CHAPTER I

INTRODUCTION
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(A) DEFINITION AND STRUCTURE OF ZEOLITES

Zeolite minerals were first discovered by the scientist Cronstedt. These minerals exhibited intumescence when they were heated in a blowpipe flame and so he named them "Zeolite". The word "Zeolite" comes from two Greek words meaning "to boil" and "a stone". The zeolites are also known as molecular sieves. The term molecular sieve was originated by J.W. Mc Bain to define porous solid materials, which exhibit the property of acting as sieves on a molecular scale. Zeolite minerals have been used in many investigations of "Zeolite structure" and properties like reversible water loss, ion exchange, adsorption etc. Such studies have contributed considerably to the present state of knowledge about zeolites.

OCURRENCE

The mineral combinations in which zeolites are found are widespread. Until about twenty years
ago, zeolite minerals were considered to occur in cavities of basaltic and volcanic rocks but after the discovery of stilbite by Cronstedt in 1756, numerous publications describe the occurrence and mineralogy of zeolite minerals in basaltic igneous rocks. All zeolite minerals known till this day are generally found in igneous rocks and only a few occur in sedimentary surroundings. There are nearly 40 species of zeolite minerals. Many of these are rare. Only a few like natrolite, analcime stilbite, heulandite and chabazite are common. They have a similar occurrence.

On account of the important properties and because of their wide applications many scientists have tried to synthesise these zeolites in the laboratory. About one hundred synthetic zeolites have been prepared but only a few have practical significance at the present time. In 1948 the first industrial research efforts were made by Milton and his associates at Union Carbide Corporation. These resulted in the synthesis and the manufacture of synthetic zeolite molecular sieves which had never existed as minerals. This controlled synthesis was a key to a research achievement of significance.
Synthetic zeolites are better suited for research and industrial applications because of their greater uniformity in composition and purity. This is particularly essential when a high degree of reproducibility is required in an industrial separation process and where minor impurities such as iron, commonly found in minerals can effect a major difference in application such as in heterogeneous catalysis.

Zeolites are crystalline hydrated aluminosilicates of group I and group II elements as found in nature or synthesized. Higher polyvalent ions like rare earths, are readily introduced by cation exchange. These particular elements are Sodium, Potassium, Magnesium, Calcium, Strontium and Barium. Properties of stilbite like the manner in which crystals of the mineral visibly lost water when heated led to the naming of the mineral as zeolite chabazite was found to have the ability to ion exchange and be able to differentially absorb molecules\textsuperscript{5,6}. 
STRUCTURE

Structurally these zeolites are "frame work" aluminosilicates which are based on an infinitely extending three dimensional net work of \( \text{Al}_4 \) and \( \text{Si}_4 \) tetrahedra linked to each other by sharing all of the oxygens.

These zeolites may be represented by the formula (oxide).

\[
\frac{M_{2/n}}{O} \text{Al}_2\text{O}_3 \times \text{SiO}_2 \times \text{YH}_2\text{O}
\]

In this formula \( x \) is generally equal to or greater than 2, since \( \text{Al}_4 \) tetrahedra are joined only to \( \text{Si}_4 \) tetraheona; \( n \) is the cation valency.

Aluminosilicate frame work contains channels and interconnected voids. These channels and interconnected voids are occupied by cation and water molecules. The cations are quite mobile and may usually be exchanged to varying degree by other cations. Exchange or dehydration in many zeolites may produce structural changes in the frame work. Ammonium and alkylammonium cations may be incorporated in synthetic
zeolite e.g. NH$_4$ (I), CH$_3$ NH$_3$, (CH$_3$)$_2$ NH$_2$, (CH$_3$)$_3$NH and (CH$_3$)$_4$N.

Since the aluminium cation in some synthetic zeolites may be substituted by gallium ion and silicon by germanium or phosphorus ions, the structural formula for zeolite is modified and is best expressed for the crystallographic unit cell as

$$M_{x/n} \left[ (AlO_2)_x (SiO_2)_y \right] \cdot nH_2O$$

where,

$M$ = is the cation of valency $n$

$W$ = number of water molecules

$x/y$ = has value 1-5 depending upon the structure.

The sum $(x + y)$ is total number of tetrahedra in the unit cell$^7,8$.

The portion within square bracket represents the framework composition.

Molecular sieves are special types of synthetic zeolites having a crystalline structure, consisting of a three dimensional aluminosilicate framework containing interconnected cavities.
Access to the cavities is through pores of a fixed diameter determined by the manufacturing conditions. The extensive adsorption surface in the cavities is accessible only to molecular species capable of passing through the pore openings. This accounts for the molecular sieving action characteristic of these synthetic zeolites. Molecules too large to enter the pores being excluded, while those of pore diameter or less are adsorbed.

The crystallography of the zeolites differ greatly from one another since they crystallize in the isometric, orthorhombic, monoclinic and hexagonal systems. Structure of zeolite A is given in Fig. 1.

Fig. 1: (A) Structure of zeolite A.  
(B) Structure of zeolite A cavity after Eberley.
CHARACTERIZATION AND IDENTIFICATION

For many years minerals were characterized and identified on the basis of chemical composition, optical properties, certain physico-chemical properties and morphology, since the advent of X-ray crystallography many early zeolite names have been discredited and much confusion that existed in the naming of zeolite minerals has been removed. The current list of zeolite minerals includes 34 species as defined by their chemical composition, structure and related physical properties. The basic frame work of 30 zeolite minerals are known.

Synthetic zeolites are also not easily characterized as well as identified because they lack definite system of chemical nomenclature. IUPAC rules can be used for naming complex compounds, which would be based on the unit cell composition. Following this rule the mineral analcime having unit cell contents of $\text{Na}_{16} (\text{AlO}_2)_{16} (\text{SiO}_2)_{32} 16 \text{H}_2\text{O}$ would be named as sodium 16 - alumino - 32 - silicate 16 water. Jadeite $\text{Na}_4 \text{Al}_4 \text{Si}_8 \text{O}_{24}$ would be named as sodium 4 - alumino - 8 silicate. Both minerals have the same anhydrous composition in terms of anhydrous
oxide mole ratios, \( \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \) synthetic zeolite type A \( \text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O} \) would be named as sodium-12 alumino-12-silicate 27 water. A nomenclature of this type is unwieldy and requires a detailed knowledge of the unit cell which is not always available.

Once a new material is properly characterised as a zeolite by means of its properties it can be identified by means of X-ray powder data and chemical composition.

