hence is equivalent to the topology of a 4-connected 3-dimensional net at least if as normally, every oxygen is shared by two tetrahedra i.e. if Boltaši\textsuperscript{6} sharing coefficient is 2.00 (if the sharing coefficient is lower, one should consider a mixed 3- and 4-connected net).

The number of theoretical nets thus obtainable is infinite. However, in the frameworks found so far in silicates, the tetrahedra form quite a small number of complex structural units (chains, rings, cages) of low potential energy.

According to this principle, Neier\textsuperscript{7} defined a small
number of complex structural units formed by a finite number of tetrahedra which may be assembled to form a complete framework. Meier excluded groups which are either (ideally) infinite or very large.

A better understanding of zeolite structure may be achieved by a brief review of the five main types of silicates and aluminosilicates. These includes Island structures.

Isolated group structures

Chain structures

Sheet structures, and

framework structures.

Framework structures are obtained by linking of \( \text{SiO}_4 \) and \( \text{AlO}_4 \) tetrahedra in three dimensions by means mutual shifting of oxygen alone. When all the the oxygen atoms are mutually shifted between tetrahedral silicon or aluminium ions, three dimensional, continuous framework result.
Fig. a-e. The structural units finite or infinite, which may be used to assemble the framework: a, co-linear; b, the chain of linear co-linear; c, the singly connected 4-rings chain; d, the doubly connected 4-rings chain; e and f, the 6-rings, single and double; g, the hexagonal sheet with h-niles; g, the 4-41-1 hexalnite unit.
CLASSIFICATION

Bragg was the first to propose the classification of zeolites. He divided zeolites into three classes on the basis of their structure and morphology.

1. Three dimensional framework structure with uniform bonding.
2. Lamellar type structure with aluminosilicate sheets weakly bonded to one another, and
3. Fibre like structure with weakly crosslinked aluminosilicate chain unit.

It should be noted because all zeolites are framework aluminosilicates and all of the zeolite structures are three dimensional.

There are about 37 types of (natural and synthetic) zeolite structures which are known for their different framework and topologies.

Structural classification of zeolite has been also proposed by Smith, Fisher and Maier and Breck.

This type of classification consists of seven groups. Within each group zeolites have a common sub-unit of structure which is a specific array of (Al-Si)O₄ tetrahedra. In this classification the Al-Si distribution is neglected,
the two simplest units are the ring of four tetrahedra (4 ring) and six ring of tetrahedra (6 ring). These sub-unit have been called secondary building units (SBU) by Meier.

The primary units are of course the SiO₄ and AlO₄ tetrahedra.

The following are the seven groups based on structural configurations.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Secondary building units (SBU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st group</td>
<td>Single four ring - S4R</td>
</tr>
<tr>
<td>2nd group</td>
<td>Single six ring - S6R</td>
</tr>
<tr>
<td>3rd group</td>
<td>Double four rings - D4R</td>
</tr>
<tr>
<td>4th group</td>
<td>Double six rings - D6R</td>
</tr>
<tr>
<td>5th group</td>
<td>Complex 4-4-1 T50₁₀ unit</td>
</tr>
<tr>
<td>6th group</td>
<td>Complex 4-4-1 T₁₀O₂₀ unit</td>
</tr>
<tr>
<td>7th group</td>
<td>Complex 4-4-1 T₁₀O₂₀ unit</td>
</tr>
</tbody>
</table>

Recently Barrer has classified zeolites into nine groups on the basis of secondary building units. These are tabulated below (Table 1)
<table>
<thead>
<tr>
<th>Group</th>
<th>Typical unit cell contains</th>
<th>Types of channels</th>
<th>Common structural element(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Analcime group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Analcime</td>
<td>( \text{Na}<em>6 \text{Al}</em>{16} \text{Si}<em>{12} \text{O}</em>{32} \cdot 16\text{H}_2\text{O} )</td>
<td>One</td>
<td>S4R, S6R</td>
</tr>
<tr>
<td>b. Wairakite</td>
<td>( \text{Ca}<em>{18} \text{Al}</em>{16} \text{Si}<em>{12} \text{O}</em>{32} \cdot 16\text{H}_2\text{O} )</td>
<td>Three</td>
<td></td>
</tr>
<tr>
<td>2. Natrolite group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Natrolite</td>
<td>( \text{Na}<em>{16} \text{Al}</em>{16} \text{Si}<em>{24} \text{O}</em>{80} \cdot 24\text{H}_2\text{O} )</td>
<td>Two</td>
<td>4-1</td>
</tr>
<tr>
<td>b. Thomsonite</td>
<td>( \text{Na}<em>4\text{Ca}<em>8 \text{Al}</em>{20} \text{Si}</em>{20} \text{O}_{80} \cdot 24\text{H}_2\text{O} )</td>
<td>Two</td>
<td></td>
</tr>
<tr>
<td>3. Heulandite group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Heulandite</td>
<td>( \text{Ca}<em>4 \text{Al}<em>8 \text{Si}</em>{28} \text{O}</em>{72} \cdot 24\text{H}_2\text{O} )</td>
<td>Two</td>
<td>4-4-1</td>
</tr>
<tr>
<td>b. Clinoptilolite</td>
<td>( \text{Na}<em>6 \text{Al}</em>{16} \text{Si}<em>{30} \text{O}</em>{72} \cdot 24\text{H}_2\text{O} )</td>
<td>Two</td>
<td></td>
</tr>
<tr>
<td>4. Phillipsite group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Phillipsite</td>
<td>( (\text{K},\text{Na})<em>5 \text{Al}<em>5 \text{Si}</em>{11} \text{O}</em>{32} \cdot 10\text{H}_2\text{O} )</td>
<td>Three</td>
<td>S4R</td>
</tr>
<tr>
<td>b. Zeolite Na-P</td>
<td>( \text{Na}<em>8 \text{Al}<em>8 \text{Si}</em>{16} \text{O}</em>{32} \cdot 16\text{H}_2\text{O} )</td>
<td>Three</td>
<td>S8R</td>
</tr>
<tr>
<td>5. Mordenite group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Mordenite</td>
<td>( \text{Na}<em>8 \text{Al}<em>8 \text{Si}</em>{40} \text{O}</em>{96} \cdot 24\text{H}_2\text{O} )</td>
<td>Two</td>
<td>T(<em>{8}^{0})(</em>{16})</td>
</tr>
<tr>
<td>b. Ferrierite</td>
<td>( \text{Na}<em>{15}\text{Mg}<em>2 \text{Al}</em>{55}\text{Si}</em>{30.5}\text{O}_{72} \cdot 18\text{H}_2\text{O} )</td>
<td>Two</td>
<td>T(<em>{8}^{0})(</em>{16})</td>
</tr>
<tr>
<td>Group</td>
<td>Typical unit cell contains</td>
<td>Types of channels</td>
<td>Common structural element(s)</td>
</tr>
<tr>
<td>---------------------</td>
<td>------------------------------------------------</td>
<td>-------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>6. Chabazite group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Chabazite</td>
<td>Ca₂Al₄Si₈O₂₄·13H₂O</td>
<td>Three</td>
<td>D₆R</td>
</tr>
<tr>
<td>b. Erionite</td>
<td>(Ca₉Mg₂Na₂₁K₂)₄Al₄Si₁₂O₇₂·27H₂O</td>
<td>Three</td>
<td>D₈R</td>
</tr>
<tr>
<td>c. Zeolite X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Fairlandite group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Fairlandite</td>
<td>Na₂₀Ca₁₂Mg₈Al₆₀Si₁₃₂O₃₈₄·23₅H₂O</td>
<td>Three</td>
<td>D₆R</td>
</tr>
<tr>
<td>(and isostructural</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zeolite X and Y)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b. Zeolite A</td>
<td>Na₁₂Al₁₂Si₁₂O₄₈·2₇H₂O</td>
<td>Three</td>
<td>D₄R, D₆R</td>
</tr>
<tr>
<td>8. Lummusite group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Lummusite</td>
<td>Ca₄Al₉Si₁₆O₴₈·1₆H₂O</td>
<td>One</td>
<td>S₄R, S₆R, S₈R</td>
</tr>
<tr>
<td>9. Pentasil group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Zeolite ZSM-S</td>
<td>NaₙAlₙSi₉₆O₁₉₂·1₆H₂O</td>
<td>S-1</td>
<td></td>
</tr>
<tr>
<td>b. ZSM-11</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
THE CAGES IN ZEOLITE FRAMEWORKS