**ALUMINOSILICATE STRUCTURE**

Although similar in chemical composition, the crystalline zeolites are completely different in structure from the gel type aluminosilicates commonly referred to as zeolites. As members of an unusual group of minerals the zeolites have been known for many years. Crystalline zeolites are complex materials chemically and structurally comprising the major group of framework silicate.\(^9\) As a result of structural studies during the last two decades there are extensive information available on the structure of zeolites. The major source of structural information is X-ray crystal structure analysis but some important information can also be obtained by IR, NMR, ESR studies.
Current concepts of silicate structure are based on the principles governing the structure of complex ionic crystals as developed by Pauling\textsuperscript{10}. The silicate minerals are all ultimately based on the tetrahedral SiO\textsubscript{4}\textsuperscript{4-} unit. This unit can be joined to a second unit i.e. Al\textsuperscript{3+} through a common O atom and the linking of a unit to one, two, three or four other units give rise to the various classes of silicates.

The Al\textsuperscript{3+} ion commonly coordinates tetrahedrally as well as octahedrally with oxygen in silicates. This has a profound effect on aluminosilicate structure and their composition. In some structures tetrahedra link to form infinite chains which give needle like fibrous crystals. In some structures tetrahedra are linked in sheets or layers, but these structures have no three-dimensional stability. Framework structures are obtained by linking SiO\textsubscript{4} and AlO\textsubscript{4} tetrahedra in three dimensions by mutual sharing of oxygen alone. These four Island\textsuperscript{11} Isolated group\textsuperscript{12} chain structure\textsuperscript{13} and framework models are used for silicate structure when all the oxygen atoms are mutually shared between tetrahedral silicons or aluminium and gives a result of three-dimensional continuous framework structure.
The class of silicate, known as tectosilicate, includes zeolites feldspathoids and is based on a structure in which each $\text{Si}^{4-}$ unit is linked to four oxygens (Pauling's first rule) as shown in Fig. 2. These units are such linked that they form a three dimensional framework of composition $(\text{SiO}_2)^n$. This structure has no residual charge. However, the replacement of the silicon ion, $\text{Si}^{4+}$, in the framework by the aluminium ion, $\text{Al}^{3+}$, produces a framework which is negatively charged and which requires the presence of cations in the interstices of the structure to bring about electroneutrality. The aluminosilicate framework so formed, can be regarded as being built by the linking of tetrahedra of $\text{SiO}_4^{4-}$ and $\text{AlO}_4^{5-}$.

The complexity of silicate structure occurs because of the various ways in which the tetrahedral groups may link by the common sharing of oxygen ions to form polynuclear complexes considerable variations in chemical composition results from the substitution of cations in tetrahedral and octahedral sites as permitted by Pauling's electrovalences rules.
Fig. 2: The tetrahedron of oxygen coordinated with silicon. In the isolated complex ion in the over all charge in 4⁻ occupancy of the tetrahedral site by Al³⁺ would produce on over all charge of 5⁻.
The degree to which substitution of Al\(^{3+}\) for Si\(^{4+}\) in the tecto-silicate frame work takes place is limited by Loewenstein's rule. He concluded from a number of observations that not more than half the available Si\(^{4+}\) in tetrahedral frame work can be replaced by Al\(^{3+}\) and that it is not possible for two tetrahedra of AlO\(_4\)\(^{5-}\) to exist adjacent to one another. Thus rigorous alternation between tetrahedra to AlO\(_4\)\(^{5-}\) and SiO\(_4\)\(^{4-}\) tetrahedra is necessary for 50% substitution and the aluminosilicate frame work becomes increasingly ordered with respect to Al and Si in approaching 50% substitution.

The zeolites possess quite open alumino-silicate frame work, with water present in the cavities and channels. They can often be dehydrated by heat and evacuation without any apperciable shrinkage of the lattice. The cations present may be readily exchanged for others merely by soaking the crystals in a solution of the appropriate salt. The zeolites are subdivided into three groups according to the nature of their alumino-silicate frame works.

1. Three dimensional frame work zeolite e.g. NaA, Faujasite, Chabazite, Analcite.
2. Hemellar zeolites e.g. Stilbite.
3. Fibrous zeolite e.g. Natrolite.
The three dimensional frame work zeolites are much less prove than the latter two groups of zeolites to structural changes during the course of ion exchange reactions. Therefore, it is to be expected that in this sense the first group of zeolites will produce exchangers more nearly approaching ideal frame work.

**ORDERING OF ALUMINIUM AND SILICON IN ZEOLITE FRAME WORK**

There are 17 varieties of $\text{SiO}_2$ and they vary in $\text{SiO}_4$ tetrahedra arrangement. In three dimensional frame work of tetrahedra $\text{Al}^{3+}$ is tetrahedrally substituted for $\text{Si}^{4+}$. In frame work aluminosilicates the ratio $O/(\text{Al} + \text{Si})$ is 2.

In addition to the frame work structures and cation siting in zeolites, there is considerable interest in the ordering of the silicon and aluminium atoms within the frame work. All evidences the most conclusive being magic angle spining n.m.r (MASNMR) presently suggests that Loewenstein's rule (which disallows $\text{Al}-\text{O}-\text{Al}$ linking) holds generally in zeolite structures having $\text{Si} : \text{Al}$ ratios greater than or equal to one. The degree to which particular structures,
with framework ratio Si : Al greater than one, shows preferred siting of aluminium is less clear. There is evidence that some structures show preference for particular types of ordering but currently there are no general rules allowing the prediction of order\textsuperscript{14}. Representation of $\text{SiO}_4$ or $\text{AlO}_4$ tetrahedra is given in Fig. 3.

**WATER MOLECULES**

All zeolites have similar open structures and contain channelways in which water is readily housed. This water differs from that contained in most minerals as when the zeolite is heated the water is given off, leaving the structure intact. After nearly complete dehydration the channels may again be filled with water or other molecules such as ammonia, iodine or alcohol. This process is selective depending on the relative sizes of the molecules and the channel ways, so zeolites are used as molecular sieves.

It is known that water molecules or salt, both aid the formation of alumino silicates. Water molecules are generally present in the channels and interconnected voids. It is seen that many of the zeolites after dehydration are permitted by very
Fig. 3
small channels system which are not interpenetrating and which may cause various diffusion blocks. In other case dehydration irreversible disturbs the frame work structure and the positions of metal cations so that the structure partially collapses and dehydration is not complete. To be used as molecular seives the structure of the zeolite must remain intact after complete dehydration. Thus we see that water molecules play on important role in the molecular structure of zeolites. Zeolites do not form in the absence of water i.e. it is impossible to synthesise an open zeolite structure equivalent to a dehydrated zeolite under anhydrous conditions. Thus the effect of water is important in the growth of zeolite crystals.