Apart of zeolite framework, which includes a cavity large enough to contain extra framework atoms, may be called a cage or channel, depending on its finite or (ideally) infinite length. There is no clear cut difference between the two, because a cage often may be considered as a part of a channel two constrictions, the free section of which smaller than the average free section of the channel.

The consideration of the following cages may be useful in describing the natural zeolite structures (Fig. ).

a. the 6-ring (usually a ring is not considered as a cage, but it is included here for completeness).

b. the double 6 ring,

c. the 3 ring,

d. the double 8 ring

e. the cancrinite cage

f.g. the sodalite cage or truncated octahedron or cube and octahedron combination, the octahedral faces of which are regular hexagons,

h. the gmelinite cage

i. the chabazite cage,

j. the leviine cage,

k. the erionite cage
1. the $\beta$-cage or truncated cubo-octa hedron - rhombic dodecahedron combination in which the cubic faces are octagons and the octahedral faces are regular hexagons.

**CATION SITES IN ZEOlITE FRAMEWORK**

Galli\textsuperscript{14} classified the cation sites in zeolites as follows:

I. The cation is coordinated by framework oxygen only.

II. The cation is coordinated by framework at two nearly opposite side and to some water molecules.

III. The cation is bound to framework oxygens on one side only, and to some water molecules.

IV. The cation is completely surrounded by water molecules.

Some examples for the different conditions follow:

I. This coordination has been found by Gard and Tait\textsuperscript{16} in offretite, where a K is in the centre of a cancrinite cage, and at bond distance from 8 out of the 12 oxygens which are in the two basal hexagonal rings of the cage, there is not enough room for water in this cage.

II. This is the typical situation in structures with narrow channels, with a cation occupying their centre. Besides fibrous zeolites, this coordination has been
found, for instance for Sr in brewsterite by Perrotta and Smith.  

III. This is the most common situation, the cation is attached to the wall of the channel and is covered by water molecules on the other side.

IV. This coordination has been described for instance by Galli for Ca in stilbite and by Galli for Mg in hassite, this is the only coordination known so far for Mg, probably because this ion is so strongly solvated in solution, that it does not lose its water molecules during the formation of the zeolite crystal.

SYNTHESIS OF ZEOLITES

Zeolites are hydrated aluminosilicates formed under hydrothermal conditions. Attempts to synthesize silicates under hydrothermal conditions began with the experiments by Schafnautle, who in 1845, reported the preparation of quartz by heating a gel silica with water in an autoclave.

Early hydrothermal investigations were confined to temperatures above 200°C and correspondingly elevated pressures. Reaction mixtures were composed of the various components in amounts corresponding to the composition of the desired product. The mixture were maintained for a
period of time at constant pressure and temperature in
the presence of large excess of water.

A new approach to zeolite synthesis was initiated by
R.M. Milton and associates in the Union Carbide Corporation.
This approach was based on starting with very reactive
components in closed systems and employing temperatures
for recrystallization, which are more typical of the
synthesis of organic compounds than they are of mineral
formations. (17-19)

Many of the synthetic zeolites are formed at tempera-
rature ranging from about room temperature to the boiling
point of water. Early attempts to synthesize zeolites
were based upon the current ideas concerning their probable
mode of formation in basaltic rocks.

Recent information on the occurrences and formation
of mineral zeolites in sediments at relatively low tempe-
ratures and their formation in marine sediments on ocean
bottoms is consistent with the relatively mild temperature
conditions used in laboratory synthesis.

**CONDITION FOR SYNTHESIS**

The conditions generally used in synthesis are:

1. Relative starting materials such as freshly co-
   precipitated gels or amorphous solids.
2. Relatively high pH introduced in the form of an alkali metal hydroxide or other strong base.

3. Low temperature hydrothermal conditions with concurrent low autogeneous pressure at saturated vapour pressure.

4. A high degree of super saturation of the components of the gel leading to the nucleation of a large number of crystals.

**ION EXCHANGE REACTION IN ZEOLITES**

"Corpora non agunt nisi fluida sive soluta" substances do not react unless in a liquid or dissolved state, this empirical rule is not universal one of the noteworthy exceptions is ion exchange. Here, a solid reacts with solution ion can be exchanged and electrolytes and even precipitates can be removed by treating the solution with a solid ion exchanger.

Ion exchange occurs in inanimate soil, sands, and rocks, and in living organisms. At first, these process remained unnoticed by chemists, geologists and biologists. Later, when ion exchange in zeolite was discovered, it was considered as an exceptional phenomenon, a miracle in which other than purely natural causes were supported to have their part.
Ion exchange has an interesting history, though investigators have shunned no efforts to discover ancient references. The earliest of those, it seems, is found in the holy Bible.

It establishing Moses priority it reads, thus Moses — succeeded in preparing drinking water from brackish water. Undoubtedly by an ion exchange technique which he developed on an industrial scale. Thomson and Way two English chemists rediscovered base exchange (cation exchange) in soil, the materials which are responsible for these phenomena were identified chiefly by Lambert and later by Wiegner as clays and zeolites.

In exchangers (zeolites) consist of framework carrying a positive or negative electric surplus charge which is compensated by mobile counter ions of opposite sign. The counter ions can be exchanged for other ions of the same sign. The exchange is stoichiometric and as a rule reversible. Ion exchange is essentially diffusion process and has little, if any relation to chemical reaction kinetics in the usual sense.

Today ion exchange is firmly established as a unit operation and is an extremely valuable supplement to other procedures such as filtration, distillation and adsorption.
The cation exchange behaviour of zeolites is affected by some particular factors. The most important of these are -

i. the electrostatic interactions between the charged framework and the counter ions depend on the size and in particular on the valence of the counter ion,

ii. the concentration ratio of the competing counter ion species in the solution,

iii. in addition to the electrostatic forces other interactions between the ions and their environment are effective,

iv. large counter ions may be sterically excluded from the narrow pores of ion exchanger,

v. the temperature,

vi. selectivity of the ion exchanger to distinguish between various counter ion species, and

vii. the nature of the solvent (it may be aqueous or organic solvents).

Most of the zeolites do not undergo any appreciable dimensional change with ion exchange.\(^2\)\(^6\)

The zeolites are relatively soft materials and thus not very abrasion resistant, their framework are less open (pre widths about 3 to 9 Å) and more rigid than those of most other ion exchangers therefore, the swell very
little and the counter ions in their pores are not very mobile, perhaps the most important property of zeolites is their small and strictly uniform pore size which gives rise to a pronounced 'sieve cation' on a molecular scale.

**ION EXCHANGE THEORY**

The treatment of ion exchange reactions in zeolites by different investigators seems to be somewhat confused because a uniform system of nomenclature has not generally been employed.$^{27}$ The ion exchange process may be represented by the following equation -

$$Z_A^+ B(Z) + Z_B^+ A(S) \rightleftharpoons Z_A^+ B(S) + Z_B^+ A(Z) \rightleftharpoons 1$$

where $Z_A$, $Z_B$ are the charges of the exchange cations $A$ and $B$. The subscripts $Z$ and $S$ refer to the zeolite and solution respectively.$^{28}$

The equivalent fractions of the exchanging cations in the solution and zeolite are defined by

$$A_S = \frac{Z_A^mYZ_A}{Z_A^mYZ_A + Z_B^mYZ_B} = \frac{Z_A^m}{Z_A^m + Z_B^m} \rightleftharpoons 1.2$$

$$A_Z = \frac{\text{no. equivalents of exchanging cation } A}{\text{total equivalents of cations in the zeolite}}$$

where $m_A^S$ and $m_B^S$ are the molalities of the ions $A$ and $B$ respectively in the equilibrium solution. Also $(A_Z+B_Z)$
\[
\alpha^A_B = \frac{A_S}{B_S \cdot A_S}
\]

The preference of the zeolite for one of the two ions is expressed by the separation factor \(\alpha^A_B\). If ion A is preferred \(\alpha^A_B\) is greater than unity. \(^{27}\)

The separation factor depends on the total concentration of the solution, the temperature and \(A_S\), it is not affected by choice of concentration units.

**KINETICS OF ION EXCHANGE**

The ion exchange process may be quite rapid and equilibrium may under certain conditions be reached almost instantaneously. On the other hand ion exchange having the ion active groups accessible only through very small pores exhibit a low speed of exchange.

It may be concluded that the ion exchange occurs instantaneously and that in the most cases the diffusion of the ions through the zeolite particle is the rate determining factor. \(^{29}\) Other factors which are of importance from an analytical point of view are that the rates of exchange increase considerably with decreasing particle size, \(^{30}-^{32}\) and increasing temperature, \(^{32}-^{34}\). The rate of uptake decreases with increasing charge and volume of ions \(^{30}-^{35}\) with
cation exchange theoretical studies of ion exchange kinetics have been published by several authors 34-36.

Boyd et al. 28 have considered not only the diffusion through the zeolite particle and the exchange reaction but also the diffusion through the solution to the surface of the zeolite, the conditions under which the film diffusion has an influence or eventually is the rate determining factor have also been discussed by Hale and Reichenberg 31 as well— as by kressman and Kitchener 34.

The rates of ion exchange have a great influence upon the efficiency of ion exchange separation thus the rate determines the stepness of the breakthrough curves. The sharpness of elution peaks and the degree of overlap in chromatographic separations.

Particle diffusion controlled exchange is more rapid when the counter ion which is initially in the ion exchanger is the faster one. For film diffusion controlled exchange the opposite holds the counter ion which is preferred by the ion exchanger is taken up at the end released at the lower rate.

THERMODYNAMICS OF ION EXCHANGE PROCESSES

Ion exchange reactions can be expressed by the equation 37. The free energy of exchange $\Delta G^\circ$ is given by
\[ \Delta G^\circ = \frac{-RT}{Z_A Z_B} \ln K_a \]  \hspace{1cm} \text{.. 1.4}

and the standard entropy, \( \Delta S^\circ \) is given by

\[ \Delta S^\circ = \frac{\Delta H^\circ}{T} - \Delta G^\circ \]  \hspace{1cm} \text{.. 1.5}

The standard enthalpy is obtained from the variation of \( K_a \) with temperature,

\[ \frac{d \ln K_a}{dT} = \frac{\Delta H^\circ}{RT^2} \]  \hspace{1cm} \text{.. 1.6}

Enthalpy changes in zeolites ion exchange reactions are generally small. The thermodynamical data should be used, with caution. In many cases complete exchange can not be obtained due to cation sieve effects. Further, in some cases equilibrium had been not reached where very dilute solutions were employed.

The ion exchange model originally proposed by Eiseman has been extended to account for the variation in ion specificity exhibited by zeolites. Interaction of the ion with the zeolite and solution phases is considered.