Nuclear magnetic resonance studies of zeolitic structure provide information on the state of water molecules in hydrated zeolite. These water molecules in zeolite molecule having large cavities exhibit the same pattern as the isolated liquid which indicates that molecules which are present in the centre of large cavities do not occupy definite lattice sites, but in the case of zeolites having smaller cavities, these water molecules appear to cluster around the cations. In analcime the sodium
cation is in contact with only two water molecules and in chabazite each calcium ion has five nearest water molecules.

In brief, the position of water molecule in the hydrated zeolite with small cavities appear well defined and coordination occurs with cation in the cavities (for example in analcime). The cation in the hydrated zeolite seems to be surrounded by as many water molecules as is spatially possible as long as they do not lie too far away from the alumino silicate frame work and the negative charge distribution.

During dehydration it appears that the water molecules lie inside the structural cages.\(^{15}\) Cation dipole interaction plays an important role in the nature and structure of the zeolitic water.

The thermal expansion of fully hydrated zeolite Sodium A was measured by the determination of the unit cell dimension from X-ray pattern over the temperature range of 185°C to 225°C. The thermal expansion coefficient based on the change in unit cell dimension with change in temperature is about the same as for quartz.
(B) SOME PROPERTIES OF ZEOLITE

(1) PHYSICAL PROPERTIES

(A) DENSITY

The density of zeolite is low, ranging from about 1.9 to 2.3 g/cc. Cation exchange with heavy ions increases the density.

(B) HARDNESS

The hardness of crystals of zeolite minerals ranges from 4 to 5 on the Moh's scale.

(C) COLOUR

Zeolites in a pure state are colourless. Crystals of some mineral specimens are so transparent that it is difficult to see them in a matrix rock. If the alkali or alkaline earth cations generally present in synthetic zeolite are exchanged by transition metal ions, the zeolite may have a colour.\textsuperscript{16–20} This colour will vary with the degree of hydration. Colour change in zeolites has been used as an indicator for the presence of water vapour.
(D) **LUMINESCENCE IN ZEOLITE**

Luminescence effect in zeolite minerals were first observed more than fifty years ago. Eight zeolites were found to fluoresce in blue, blue green, yellow green, white yellow and blue white when illuminated by 3650 Å UV radiation\textsuperscript{21}.

(E) **DIELECTRIC PROPERTIES**

The dielectric behaviour of zeolite NaA over a range of temperature and with controlled water contents has been reported. The dielectric properties of zeolite A were studied as a function of time after the adsorption of a small amount of water.

(F) **ELECTRICAL CONDUCTIVITY**

The conductivity was found to depend strongly on the cation size and the size of the channels within the zeolite structure. Zeolite contain mobile cations which are located in sites in cavities, on the channel walls and free within the channels coordinated with water molecules.

The electrical conductivity exhibited by zeolites is ionic and arises from the migration of
cations through the zeolite framework. The electrical conductivity of various forms of the synthetic zeolites was measured\textsuperscript{22}. In zeolite A conductivity increases with hydration until about five water molecules are present within the cell. This is equivalent to the hydration of the four mobile sodium ions, which are located in sites II and III near the oxygens 8 rings that forms the apertures into the α cavities. These sites appear to possess the highest adsorption energy.

(2) CHEMICAL PROPERTIES

(A) ION EXCHANGE IN ZEOLITE

The first chemical property of zeolites viz cation exchange was investigated by Eiclochorn\textsuperscript{23} about 100 years ago. This led to the development of synthetic amorphous alumino silicates as commercial cation exchange materials (permutes) in the early 20\textsuperscript{th} century. These were primarily used in water softening\textsuperscript{24}. One application for commonly occurring zeolite minerals is in the selective removal of radioactive ions from radioactive waste materials\textsuperscript{25}. The cation exchange behaviour of zeolite is based on the following:
(1) The nature of the cation species and size of both anhydrous and hydrated zeolite and cation charge.

(2) The concentration of the cation species in solution.

(3) The temperature.

(4) The anion species associated with the cavities in solution.

(5) The solvent (most exchanges have been carried out in aqueous solutions although some work has been carried out in organic solvents).

(6) The structural characteristics of a particular zeolite.

In the crystalline zeolites, ion exchange is controlled by diffusion of the ion within the crystal structure.

The isomorphous replacement of silicon atoms by aluminium within a zeolite lattice gives rise to a net negative charge on the framework. Although this negative charge is partially delocalised over the whole of the framework, pockets of localised
charge are still found through out the lattice. These pockets of charge may be effective as adsorption centers or as catalytically active sites. 26-28

A more obvious consequence of the presence of this net negative charge on the lattice arises from the need for electroneutrality to be preserved within the zeolite. This can only occur by the zeolite crystals including cations within the molecular sized channels and cages which comprise their structure. This behaviour is not unique to zeolites, the layer or sheet silicates are just one example of another set of materials, which contain occluded cations within their structure to counterbalance the anionic charge on the layers. 29,30 Zeolites manifest a great variety of ion exchange characteristics. These make them particularly interesting to study as models of the ion exchange process31. The high crystallinity of the materials means that the channels and cages which characterise a particular zeolite structure are clearly defined both in their dimensions and in their shapes.

It is also possible for ions to exchange only partially because the volumes of the ions are
such that these completely fill the intercrystalline space in the channels before one hundred percent exchange can be attained.

In addition to the interesting ion exclusion properties which characterise the zeolites isomorphously changing the silicon aluminium ratio in the frame work alters the selectivity of the zeolite for one ion over another sometime in unexpected ways. Also if the silicon aluminium ratio is raised to a high enough value (more than 80) the materials then becomes hydrophobic resulting in complete reversals in selectivity trends for large organic cations.

Zeolites differ from clays in one very important respect, their rigid three dimensional frame work does not allow appreciable ion exchange. Nevertheless, the size of the channels and cages within zeolites are such that intracrystalline water is occluded readily; consequently, the cations are mobile. Therefore, zeolites are able to participate in exchange reactions. It has been shown that if this water is removed, the rates of exchange decrease drastically.
THEORY OF ION EXCHANGE AND THERMODYNAMICS OF ION EXCHANGE PROCESSES

The treatment of ion exchange reactions in zeolites by different investigations seems to be somewhat confused because of non-employment of uniform system of nomenclature\textsuperscript{40}. The ion exchange process is represented by the following equation.

\[ Z^+_A B^+_Z + Z^+_B A^+_Z \rightarrow Z^+_A B^+_S + Z^+_B A^+_S \]  \hspace{1cm} (1)

Where \( Z_A \) and \( Z_B \) are the charges of the exchanging cations \( A \) and \( B \). The subscripts \( Z \) and \( S \) refer to the zeolite and solution respectively.\textsuperscript{41}

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

\[ A_S = \frac{Z_A M^A Y^A Z_A}{Z_A M^A Y^A Z_A + Z_B M^B Y^B Z_B} = \frac{Z_A M^A}{Z_A M^A + Z_B M^B} \]  \hspace{1cm} (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 \((A_Z + B_Z) = 1\) and \((A_S + B_S) = 1\).