For the uni-univalent ion exchange reactions

\[ \Lambda_5^+ + Z_2^+ \rightleftharpoons \Lambda_2^+ + Z_5^+ \]  \hspace{1cm} \text{.. 1.7}

where \( S \) and \( Z \) represent the solution and zeolite phases.
The free energy of the reaction is considered to be consisting of two terms,

$$
\Delta G^* = (\Delta G_2^A - \Delta G_2^B) - (\Delta G_3^A - \Delta G_3^B)
$$

The first term in this expression represents the difference between the free energy of $A^+$ and $B^+$ in the zeolite while the second term represents the free energy difference of hydration of the ions $A^+$ and $B^+$ in solution. The first term is more important if the force fields in the zeolite are very strong (zeolites with a high framework charges and correspondingly low Si/Al ratio) and small ions are preferred. If the fields are weak (as in zeolites with a high Si/Al ratio) the second term is more important and large, weakly hydrated cations are preferred. The model proposed by Sherry\textsuperscript{41} considers the entropy change that occurs in the zeolite phase and the corresponding difference in entropy of hydration of the ions in the equilibrium solution. Transfer of water to the zeolite decreases the entropy because water molecules adsorbed in zeolite have fewer degrees of freedom. The water content of the zeolite decreases with increasing atomic number of the univalent alkali metal ion present.\textsuperscript{42}
MOLECULAR SIEVE PROPERTIES OF ZEOLITES

In 1952, McBain proposed the term molecular sieve when he noticed chabazite to have the ability to adsorb different molecules. Three categories of molecular sieves have been distinguished by Barrer according to the minimum diameter of the pores governed in principle by the framework Al-Si-O ring. These apertures range may be from 0.3 nm to 1.01 nm. By a useful choice of the zeolites it is possible to separate many mixtures.

In order to correlate the crystallographic pore size of zeolite with dimensional parameter of various adsorbates, a scale of molecular dimension is established the effective diameter of the windows controlling access to the channels network. Following methods are used for varying the molecular sieve behaviour of a zeolite:

1. **By Ion Exchange**

   Changing the cation in a zeolite may effectively alter the pore diameter. This variation may take place in both direction either positive or negative. For example, consider the effect of Na⁺/Ca²⁺ exchange on the adsorption behaviour of N₂ on zeolite A for adsorption at 77°K. No N₂ was adsorbed by NaA. The windows of zeolite A are
open for adsorption of nitrogen when 23 to 28% exchange of Ca\textsuperscript{++} has taken place and the increase in pore size by Ca\textsuperscript{++} exchange does not occur in a linear fashion.

**Pre-adsorption**

It is known from X-ray examination that the water molecules in zeolites are not held by ordinary valence bond but merely fit into the vacant species in the lattice of aluminium and silicon metal atoms. On dehydration the water is removed and the space can be filled by other molecules. Dehydrated zeolites are therefore good adsorbing agents.

It is a second method for altering the molecular sieving effect of zeolite by is by pre-adsorption of polar molecules. It is assumed that the strong reaction between the zeolite cation and dipole movement of ammonia or water produces a diffusion block by clustering of water of ammonia molecules about the cation in channels. Similar results have been observed with chabazite and mordenite.

In the case of large pore zeolite such as \( x \), the effective pore size may be controlled by the formation of a stable inorganic complex. If copper is exchanged into the cation positions in the zeolite and subsequently treated with pyridine, a very stable pyridine cation complex is formed. The adsorption of gases and vapours on this materials is
evidence of considerable decrease in the pore size due to blocking by the cation complex. 48

Pore Closure

A third method for varying the molecular sieve behaviour of a zeolite is by the mechanism of hydrolytic pore closure. This technique reduces the effective pore size for critical molecules. 49

Decationisation

Complete removal of cations from the zeolite framework alters the local electrical field and field gradient consequently reduced any interaction with a molecule of permanent electrical moment.

The Kinetic Diameter

For spherical and non-polar molecules the potential energy of interaction, \( \phi(r) \) is well described by the Lennard-Jones potential

\[
\phi(r) = 4\varepsilon \left[ (\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6} \right]
\]

The parameters, \( \sigma \) and \( \varepsilon \) are constant which are characteristic of the molecular species and are determined from second virial coefficients. At large separations the attractive component \( (\varepsilon/\sigma)^6 \) is dominant and describes the
induced dipole attraction. At small separations the repulsive component is dominant. When the potential equals 0, the diameter $r$ is equal to $a$. The kinetic or collision diameter is the intermolecular distance of closest approach for two molecular colliding with zero initial kinetic energy. The maximum energy of attraction occurs at $r_{\text{min}}$ where $r_{\text{min}} = 2^{1/6}a$. There are several examples of molecular sieving\textsuperscript{51,52}

In assessing the apparent pore size of molecular sieve zeolites, the critical dimensions for spherical molecules are given by the pore value of $r_{\text{min}}$. For diatomic molecules $r_{\text{min}}$ is based upon the Vander Waals length, and represents the molecule in all orientations. For long molecules such as hydrocarbons, the dimension is minimum cross sectional diameter. It is preferred to use 6 values, where available for non-polar spherical molecules and 6 values obtained from minimum cross-sectional diameters for more complex molecules such as n-paraffins.

**ION EXCHANGE CAPACITY**

Ion exchangers are characterized in a quantitative manner by their capacity which, in common usage, is defined as the number of counter ion equivalents in a specified amount of the materials. Capacity and related data are primarily used for two purposes for characterizing ion
exchange materials and for use in the numerical calculation of ion exchange operations. In the first case, the capacity should be defined, if possible, in such a way that it is a characteristic constant of the materials and is independent of the experimental conditions. In the second case it is usually more practical to use other definitions or quantities which reflect the effect of the operating conditions. A Glossary of the most common definitions is given.

Number of ionogenic groups per specified amount of ion exchanger.

**ION EXCHANGE EQUILIBRIA**

When an ion exchanger is brought into contact with an electrolyte solution by shaking a given quantity of exchanger with the solution, exchange of ionic will take place until equilibrium is attained. At equilibrium the solution contains generally the same ionic species as it originally did. Although the concentrations of these species have changed, together with additional ions previously attached to the exchanger. The same ionic species as in the solution are found in the ion exchanger, but the concentrations differ from those in the solution only in exceptional cases. A quantitative uptake of ions can be obtained when a moderate amount of ion exchanger is shaken with a solution. As a rule, precipitation of the solution through an ion exchange
column is necessary to ensure a quantitative uptake.

Because of their great practical importance, ion exchange equilibria have been the object of numerous investigations with both inorganic and organic ion exchangers. 54

APPLICATIONS OF ION EXCHANGE

Because of the particular selectivity forces of materials separation with ion exchange is used mostly in inorganic chemistry, organic chemistry which form salts with the oppositely charged ions in another phase can be separated too. Almost all ion exchanger reactions require aqueous solvents. Some of the most important applications of ion exchange reaction are as follows:

1. Determination of Total Concentration

A very important field for the employment of the ion exchange method is determination of the total concentration studies of this method, which is extremely rapid and accurate, were first reported by Amuelson. 55

The solution to be analyzed is merely passed through a column of the cation exchanger and after washing with water, the resulting solution is titrated with standard alkali.
2. Separation of Similar Ions from One Another

Ion exchange reaction is being used to separate similar ions from one another because the different ions undergo exchange reactions to different extents. For instance, a mixture Li⁺, Na⁺ and K⁺ ions can be separated by passing their solution through a cation exchanger subsequently 0.1 M HCl has been used as an eluent.

3. Purification of Direct Cotton Dyes

A method for the purification of direct cotton dyes, which may be of interest also from an analytical point of view, has been devised by Richardson. The method is based on the fact that the large organic anions of a dye with an average diameter of 30 Å or larger are prevented from entering the resin phase.

4. Separation of Sugars

McGready and Hassid isolated and purified glucose-1-phosphate with the aid of ion exchange resins. These sugars are first of all converted into borate complexes

\[
\begin{align*}
\text{C} - \text{OH} + \text{H}_3\text{BO}_3 & \rightarrow \text{H}_2\text{O} \\
\text{C} - \text{OH} & \rightarrow \text{C} - \text{O} \quad \text{B} \quad \text{OH} \\
& \quad \text{OH} \quad \text{H}^+ \\
\end{align*}
\]
Monodiol boric acid

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{Monodiol boric acid} \\
\text{H}^+ & \quad \text{B-OH}
\end{align*}
\]

Bisdiol boric acid

Separation of borate complexes of sugar have been achieved on 11 x 0.9 cm columns of 200-400 mesh Dowex 1 resin.

Similarly, disaccharides can be separated from monosaccharides and the individual compounds of hexose and pentose mixture resolved.

5. Analysis of Natural Water

Lur'e and Stefanovich used a cation exchanger of sulphonlic acid type to concentrate calcium and magnesium from natural waters. Elution was performed by means of HCl.- This principle was also used in a careful investigation by Rydani\textsuperscript{58} who extended the method to include Na\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, Fe\textsuperscript{3+}, Mn\textsuperscript{2+}, Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-} and PO\textsubscript{4}\textsuperscript{3-}. The method was checked by analysis of synthetic 'lake waters'.

6. Analysis of Milk, Beer and Apple Juice

Granston and Thompson\textsuperscript{59} devised a method for the determination of copper in milk by the use of a cation exchange
resin and synthetic zeolite. The copper in milk is transferred to cupric ions by addition of perchloric acid to pH less than 3.0. This accomplishes the precipitation of the protein and fat will be carried into the curd.

Preliminary experiments on the concentration of tin, copper, and iron from milk by means of cation exchange resin have been reported. Furthermore, the method has been successful for determination of sodium and potassium in apple juice.

7. Isolation of Radioelements from Urine

As an example of the application of a simplified technique for ion exchange process introduced by Schubert, Russell and Parable for the determination of radioelements in urine by this method the amount of dangerous radioelements which may have accumulated in the body of an exposed individual is conveniently ascertained.

8. Isolation of Amino Acid

One of the earliest applications of ion exchange to laboratory problems was that of Whitcomb, who in 1932 studied the uptake of different organic cations and amino acid. The basic amino acids histidine and lysine were found to be quantitatively retained in a column containing
synthetic zeolite (permamit) in the sodium form, whereas several natural amino acids passed into the effluent. The procedure has been utilized for the selective uptake of basic amino acids. Archibald\textsuperscript{64} investigating the occurrence of glutamine in liver extracts found that it could be freed from arginine by this method. Ninety per cent of the glutamine, but no arginine was found in the effluent.

According to Bristol and Foucaud\textsuperscript{65} ornithine, lysine, arginine, and histidine may be almost quantitatively removed by means of permamit. Based on this principle investigation were performed on the amino acid composition of human serum.

Dubnaff and Borsook\textsuperscript{66} determined glycocyamine in biological fluids and tissue extracts. Since arginine interferes with the glycocyamine reaction, it was removed by means of sodium zeolite.

Some early experiments on ion exchange chromatography of amino acids by means of synthetic zeolites were published by Felix and Warg\textsuperscript{67} by Sadikov and Lindkvist Ruisakov\textsuperscript{68} as well as by Kapuva\textsuperscript{69}.
ABSORPTION AND DIFFUSION PHENOMENA ON ZEOLITE

The ability of zeolites to adsorb considerable volumes of adsorbate molecules in place of zeolitic water present in the crystal on formation was quickly demonstrated by early studies. The molecular volume and shape of the adsorbate molecules were found to have an influence upon the amounts which would be taken up by the zeolite. Crystalline zeolites were soon shown to be porous crystals permeated by channel networks. The free dimensions of which were strictly controlled by the position of the framework oxygens. Thus the molecular sieving character of zeolites could be fully explained. The behaviour of a given zeolite acting as an adsorbent diffusion medium and molecular sieve is also regulated by the size, charge, and locations of the cations present in the structure.

In one respect, the adsorption of gases and vapours by zeolite solids is not as complex as adsorption phenomena on amorphous, less defined solids. This is due to the regularity in the internal pore system.

Zeolites are high capacity selective adsorbents for two reactions -

1. They separate molecules based upon the size and
configuration of the molecules relative to the size and geometry of the main apertures of the zeolite structure.

2. Zeolites adsorb molecules in particularly those with a permanent dipole movement and which have other intraction effects with a selectivity not found in other adsorbents.

In dehydrated crystalline zeolites adsorption of gases or vapours depends on equilibrium pressure, temperature and nature of the micropores in the zeolite crystals and the nature of gas or vapours adsorption process involved a decrease in free energy and in entropy $\Delta H$ change, must also be negative. Since the change in entropy is negative, hence the adsorption process is exothermic and heat is evolved. The heat of adsorption is derived from the clausius clapeyron equation.

Isotherm Equation to the Zeolite Adsorption

Several attempts have been made to derive a standard adsorption equation, which would apply to the adsorbed phase in zeolites under all conditions. Although several at the equations have some degree of broad applicability no universal adsorption equation exists. The Langmuir equation originally applied to the adsorption of molecules
in a monolayer on an open surface. The classical interpretation of the type I isotherm is based upon this model.

Since zeolites exhibit the type I isotherm, the Langmuir equation has been applied with some degree of success.

Contrary to the usual interpretation of the type I isotherm, the break in the isotherm corresponds to the filling of the microvoids and not the completion of monolayer.

According to the Langmuir equation

\[ 0 = \frac{X}{X_m} = \frac{B_p}{1 + B_p} \]  \( \ldots \) 1.11

This model assume that adsorption potential is uniform and no energetic heterogeneity exists. But this is not true in most of zeolite adsorption cases. In equation 1.11, \( X \) represents the quantity adsorbed in the solid at pressure \( p \).