The exchange isotherm is a plot of \(A_Z\) as a function of \(A_S\) at a given total concentration in the equilibrium solution and at constant temperature.

The exchange isotherm for exchange of cations in zeolites may be classified into five types. Families of isotherms can be used to develop empirical selectivity series. Since the selectivity generally changes with the degree of exchange, such a series is at best qualitative. The preference of the zeolite for one of the two ions is expressed by the separation factor, \(\alpha_{A_B}^A\), defined by

\[
\alpha_{A_B}^A = \frac{A_Z}{A_S} \frac{B_S}{B_Z}
\]

(3)

If ion \(A\) is preferred, \(\alpha_{A_B}^A\) is greater than unity. 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. If \(\alpha_{A_B}^A = 1\), the exchange is ideal and obeys the law of mass action. The isotherm deviates from the diagonal line, represented as \(\alpha_{A_B}^A = 1\) and this shows a selectivity for one of the two ions. The ultimate base exchange capacity of a zeolite
depends on the chemical composition, a higher exchange
capacity is observed with zeolites of low $\text{SiO}_2/\text{Al}_2\text{O}_3$
ratio. The exchange capacity has been measured as
part of a characterisation procedure in determining
ion exchange equilibrium.

**THERMODYNAMICS OF ION EXCHANGE PROCESS**

Ion exchange reactions can be expressed by
equation 1. The free energy of exchange $\Delta G^0$ is
given by

\[
\Delta G^0 = \frac{-RT}{Z_A Z_B} \ln K_a
\]  
(4)

and the standard entropy $S^0$ is given by

\[
\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}
\]  
(5)

The standard enthalpy is obtained from the
variation of $K_a$ with temperature

\[
\frac{d \ln K_a}{dT} = \frac{\Delta H^0}{RT^2}
\]  
(6)

Enthalpy changes in zeolites ion exchange
reactions are generally small. This (Thermodynamics)
data should be used, with cations.
The ion exchange model originally proposed by Eiseman\textsuperscript{42} has been extended to account for the variation in ion specificity exhibited by zeolites.\textsuperscript{43,44} Interaction of the ion with the zeolite and solution phases is considered.

For the uni-univalent ion exchange reactions

\[ \lambda_s^+ + b_z^+ \rightleftharpoons \lambda_z^+ + b_s^+ \]  \hspace{1cm} (7)

Where \( s \) and \( z \) represent the solution and zeolitic phase.

Free energy of the reaction is considered to be consisting of two terms.

\[ \Delta G^\circ = (\Delta G_z^H - \Delta G_z^B) - (\Delta G_b^A - \Delta G_b^B) \]  \hspace{1cm} (8)

The first term in this expression represents the difference between the free energy of \( \lambda^+ \) and \( b^+ \) in the zeolite, while the second term represents the free energy difference of hydrous ions \( \lambda^+ \) and \( b^+ \) in solution.

The first term is more important if the force fields in the zeolite are very strong (zeolites with a high frame-work 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{45} considered 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 favour degree of freedom. The water content of the zeolite decreases with increasing atomic number of the univalent alkali metal ion present.\textsuperscript{46}

In the crystalline zeolites, ion exchange is controlled by diffusion of the ion within the crystal structure. The extent of exchange for spherical particles follows in the initial steps relationship,\textsuperscript{47}

\[
\frac{\Delta T}{Q_{\infty}} = \frac{Q_{0}}{Q_{0} - Q_{\infty}} \frac{25}{V} \frac{\sqrt{D_{it}}}{r} = \frac{6}{r} \frac{\sqrt{D_{it}}}{r} \quad \text{-- (9)}
\]

Where $Q_{0}$ and $Q_{\infty}$ are the amount of exchange at time $t$ and equilibrium ($\infty$) respectively.

$Q_{0} = \text{concentration of tracer ion initially present.}$
and \( S, V \) and \( r \) represent the surface area, volume and radius of the exchanger particles. The biggest practical problem in determining the diffusion coefficient is the measurement of the surface area. To determine the surface area, two methods have been used, one involving gas adsorption and another involving a projection. A better method would be one which is independent of the surface area. The apparent diffusion coefficient \( D_i \) is related to interdiffusion of the two exchanging cations or interchange of cation \( A \) and \( B \) with the same valence. \( D_A^i = D_B^i = D_i \), and is independent of the composition. The apparent diffusion coefficient varies with temperature according to the Arrhenious equation for zeolite. \( D_i \) varies from 1 x \( 10^{-8} \) to 1 x \( 10^{-13} \) \( \text{cm}^2 \text{Sec}^{-1} \). To determine the activation energy \( E \) Arrhenious equation can be used.

\[
D_i = D_0 \exp \left( -\frac{E}{RT} \right) \quad (10)
\]

The value of \( D_i \) is obtained from a plot of \( Q_T/Q_\infty \) versus \( \sqrt{T} \) using the slope of the initial portion of the curve.
The range of ion exchanged zeolites that have been studied has been extended by Angell and Schaffer. 49

(B) ADSORPTION AND DIFFUSION OF GASES IN ZEOLITES

The term molecular sieve is wholly appropriate if one considers the exterior surface of the crystal as the 'sieve'. Only molecules of a specific size and/or shape may diffuse through the surface of the crystal into the intercrystalline voids and channels.

Zeolite A shows a cubic (100) face containing a regular net work of 4.2Å apertures. The ability of zeolites to adsorb considerable volumes of adsorbate molecules, in place of zeolitic water present in one crystal on formation was quickly demonstrated by early studies. For the following reasons the zeolites have high capacity for selective adsorption.

(i) Size and configuration of the molecule relate to the size and geometry of the main apertures of the zeolite structures.
(ii) Zeolites adsorb molecules, in particular those with a permanent dipole moment, and have other selective interactions.

The basic principles of physical adsorption on solids are described in detail elsewhere.\textsuperscript{50-55} The molecular volume and shape of the adsorbate molecules were found to have an influence upon the amount which could be taken up by the zeolite. Crystalline zeolites were soon shown to be porous crystals permitted by channel networks, the free dimensions of which were strictly controlled by the positions of the framework oxygens. Thus, the molecular sieving character of zeolites could be fully explained. The behaviour of a given zeolite acting as adsorbent, diffusion medium and molecular sieve is also regulated by the size charge and locations of the cation present in the structure.