The coefficient \( B \) is constant at constant temperature. In the zeolites, the point corresponding to void filling is given by \( X_m \). At low pressures the term \( B_p \) may be neglected in comparison to unity. Thus equation is simplified to

\[ X = X_m B_p \]  \( \ldots \) 1.12

Here adsorption is proportional to pressure (Henry's law) and the isotherm is a straight line. At high pressure, the value \( B_p \) is very large relative to one and the equation
reduces to \( \frac{P}{X} = \frac{1}{X_m} \). The isotherm becomes horizontal at high pressures.

The **Langmuir equation** may be rewritten as

\[
\frac{P}{X} = \frac{1}{X_m} \beta + \frac{P}{X_m}
\]

... 1.13

The value of \( P/X \) plotted against \( P \) yields a straight line with \( 1/X_m \) as the slope.

The classical **BET equation**, used for many years to evaluate surface areas and heats of adsorption for many adsorbent adsorbate systems, is not applicable to zeolites. Basically this equation was developed for multilayer adsorption; for a monolayer, such as in zeolites, it reduces the Langmuir equation.

Reikert \(^{70b}\) shows that for adsorption of \( \text{CO}_2 \) on zeolite \( \text{H}, \) the isotherm at \(-30^\circ\text{C}\) may be represented as the sum of two individual Langmuir isotherms, one for each of two different types of sites.

The **Volmer equation**

\[
K_v = P \frac{(1 - \theta)}{\theta} \exp \left[ - \frac{\theta}{1 - \theta} \right]
\]

... 1.14

assumes that the equilibrium gas phase behaves as a two-dimensional gas without any lateral interaction. This
equation is not applicable in most cases \[71, 72\].

In another model, the isotherm equation is based upon a virial equation by the application of solution thermodynamics. The term \(\mathcal{A}\) which is the pressure that would have to be applied to the dehydrated zeolite to reduce its chemical potential to that of the zeolite when adsorption has taken place. This equation is based on the osmotic rates \(\mathcal{A} = \frac{\kappa}{c} \frac{C}{RT}\). \[73\]

\[
\frac{\mathcal{A}}{c} = 1 + A_1 c + A_2 c^2 + \ldots + A_n c^n \quad \ldots \quad 1.15
\]

where \(c\) is the concentration of adsorbate in the zeolite.

The polyanion potential theory was one of the earliest empirical theories developed for treating adsorption. It was modified by Dubinin and Redushkevich for application to microporous adsorption and void filling \[74, 75\]. In polyanion theory the characteristic curve is the relationship between the work of adsorption \(W\) and the filled volume of the adsorption space \(V\), and \(A\) is given by

\[
A = kT \ln \frac{P_s}{P} \quad \ldots \quad 1.16
\]

and

\[
h = a V
\]

where \(a = \) the amount of adsorbate in millimoles/g at
temperature $T$ and equilibrium pressure $P$. The molar volume of the adsorbate is $V$ and $P_s$ in the saturation vapour pressure. This equation takes the form of

$$W = W_0 \exp \left[ - \frac{KA^2}{\beta^2} \right]$$

... 1.18 ...

This is applied to microporous adsorbents such as carbon and in many instances to zeolites. The volume occupied by adsorbed phase $W$ at a given temperature $T$ and pressure $P$ is given by the equation

$$W = W_0 \exp \left[ - \frac{B}{\beta^2} \left( T \log \frac{P_s}{P} \right)^2 \right] = aV$$

... 1.19 ...

$W_0$ is a constant and gives the volume of the adsorption space or pore volume. $B$ is a constant which is independent of temperature and characteristic of the adsorbent porous structure. The constant $\beta$ is an "affinity constant". At low temperatures below the boiling point of the liquid, $V$ can be taken as equal to the molar volume of the bulk liquid. Experimentally, equation 1.19 is used in the following form, 75, 76.

$$\log W = \log W_0 - \frac{B}{2.303\beta^2} \left( T \log \frac{P_s}{P} \right)^2$$

... 1.20 ...

In order to evaluate $W_0$ and $B$, the equation is expressed as

$$\log a = c - d \left( \log \frac{P_s}{P} \right)^2$$

... 1.21 ...

when log $a$ is plotted against $\left( \log \frac{P_s}{P} \right)^2$ the curve should
be linear, for the equation to be applicable.

\[
C = \log \frac{W}{V} \quad \text{and} \quad D = \frac{0.434 B T^2}{\beta^2}
\]  .. 1.22

A single characteristic curve was applied to all of the low molecular weight hydrocarbon including n butane by using a reduced adsorption potential. Isotherm equation given by simple expression

\[
V = K_p h
\]  .. 1.23

and

\[
\log V = h \log P + \text{constant}
\]  .. 1.24

This equation has some limited applicability to zeolite adsorption. Loughlin and Ruthven have determined a new isotherm equation with the help of thermodynamics. This equation was found to be unsatisfactory for high adsorbate loadings or above a value of Θ = 0.7.

**The Heat of Adsorption**

All adsorption processes involving physical adsorption are exothermic, that is they evolve heat. For adsorption to take place, the free energy change must be negative. From the thermodynamic relation

\[
\Delta G = \Delta H - T \Delta S
\]  .. 1.25

The change in enthalpy, \( \Delta H \) is negative since the change
in entropy, $\Delta S$ is negative because the adsorbate molecules are in a more ordered configuration. There are three terms referring to the heat of adsorption.

i. The isothermal integral heat of adsorption. This is the total heat involved in the adsorption process from zero adsorbate loading to some final adsorbate loading at a constant temperature.

\[ \Delta \tilde{H} = (\tilde{H} - \tilde{H}_g) \quad \cdots \quad \text{1.23} \]

where $\tilde{H}_g$ is the molar enthalpy of the adsorbate gas and $\tilde{H}$ is the partial molar enthalpy of the adsorbate. The differential heat of adsorption is dependent upon pressure, temperature and adsorbate coverage or loading.

ii. The differential heat of adsorption, $\Delta \tilde{H}_d$. This is the change in integral heat of adsorption with a change in adsorbate loading.

iii. The isosteric heat of adsorption is derived from adsorption isosteres. It is obtained from plot of the log of the pressure $V_P$, the reciprocal of the absolute temperature, $1/T$ at constant adsorbate loading by means of Clausius-Clapyron equation. From the pairs of the isotherms $q_{iso}$ may be calculated by

\[ q_{iso} = 4.58 \frac{T_1^2}{T_2 - T_1} \log \frac{P_2}{P_1} \quad \cdots \quad \text{1.24} \]
The isosteric heat is related to the differential heat of adsorption by

\[-q_{iso} = \Delta \tilde{H}\]  

It can be demonstrated that the isosteric and differential heat are identical. One can also obtain the integral heat of adsorption from isosteric heats. Iso-

steric adsorption heats which are obtained from a family of adsorption isosteres, are plotted as a function of the adsorbate loading and by a subsequent graphical integration the isothermal integral heat of adsorption is evaluated. The differential entropy of adsorption can be determined from the logarithmic plots since it is equal to the product of the absolute temperature and isosteric heat of adsorption.

**Zeolite Adsorbate Interaction Energies**

At low levels of adsorption, the initial adsorption heat \(\Delta \tilde{H}\) has been related to several component interaction energies. These include dispersion and short range repulsion energies, (energies)\(^1\) polarisation energy and additional components attributed to electrostatic interactions. These are caused by the interaction of the local electrostatic fields in the zeolite with molecules possessing permanent dipole moments or quadrupole moments. The magnitude of these interactions has been estimated and related to \(\Delta \tilde{H}\).
This dispersion and repulsion energy terms are found universally but the electrostatic terms depend on the characteristics of the adsorbate and adsorbent, and dispersion and repulsion energies are also estimated.\textsuperscript{80,81,80-81}

**Character of Adsorbed Phase in Zeolites**

The techniques employed in characterizing the adsorbed molecules in zeolite include:

1. Spectroscopic methods, infra-red spectra, Raman spectra, reflectance spectra in the visible and ultra-violet regions electron spin resonance (nmar)(II).
2. X-ray crystal structure studies to determine the location of adsorbed molecules and their interaction with the internal zeolite surface atoms and cations.
3. Thermochemistry - heats and entropies of adsorption.

**Effect of Ion Exchange**

As exhibited by the previous examples, changing the cation in a zeolite may effectively enlarge the pore openings by diminishing the cation population or reorienting of cations which are normally located near these openings. Variations in both a positive and negative direction may
take place. For example, in zeolite A divalent ion exchange opens the aperture to full diameter whereas exchange with a larger univalent ion diminishes the aperture size. Potassium ion exchange in zeolite A reduces the effective adsorption pore size to the point where only small polar molecules are adsorbed. This reduction does not occur gradually with increasing exchange but rather suddenly at a level of about 25 per cent potassium exchange. Similarly, the increase in adsorption pore size by calcium exchange does not occur in a linear fashion but rather abruptly at a level of about 30 per cent exchange. Similar effects are exhibited by the zeolite Chabazite.
Applications of Adsorption Processes in Zeolites

Molecular sieves have several advantages over other adsorbents because of the following:

i. They adsorb small molecules and reject those that can not pass through the pores.

ii. They have a high adsorption capacity at elevated temperature.

iii. They have a high adsorption capacity at low adsorbate concentrations.

iv. They have an unusually high affinity for unsaturated organic compounds.

v. They have an unusually high affinity for polar molecules.

vi. They will adsorb water in presence of other adsorbates.

APPLICATIONS OF ZEOLITE

The first practical use of zeolites probably dates back to about 2000 years. When natural zeolites as rock was quarried for use as boiling stones. Although zeolites were not recognized as new minerals species till about 200 years ago, the first chemical property of zeolite viz.
cation exchange was investigated by Richmor about 100 years ago. This led to the development of synthetic amorphous aluminosilicates as cation exchange materials. These were primarily used in water softening. Their other well known uses are:

1. **Purification of Water**

Water which reacts with soap and produces an insoluble precipitate is said to be hard. Water containing salts of calcium or magnesium or indeed, of any of the metals other than sodium and potassium has this property. The precipitate formed consists of the stearates of calcium and magnesium. Soap consists of sodium stearate which is soluble in water and this reacts with any soluble calcium salt according to the equation:

$$2\text{NaSt} + \text{Ca(HCO}_3\text{)}_2 = 2\text{NaHCO}_3 + \text{CaSt}_2$$

Where St is stearate radical (C₁₇H₃₅COO⁻).

Hard water is, therefore, obviously unsuitable for washing purposes. For until the calcium in the water has been removed by combining with the soap, the water cannot exert its detergent action which depend upon its being free in solution. Hard water accordingly causes great wastage of soap.
This inconvenience of hard water have led to the development of a process designed to remove from water the substances which cause its hardness. The process which is most efficient and most widely used is the permun-rit process. This is never used to soften a whole town's supply, but a softening plant is attached to the water inlet pipe of an individual private house or factory. The softening is accomplished by allowing the water to flow over a bed of granulated hydrated aluminium silicate. This substance may be made artificially, but is usually obtained from mineral zeolite. The commonest form of this zeolite is greensand. A reaction takes place between the zeolite and calcium and magnesium salts of the water (which we will regard for the purposes of the equation as calcium bicarbonate) resulting in the $\text{Ca}()_{2} \text{HCO}_{3} \text{+ Na}_2 \text{Al}_2 \text{Si}_4 \text{O}_8 \cdot x \text{H}_2 \text{O} \rightarrow \text{CaAl}_2 \text{Si}_2 \text{O}_8 \cdot x \text{H}_2 \text{O} + 2 \text{NaHCO}_3$.

Conversion of the sodium aluminium silicate into calcium aluminium silicate while sodium bicarbonate goes into solution. The issuing water contains no calcium or magnesium salts and the trace of sodium present is quite innocuous.

The zeolite is then regenerated by running over it for five minutes a converted solution of common salt. The high concentration of this causes the reaction to proceed
almost to completion.

$$2\text{NaCl} + \text{CaAl}_2\text{Si}_2\text{O}_8\cdot\text{XH}_2\text{O} \rightarrow \text{CaCl}_2 + \text{Na}_2\text{Al}_2\text{Si}_2\text{O}_5\cdot\text{XH}_2\text{O}$$

The sodium zeolite is once more formed and the calcium goes into solution as the chloride and is run to waste.

The zeolite can then again be used to soften more hard water until it once more needs regeneration.

2. Catalysis by Zeolites

Many chemical reactions, both inorganic and organic, can be catalyzed by zeolites. This is true for reactions of gases and of liquids and solutes. Catalysis of reactions of liquids and solutes by ion exchangers (zeolite) can usually be explained in terms of the catalytic activity of the counter ions and is analogous to homogeneous phase catalysis by dissolved electrolytes. The catalytic activity of ion exchanger thus is directly related to the ion exchange properties. It has been found that the dissolved electrolyte can be replaced by an ion exchanger which contains the catalytically active ion as the counter ion. The reaction now occurs in the pores of ion exchanger where the active sites are located. 

Sucrose inversion 86-92

93-103

Acetone hydration of acetylene derivatives 104

95-102

Benzenoid condensation 105 and many other ion exchange reactions 103.
can thus be catalyzed by zeolites.