Zeolite frameworks contain cavities of many kinds. These voids are frequently polyhedral and many zeolite structures can be built by staking one or more types of polyhedra are found in zeolite \( \alpha \) and \( 26 \) hedra type \( \text{II} \) in Faujasite. The free dimensions of these \( 26 \) hedra are \( 1.14 \) and \( 1.18 \) nm
respectively. Therefore these are capable of accommodating clusters of small molecules (e.g. about 30 \( \text{H}_2\text{O} \)).

It was concluded that although the pore filling rule of Gurvitsch applies in many cases, there are exceptions which are caused by interaction of the zeolite crystals and certain adsorbate molecules.

The term 'monolayer equivalent' is sometimes used to express the adsorption capacity of zeolites. All the molecules filling the intercrystalline voids are assumed to be spread out in a close packed monolayer. Different zeolites show different properties of adsorption.\(^{56-60}\)

Zeolites are classified into seven groups based on framework topology. In cage structures such as zeolite A, chabazite, and faujasite, the channel network allows three-dimensional diffusion of all guest molecules small enough to enter the channel system. In heulandite, two-dimensional diffusion of adsorbate molecules occurs. In Mordenite however, channels cross link the main channels and
are wide enough for adsorbate diffusion to occur, so diffusion is strictly one dimensional in character. In zeolites with one dimensional channel net works adsorption and diffusion are sensitive to the presence of entrained impurities in the channels. 61-68

The extent of adsorption in zeolites increases by increase of pressure and decrease of temperature. At low temperature, the adsorption of gas increases rapidly as the pressure is raised. At higher temperatures, this increase is less marked. An examination of phenomena associated with the adsorption of gases in zeolites shows that there are two different types of adsorption. The first type, known as Vander Waals adsorption or physical adsorption, is exhibited particularly at low and moderately low temperatures. The second type of adsorption is referred to as activated adsorption or chemisorption. Chemisorption occurs in limited cases only and it is generally observed at moderately high temperature. In case of zeolites, both chemisorption and physical adsorption depend on the type of cation present. Zeolite A does not adsorb molecules with a kinetic diameter greater than 3.6 Å at 77°C and 4.0 Å at 300°C.
SYNTHETIC METHODS FOR PREPARATION OF ZEOLITES

Methods currently used to prepare zeolites require

(1) Reaction starting materials either as freshly prepared gels or amorphous solids.

(2) Selective high PH obtained by using an alkali metal hydroxide and/or organic base.

(3) Either low temperature hydrothermal conditions at atmospheric pressure or high temperature hydrothermal conditions (when temperature is less than 300°C).

(4) A high degree of supersaturation of the components in a gel phase.

(5) Crystallization times from a few hours to several days.

The most common starting materials are sodium silicates or colloidal silanes formed into gels with sodium aluminate additions. These methods have been described in detail in literature. These products are extracted counterparts of the natural materials. As ion exchanger, they are of
little practical importance. However, they are very useful as highly specific adsorbents.

The pore size of these materials can be adjusted to a certain degree by converting the materials to other ionic forms.

(C) **CLASSIFICATION OF ZEOLITES**

Early observation shows that zeolites were classified into three groups based upon their ability to adsorb or exclude certain molecular species (Table 1). This type of classification was given by Barrer following his initial studies. This classification defined the approximate interstitial channel dimensions.

As the studies on zeolites went on new zeolites came into existence. During this period three types of zeolitic frame work were considered to exist and thus the zeolites were classified according to the frame work.

(1) Three dimensional frame work structure with uniform bonding.
TABLE - 1: THREE CATEGORIES OF MOLECULAR SIEVE ZEOLITES.

CLASS - 1

Do not occlude isoparaffins or aromatics.

Chabazite

- Occludes n paraffins slowly

Gadolinite

- Occludes CH₄, C₂H₆, and molecules of smaller cross section very rapidly.

Synthetic Zeolite

(Ba,Al₂Si₄O₁₂ n H₂O)  - Diameter of narrowest cross section of interstitial channel between 4.83 and 5.58 Å.

CLASS - 2:

Mordenite (Na-rich)

- Does not occlude n paraffins isoparaffins or aromatics, occludes CH₄ and C₂H₆ slowly. Occludes N₂O₂ and molecules of smaller cross section rapidly, diameter of narrowest cross section of interstitial channel between 4.0 and 4.89 Å.

CLASS - 3:

Ca and Ba rich mordenite

- Do not occlude hydrocarbons including CH₄, C₂H₆ occlude Ar, N₂ and molecules of smaller cross section. Diameter of narrowest cross section of interstitial channel between 3.84 and 4.0 Å.
(2) Lamellar type structure with alumino silicate sheets bonded to one another.

(3) Fiber like structure with weakly cross linked alumino-silicate chain units.

This classification introduced by Bragg, has been used until recent years.\textsuperscript{72,73}

Following this classification it so happened that many of the zeolites known were not properly classified. In some instances no direct relationship between habit and detailed structure exists. For example the mineral Frionite is fibrous in habit but has robust, three dimensional structure, so such type of classification could not be continued.

The mineralogist, E.S. Dana employed a classification of the minerals and zeolites which were based on chemical composition, optical properties, cation polysilico chemical properties and morphology. For example zeolite minerals were classified as highly acid species (i.e. high in silica content) followed by metasilicate and orthosilicates.
Early interpretation of the physical and chemical properties of zeolites were based upon structural information. Extensive informations have been obtained on the crystal structure of 35 different new zeolites since the last ten years. But till now nearly one hundred synthetic type zeolites have been reported. Zeolites are classified into groups according to common features of the alumino silicates framework structure. Structures of zeolites have been classified by Smith, Fisher, and Breck.

The properties which are structure related include

(1) High degree of hydration and the behaviour of zeolitic water.

(2) When dehydrated - large void volume and low density.

(3) Stability of the crystal structure.

(4) Cation exchange properties.

(5) Uniform molecular sized channels in the dehydrated crystals.

(6) Various physical properties such as electrical conductivity,
(7) Adsorption of gases and vapours, and

(8) Catalytic properties.