3. As drying agents and adsorbers

Mordenite, like many other natural and synthetic zeolites, is used in drying and purification of acidic gases. In view of its particular resistance to thermal cycles in acidic environments.

Minato and Tamura\(^{107}\) devised an oxygen generator based on the differential adsorption of \(N_2\) and \(O_2\) on natural mordenite from the tuffs of Itado, Akita Pref., Japan.\(^{108}\) After a pre treatment column for the removal of \(H_2O\), \(CO_2\) and \(SO_2\), the air enters a zeolite column, which adsorbs \(N_2\). So that a gas with upto 93% of \(O_2\) is obtained.

The sedimentary chabazite from Bowie, Arizona is used not only for the adsorption of \(H_2O\), \(CO_2\), \(H_2S\) in industrial gases, but also for the separation of \(CO_2\) from \(NH_3\) gas produced by decaying garbage in landfills. A plant of this type with chabazite beds is active in Los Angeles.\(^{109}\)

4. Removal of Ammonia from Waste Water

The interesting property of phillipsite as an ammonia adsorber\(^{110}\) suggests an application for the removal of ammonia from waste water. From this point of view phillipsite
is superior to clinoptilolite and inferior to merlinerite or Linde W but the first is not available in nature as large masses and the synthetic Linde W is certainly more expensive than a sedimentary phillipsite, subsequently Sherman and Ross\textsuperscript{111} patented a process of this type based on natural and synthetic phillipsite.

A similar application, ammonia removal during coal gasification was proposed by Hayhurst\textsuperscript{112} who demonstrated that phillipsite was better than mordenite, chabazite, clinoptilolite or ferrierrrite for this particular task. Banerjee\textsuperscript{113-114} and co-workers have also succeeded in adsorbing ammonia in hydrophilite and stilbite.

5. Estimation of Vitamin

A synthetic zeolite (Decalso)\textsuperscript{115} was used in early investigations by Cerecedo and co-workers in order to take up thiamine from solutions obtained from extraction of rice polishings, yeast or wheat germ\textsuperscript{116-117}

Fujiwara and Shimizu\textsuperscript{118} found that a pyridine treated zeolite has affinity for riboflavin compared to potassium zeolite and that riboflavin where retained on the former type of exchanger is easily eluted by washing with water without any linkage of thiamine.
Riboflavin is retained to only a slight extent by a synthetic zeolite in the potassium form\textsuperscript{119} and may therefore, be determined in the effluent from the column.

A synthetic zeolite has also been used for the isolation of vitamin K\textsubscript{4}\textsuperscript{120}. The reaction of this substance seems to be due to a "Physical Adsorption".

\textbf{MISCELLANEOUS APPLICATIONS}

As sedimentary clinoptilolite is available as large masses which can be excavated at low cost in quarries it has been widely studied and deployed building stones, soil conditioner, paper filling, dietary supplement for pigs and roosters, and in waste water purification, dehydration, gas separation, etc.

Torii\textsuperscript{121} reports on the increased agricultural crops obtained in Japan, when clinoptilolite (1 ton/1000 m\textsuperscript{2}) was added to the soil, retention of ammonia and potassium could be the cause of the favourable effect. Clinoptilolite is also used in agriculture as a chemical carrier both for herbicides and fertilizers.

Torii\textsuperscript{121} reports that 3300-4000 tons per month of clinoptilolite are used in Japan as paper filler. The
The literature on the use of clinoptilolite as dietary supplement is so wide.

Torii\textsuperscript{121} presents interesting data on the advantages in feeding pigs with a diet including 6\% of this zeolite, especially in the first month. Hayhurst and Willard\textsuperscript{122} showed that roosters raised with a diet including 75\% clinoptilolite showed increased weight gain over a seven weeks period, no toxic effects were observed. Olver\textsuperscript{123} reported on the influence of this dietary supplement on laying hens.

Mercer and Ames\textsuperscript{124} reported the use of clinoptilolite beds for recovering cesium from radioactive waste water, and ammonia from municipal waste water. Murphy \textit{et al.}\textsuperscript{125} Torii\textsuperscript{121} and Sheppard \textit{et al.}\textsuperscript{126} similar is the application proposed by Bower and Turner\textsuperscript{127} to add some clinoptilolite to the plastic shipping bags containing goldfish to reduce ammonia concentration during transport.

The most common industrial use of clinoptilolite is probably to fill drying beds for the dehydration of liquids and gases. For instance before a catalytic reaction Klopp \textit{et al.}\textsuperscript{128} report widely on this kind of use of Hungarian clinoptilolite and Torii\textsuperscript{121} for the zeolite from Japan. Both authors mentioned the possibility of filling drying cartridges
in compression type refrigerators.

Galabova et al.\textsuperscript{129} studied an oxygen enrichment of air using clinoptilolite, but Minato and Tamura\textsuperscript{118} obtained better results with mordenite.

**SCOPE OF THE PRESENT WORK**

In the present investigations, the author has studied some cation exchange and adsorption properties of a new commercial material 'Deolite'. A number of cation exchanged and adsorbed derivatives has been studied to extent the commercial applications of this material.

Cation exchanged derivatives of 'Deolite' have been prepared with the mono and divalent cations like $\text{K(I)}$, $\text{NH}_4(I)$ and $\text{Ca(II)}$ and adsorbed derivatives with phosphoric acid, tricresyl phosphate and normalbutyl phosphate. These cation exchanged forms and the original Deolite have been tried as adsorbent for a gaseous adsorbate like ammonia. The aim has been to use them as anti-pollutents by studying the extent of adsorption. The thermal behaviours of these new cation exchanged and adsorbed Deolite derivatives have been followed by TG analysis, IR spectroscopy and X-ray diffraction analysis have helped to elucidate their structures.
The work attempts to establish the following facts.

1. The new zeolite like material Deolite can be used effectively as a cation exchanger for K(I), NH₄(I) and Ca(II), the extent of exchange with the three different cations differs due to the cations used for exchange.

2. All the exchanged forms as well as Deolite are capable of adsorbing ammonia through either physical or chemical processes. The extent of adsorption varies with cation exchanged forms due to difference in properties of these forms.

3. Phosphorus containing compounds have been used for interaction to prepare phosphatic derivatives which may have future applications as fertilizers and catalysts.

Analytical data, for composition studies, IR and X-ray diffraction characteristics of Deolite and its prepared derivatives with various cations recorded and other reagents yield important informations regarding the potential industrial applications of these samples. Thermal studies contribute to the knowledge of thermal behaviours of these samples.

This thesis therefore, aims to make a small contribution to the study and application of an industrially useful material like Deolite.
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