The classification which is used now a days is based on the frame work topology of the zeolites for which the structures are known. Here the zeolites are classified into seven groups. Within each group zeolites have a common subunit of structure which is a specific array of \((\text{Al, Si})\text{O}_4\) tetrahedra. Here the Si-Al distribution is neglected for example the two simplest units are the ring of four tetrahedra (4 rings) and ring of six tetrahedra (6 rings) as found in many other frame work alumino silicates. Meier\(^{77}\) has called these subunits as the secondary building units (S.B.U.). The primary units are the \(\text{SiO}_4\) and \(\text{AlO}_4\) tetrahedra. Some of the SBU are properly involved in crystal growth process. The secondary building units as proposed by Meier are shown in Fig. 4. These are associated with characteristic configurations of tetrahedra.
Fig. 4: Secondary building units (S B U)

(a) Single four ring (S 4 R).
(b) Single six ring (S 6 R).
(c) Single eight ring (S 8 R).
(d) Double four ring (D 4 R).
(e) Double six ring (D 6 R).
(f) Complex 4-1 ($T_{50}^{10}$) unit.
(g) Complex 5-1 ($T_{80}^{16}$) unit.
(h) Complex 4-4-1 ($T_{100}^{20}$) unit.
These seven groups are:

<table>
<thead>
<tr>
<th>Group</th>
<th>Secondary</th>
<th>building unit (S B U)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Single 4 ring</td>
<td>S 4 R</td>
</tr>
<tr>
<td>2</td>
<td>Single 6 ring</td>
<td>S 6 R</td>
</tr>
<tr>
<td>3</td>
<td>Double 4 ring</td>
<td>D 4 R</td>
</tr>
<tr>
<td>4</td>
<td>Double 6 ring</td>
<td>D 6 R</td>
</tr>
<tr>
<td>5</td>
<td>Complex $4 - 1 T^{5} O^{10}$ Unit</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Complex $5 - 1 T^{6} O^{16}$ Unit</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Complex $4 - 4 - 1 T^{10} O^{20}$ Unit</td>
<td></td>
</tr>
</tbody>
</table>

In other classification, each group has been named after a representative member. An arbitrary designation by number is preferable since no single member is more representative than any other. Zeolite classification after BARRER is given table 2.

(D) **COMMERCIAL USES**

At present about 34 species of mineral zeolites and about 100 types of synthetic zeolites are known but out of these only few have practical significance. Zeolites, natural as well as synthetic, are widely used for their molecular sieve action.
TABLE 2: ZEOLITE CLASSIFICATION AFTER BARRER

<table>
<thead>
<tr>
<th>GROUPS</th>
<th>IDEALISED UNIT CELL COMPOSITION</th>
<th>COMMON STRUCTURAL ELEMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Analcime Group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A) Analcime</td>
<td>Na$<em>{16}$ (Al$</em>{16}$ Si$<em>{32}$ O$</em>{96}$) 16 H$_2$O</td>
<td></td>
</tr>
<tr>
<td>(B) Wairakite</td>
<td>Ca$<em>8$ (Al$</em>{16}$ Si$<em>{32}$ O$</em>{96}$) 16 H$_2$O</td>
<td>S 6 R, S 4 R</td>
</tr>
<tr>
<td>2. Natrolite Group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A) Natrolite</td>
<td>Na$<em>{16}$ (Al$</em>{10}$ Si$<em>{24}$ O$</em>{80}$) 16 H$_2$O</td>
<td></td>
</tr>
<tr>
<td>(B) Thomsonite</td>
<td>Na$<em>4$ Ca$<em>8$ (Al$</em>{20}$ Si$</em>{20}$ O$_{80}$) 24 H$_2$O</td>
<td>4 - 1</td>
</tr>
<tr>
<td>3. Heulandite Group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A) Heulandite</td>
<td>Ca$<em>4$ (Al$<em>8$ Si$</em>{28}$ O$</em>{72}$) 24 H$_2$O</td>
<td>4 - 4 - 1</td>
</tr>
<tr>
<td>(B) Clinoptilolite</td>
<td>Na$<em>6$ (Al$</em>{16}$ Si$<em>{30}$ O$</em>{72}$) 24 H$_2$O</td>
<td></td>
</tr>
<tr>
<td>4. Phillipsite Group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A) Phillipsite</td>
<td>(K, Na)$<em>5$ (Al$<em>5$ Si$</em>{11}$ O$</em>{32}$) 10 H$_2$O</td>
<td>S 4 R</td>
</tr>
<tr>
<td>(B) Zeolite Na P</td>
<td>Na$<em>8$ (Al$</em>{18}$ Si$<em>{18}$ O$</em>{32}$) 16 H$_2$O</td>
<td>S 8 R</td>
</tr>
<tr>
<td>5. Mordenite Group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A) Mordenite</td>
<td>Na$<em>8$ (Al$</em>{18}$ Si$<em>{40}$ O$</em>{96}$) 24 H$_2$O</td>
<td>5 - 1</td>
</tr>
<tr>
<td>(B) Ferrierite</td>
<td>Na$<em>{1.5}$Mg$<em>2$ (Al$</em>{5.5}$ Si$</em>{30.5}$ O$_{72}$) 18 H$_2$O</td>
<td></td>
</tr>
</tbody>
</table>

Contd...2.
<table>
<thead>
<tr>
<th>Groups</th>
<th>Idealised Unit Cell Composition</th>
<th>Common Structural Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>6. Chabazite Group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A) Chabazite</td>
<td>Ca$_2$(Al$_4$Si$<em>4$O$</em>{24}$) 13 H$_2$O</td>
<td></td>
</tr>
<tr>
<td>(B) Erionite</td>
<td>(Ca, Mg, Na$_{21}$K$<em>2$) 45 (Al$<em>4$Si$</em>{27}$O$</em>{72}$) 27 H$_2$O D6R S8R</td>
<td></td>
</tr>
<tr>
<td>(C) Zeolite L</td>
<td>K$_6$ Na$<em>3$ (Al$<em>9$ Si$</em>{27}$ O$</em>{92}$) 21 H$_2$O</td>
<td></td>
</tr>
<tr>
<td>7. Faujasite Group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A) Faujasite and ISO Structural Zeolites X, Y</td>
<td>Na$<em>{12}$Ca$</em>{12}$Mg$<em>{11}$ (Al$<em>5$9 Si$</em>{133}$ O$</em>{38}$) 26 H$_2$O S4R, S6R, S8R D6R</td>
<td></td>
</tr>
<tr>
<td>(B) Zeolite A</td>
<td>Na$<em>{12}$ (Al$</em>{12}$ Si$<em>{12}$ O$</em>{48}$) 27 H$_2$O D4R, S4R, S8R</td>
<td></td>
</tr>
<tr>
<td>8. Laumonite Group</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ca$<em>4$ (Al$<em>8$ Si$</em>{16}$ O$</em>{48}$) 16 H$_2$O S4R, S6R, S8R</td>
<td></td>
</tr>
<tr>
<td>9. Pantasil Group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeolite Z SM - 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z SM - 11</td>
<td>Na$<em>n$ (Al$</em>{19}$ Si$<em>{196}$ O$</em>{192}$) 16 H$_2$O 5 - 1</td>
<td></td>
</tr>
</tbody>
</table>
These zeolites possess important properties like (1) stability (2) dehydration behaviour (3) cation exchange behaviour and (4) adsorption behaviour of gases and vapours. On account of these properties these zeolite minerals as well as synthetic zeolites have a wide range of applications embracing both laboratory and industrial fields. The first practical use of zeolite probably dates back to about 2,000 years, when natural zeolite rock was quarried for use as building stone\textsuperscript{78} although zeolites were not recognized as a new mineral species until about 200 years ago. The first chemical property of zeolites viz. cation-exchange was investigated by Eichhorn about 100 years ago.\textsuperscript{79} This led to the development of synthetic amorphous alumino silicates as commercial cation exchange materials (permutites) in the early 20\textsuperscript{th} century. These were primarily used for water softening.\textsuperscript{80} Some of the important applications are summarized below.

1. **WATER SOFTENING**

Water softening is still the largest industrial application based on ion exchange. Now there is an increasing demand not only for
softened water but also for pure or demineralized water. Large amounts of such water are essential to many technological industries such as those producing medicinal agents, electrical power, electronic components, processed food stuffs and producing fabricated metals. Many scientific workers are trying to utilize ion exchange method to get potable water from other inadequate raw supplies.

The treatment of water has always been the dominant area of ion exchange applications. Hard water which contains principally Ca(II) and Mg(II) ions cause scale in power plant boilers, water pipes and domestic cooking utensils. Hard water also cause soap precipitation producing an undesirable gray curd and a waste of soap. Water softening involves the interchanges of one hard ion Ca(II), for another soft ion of like charge, Na(I), on the zeolite. Typically hard water is passed through a bed of sodium form zeolite and softened.

2. **NUCLEAR WASTE TREATMENT AND STORAGE**

The use of zeolites to remove radio isotopes was first studied in the sixties by Ames.\textsuperscript{81} Mercer
and Amer$^{82}$ have recently provided a detailed description of the present uses of zeolites in U.S.A. Included among these uses are (1) decontamination of low and medium level waste, (2) removal of $^{137}$Cs from high level radioactive waste.

3. **FIXATION OF FISSION PRODUCTS INTO ZEOLITES PRIOR TO LONG TERM STORAGE**

The primary clean-up problem in the U.K. is the removal of fission products released into storage ponds during the handling and storage of spent fuel elements from nuclear reactors. The ponds contain water held at pH 11.4 with respect to NaOH and $\text{Na}_2\text{CO}_3$. This presents a challenge to zeolite selectivity in the removal of radio-isotopes (such as $^{137}$Cs and $^{90}$Sr) present at less than milligramme concentrations. World wide clean-up problems vary with reactor type and national inclination, but all reactors face the problem of fission product containment. This use is in marked contrast to their application in agriculture, where the aim is to employ the zeolite as a source of nutrients especially ammonium (I) and potassium (I)$^{83-90}$. 
4. **IN UTILISATION OF ALTERNATIVE ENERGY**

Zeolites can find a very ingenuous use in tapping solar energy for refrigeration because of their extremely non linear adsorption isotherms. Tchrnev suggests their use for air conditioning and for water heating by making use of hydration/rehydration energy cycle. This application of zeolites in utilisation of alternative energy was reported by Pande. The zeolite is sealed in a blackened air tight solar absorber that gets heated by the Sun during the day. At about 100°C water vapour starts desorbing from the zeolite and its partial pressure begins to rise. When the pressure reaches a value determined by the condenser temperature, the vapour begins to liquify, heat is rejected to the outside and the liquid water is stored in a storage tank and the evaporator, all form a single air tight sealed system. During the night the zeolite gets cooled to the ambient temperature and is ready to absorb water even at low partial pressure. Liquid water is now introduced into the evaporator where it absorbs heat from the space to be cooled and converted into water vapour. The zeolite adsorbs this water vapour not allowing increase in its partial pressure. At the end of the day the zeolite is loaded with water and is ready for the beginning of a new cycle the
next day. This novel use of zeolite first proposed by Tchernev\textsuperscript{93} though at laboratory stage, holds a promise of a cheap solar refrigeration technique.

5. REMOVAL OF AMMONIA FROM WASTE WATER

The early work of Ames and Moiler\textsuperscript{81,82} demonstrated that clinoptilolite had a high selectivity towards the ammonium (I) ion and so could be used to treat sewage and agricultural effluents. The spent clinoptilolite is capable of regeneration. The ammonia which is released during the process could be converted to give a useful fertilizer.\textsuperscript{94,95} Treatment of waste water with clinoptilolite is increasing world wide. Other natural zeolites have also been considered.\textsuperscript{96-98} Nastro and Clella recently reported useful NH$_4$(I) uptake by Phillipsite tuff.\textsuperscript{99} While Kliewe and Semmens favour Phillipsite over clinoptilolite mordenite and erionite for this purpose.

The Japanese have concentrated on the production of smaller waste water treatment units. These are often for a specialised purpose, such as in fish forming where the build up of ammonium (I) ion is toxic to the fish. This is being developed in the U.S.A. as well.\textsuperscript{100-104}
6. Now-a-days in case of minerals fields we see that the demand for natural resources is increasing but the natural resources and quantity of raw materials are decreasing. This is evident in many aspects of extraction of metallurgy where good quality are are being rapidly depleted and man is forced to utilize, new and more efficient processing technique. In many such applications, ion exchange has proved useful. It is hoped that the technique will be used on an ever increasing scale in the future.

7. These zeolites have wide potential application in agriculture and horticulture. Nutrients, which are essential for the plant growth may be introduced to soil and other fertile media in an accessible and efficient form, from which they may be used at a controllable rate. Corn yields have been improved in laboratory trials and favourable fields trials for wheat cultivation are reported for clinoptilolite addition.\textsuperscript{105,106} Extensive studies have been made on the same zeolite to improve, production of many green house crops (such as tomatoes and house plants)\textsuperscript{107} and market garden products (such as onions and carrots). Bulgarian workers successfully used clinoptilolite to grow straw berries on a commercial scale.\textsuperscript{108-116}

8. Ion exchangers act as homogeneous catalysts in many important organic chemical reactions in the
solution. These include esterification, ester hydrolysis, hydration of alkenes, dehydration of alcohols and condensation reactions. The largest industrial application of zeolite as catalyst is for high temperature cracking and reforming of hydrocarbons gases and vapours in oil refining. Cracking catalyst containing crystalline zeolite molecular sieves were first used in 1962. And for this account an annual saving of more than £ 250 million in operating expenses and several hundred million more in capital investment have been reported.

Zeolite catalysis have been applied to the following four general areas of industrial process, petroleum processing, petrochemicals, chemical synthesis and pollution control. Many other applications have also been suggested using zeolites as catalysts and as adsorbents. Adsorption studies of zeolites with industrial potential are listed. 119-128

9. Synthetic zeolites are important ingredients of many commercial detergents as an ion exchange agent (builder), replacing (at least in part) the environmentally undesirable sodium tripoly phosphate. An unspecified zeolite has been used to take potassium out of sea water, 129, 130 while
the selectivity of clinoptilolite for some heavy metal ions, such as Ba(II), Pb(II), may be useful as it enhances its use in sewage treatment by its ability to fix metals.\footnote{131}

The principal divalent ions in water which are harmful in the laundry process are Ca(II) and Mg(II).\footnote{132} For ideal detergent performance, the Ca(II) concentration should be below $1 \times 10^{-5} \text{M}$ and that of Mg(II), below $1 \times 10^{-4} \text{M}$. A combination of zeolite $A$ and $X$ results in a synergistic effect. Zeolite $A$ is more effective in removing Ca(II) and zeolite $X$ is more effective in the removal of Mg(II).

10. In the year 1945 Barrer\footnote{133} suggested a method for separating gas and liquid. He demonstrated that by using three types of zeolites, the separation of gases, vapours and liquids could be achieved by adsorption. This has been used for the separation and recovery of normal paraffin hydrocarbon from various hydrocarbon feedstocks such as natural gasoline and kerosene. Acid modified clinoptilolite has been used to remove organic sulphur compounds from petroleum products.\footnote{134,135}
11. Zeolites are used as drying agents, because of their great affinity for water and the fact that water molecules can enter the pores of all types of zeolites, they are widely employed as drying agents for gases, liquids and are among the best of adsorption driers. 136

12. In medicinal fields also, these zeolites play an important role. Considerable use is being made of ion exchangers particularly in pharmaceutical composition. They control slow release of drugs and other chemicals into the body.

13. Zeolites have been introduced into halogenated polymers as smoke suppression agents. 137, 138


15. Kato suggests the use of clinoptilolite as a polishing agent in tooth paste. 139


17. Resin or rubber can be impregnated with zeolites which in turn isolate a reactive chemical or catalyst from the solution. The latter is released whenever it is needed in any particular reaction. In this composition, referred to as chemically
loaded molecular sieves, the chemical is isolated by adsorption within the zeolite cavities. Release of chemicals when desired is achieved by (a) displacement with water (b) heating, or (c) by leaching with dilute acid. Release is accomplished over a narrow temperature range. The release temperature can be modified by changing the adsorption characteristics of the zeolite.\textsuperscript{140}

18. Zeolites are used as Electrical conductors. Mobile cations located in zeolite channels, impart ionic electrical conductivity.\textsuperscript{141} The conductivity depends on the composition, cation type and degree of hydration. This property has a potential use in solid state batteries and conducting paper. Certain ion exchanged forms of zeolites are used in the fabrication of electrodes for fuel cells.\textsuperscript{142,143} Many electrical uses require high purity silicon. Zeolites are also used for ultra high purification of silane for semiconductor silicon.\textsuperscript{144}

19. H Lee\textsuperscript{145} suggests some new applications for zeolites in separation and purification processes. One of the best known uses, of course includes the drying of gases and liquids, such as the drying of cracked gas.
20. **ANIMAL FEED ADDITIVES**

The beneficial effects of clinoptilolite supplementation in pigs have been known in Japan for many years. Pigs fed with clinoptilolite in their diet show significant gain in weight and are less subject to disease.

An early report showed that both chabazite and clinoptilolite helped protein digestion in cattle, sheep and goats.\(^{146}\) Part of success seems to be derived from controlled ion exchange process. The effects arise from the pick-up of harmful NH\(_4\) (I) ions released by intestinal flora. Petkova demonstrated the presence of higher levels of blood total proteins, globulins and mineral elements in pigs receiving Ca(II) - K(I) clinoptilolite in their feed.\(^{147,148}\)

21. **DETERMINATION OF MORPHINE IN URINE**

A synthetic zeolite (4A zeolite or permutit) has been used by Oberst\(^{149}\) to free morphine from substances which interfere with its colorimetric determination in urine.
22. **DETERMINATION OF AMMONIA IN URINE**

According to Folin and Bell\(^{150}\) was the first application of ion exchange separation in analytical chemistry.

These are some of the most important commercial uses of zeolites.

From these discussions above it is clear that the materials classified as zeolite molecular sieves are very useful in a wide range of chemical and industrial processes covering almost unlimited areas of technological development.

The structural consideration of the crystalline inorganic ion-exchangers play an important role in deciding their fields of applications. For characterizing zeolites, the methods generally used are those for composition and frame work structure determination. In the present study, the various cation-exchanged and interacted samples of synthetic zeolite 4A have been characterized by (a) determining the major constituents, and (b) discussing the IR Spectrophotometric, X-ray diffraction and Thermogravimetric properties.
In chapter II and III, details of the experimental work undertaken, along with the physicochemical principles of the methods used have been discussed, followed by the interpretation of these results.
(5) **SCOPE OF THE PRESENT INVESTIGATIONS**

The present work is devoted to the study of the synthetic zeolite 4A and its derivatives. Synthetic zeolite 4A corresponds to \( \text{Na}_{12} \text{Al}_{12} \text{Si}_{12} \text{O}_{48} 27 \text{H}_2\text{O} \).

Cation exchanged samples of zeolite 4A have been prepared with the following cations:

1. Copper (II)
2. Iron (II)
3. Mercury (I)
4. Cerium (IV)
5. Vanadyl (II)

These cation exchanged forms and zeolite \( 4A(\text{Na}_{12} \text{Al}_{12} \text{Si}_{12} \text{O}_{48} 27 \text{H}_2\text{O}) \) have been made to interact with some organic reagents like chromazurol and Eriochrome Black T. Thermal behaviours of these new cation exchanged and interacted zeolite derivatives have been studied by Thermogravimetric, Infrared Spectrophotometric and X-ray Diffraction analysis, this has helped to elucidate their structure, both as a result of cation exchange and interaction with organic reagents.
The work attempts to establish the following facts:

Zeolite 4A (Na$^{12}$ Al$^{12}$ Si$^{12}$ O$^{48}$ 27 H$_2$O) can be used effectively as a cation exchanger for some of the new cations used.

The extent of exchange with different cations differs from one cation to another.

All the exchanged forms as well as zeolite 4A form coloured derivatives after interaction with analytical reagents. The nature of interaction varies with the cation exchanged forms. Basically the complexes formed depend on the properties of the cations in the exchanged derivatives. Such studies involving interaction between metal ion and complexing agents on a solid support such as zeolite type adsorbents, have not been reported widely so far. The Thermal, X-ray diffraction and I.R. Spectrophotometric data of the new derivatives throw some light on their basic characteristics like structure and stability.

The exchanged and interacted forms of 4A zeolites may find possible uses as inclusion complex species in catalytic processes.
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