CHAPTER-I

1.1) Introduction and Definition of the Terms.
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1.3) Classification of Zeolites.
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1.1) INTRODUCTION

Zeolites are crystalline, hydrated Aluminosilicates of group I and group II elements, particularly, sodium, potassium, magnesium, calcium, strontium and barium. Structurally the zeolites are “framework” aluminosilicates which are based on an infinitely extending three dimensional network of Si(O/2)₄ and Al(O/2)₄ tetrahedra linked to each other by sharing all of the oxygens. Where O/2 represent the bridging oxygen atoms⁴.

In nature zeolites are formed during and after burial generally by reaction of pore water (enriched in alkalies) with solid aluminosilicate materials (e.g. volcanic rocks, glass, feldspar, biogenic silica, clay minerals). The close connection between hydrothermal epidotization and prernitization⁵ and the formation of zeolites was discussed by Eskola⁶ as a distinct reaction series with distinct temperature and pressure conditions. The detailed studies of Cl. N. Fenner⁷ of the sediments in the hot springs of yellow stone national park gave the important result that the molecular ratio of R₂O to Alumina indicates the evolution of the hydrothermal and metasomatic process in zeolitisation, where R stands for group IA and IIA elements.

Zeolites are essentially crystalline, cross-linked polymeric macromolecules. These can be represented by the empirical formula-M₂ₙ₋₅O₂Al₂O₃₄₂ₓSiO₂₄₋₅ₓWH₂O. Where n is the cation valency, X is equal to or greater than two. W represents the water contained in the voids of the zeolites⁸.

The framework contains channels and interconnected voids, which are occupied by the cations and water molecules. The cations are quite mobile and may usually be exchanged, to varying degrees, by other cations. The structural formula of a zeolite is based on the crystal unit cell. The smallest unit of structure is represented by-

\[ \text{M}_{x₀} \left[ \text{AlO}_2 \right]_x \left( \text{SiO}_2 \right)_x \text{WH}_2 \text{O} \]

where \( n \) is the valence of cation \( M \), \( W \) is the number of water molecules per unit cell, \( X \) and \( Y \) are the total number of tetrahedra per unit cell, and \( Y/X \) usually has values of 1-5. However recently high silica zeolites have been prepared in which \( Y/X \) is 10 to 100 or even higher and in one case, molecular sieve silica has been prepared⁹. The
term "Molecular Sieve" was originated by J.W. McBain to define porous solid materials, which exhibit the property of acting as sieves on a molecular scale\textsuperscript{6}.

The porous framework of the zeolite enables them to act as molecular sieves\textsuperscript{7}. The zeolite channel systems, which may be one, two or three-dimensional and may occupy more than 50\% of crystal volume are normally filled with water. When water is removed other species such as gaseous elements, ammonia, alkali metals, vapours, hydrocarbons, alcohols and many other organic and inorganic species may be accommodated in the intracrystalline space, depending on pore diameter and molecular dimensions. This process is often highly selective and gives rise to the alternative names for zeolites "Molecular Sieves"\textsuperscript{8}.

The zeolite crystal structure consists of a three dimensional framework of SiO\textsubscript{2} and AlO\textsubscript{2} tetrahedra. The alumina tetrahedron is slightly larger than the silica tetrahedron in the zeolite structure. However, the aluminium ion can isomorphously replace the silicon ion in the silicon tetrahedron. The alumina tetrahedron carries negative charge and therefore a positive charge supplied by a metal cation must be associated with each alumina tetrahedron in the crystal. These metal cations in the zeolite structure are responsible for the very strong and selective adsorption forces, which are unique with molecular sieves\textsuperscript{9}. Aluminate tetrahedra can not be neighbours in the framework of hydrothermally prepared zeolites, i.e. Al-O-Al linkages are forbidden. This requirement is known as Lowenstien rule\textsuperscript{10}.

Most zeolites may be dehydrated to some degree without major alteration of their crystal structure. They may subsequently be rehydrated, that is, adsorb water from the vapour or liquid phase. The reversible dehydration property of zeolites was discovered in 1857.

The water binding in the crystal structure of the zeolites is not properly determined by independent mobility of the water molecule in the framework of the aluminosilicate, but the water is loosened, partially or totally from crystal structure and re-established without considerable changes\textsuperscript{11}. The isothermal dehydration, which has already been studied by G. Tammann\textsuperscript{12}, is continuous for the vapour pressure and water loss. He exposed zeolite at constant temperature over dilute H\textsubscript{2}SO\textsubscript{4} until
equilibrium was established between the water vapour pressure and the zeolite. Subsequently the water content of the exposed zeolite sample was determined. The dehydration equilibrium is, with in certain limits, ideally reversible if a partially dehydrated zeolite is cured in surrounding with a higher water vapour tension it resorts water to equilibrium. The equilibria in such experiments are generally attained from both the sides in order to avoid false “non-equilibria”. The last water molecules however, are very firmly fixed in the structure and can be driven out only by relatively intense heating\(^{13}\). The physical and optical properties of the zeolite change with degree of dehydration. The crystallographic homogeneity is always preserved even with the complete expulsion of water content. E. Mellard\(^{14}\) observed that on removal of water from zeolites the crystal remained transparent and homogeneous if they were imbedded in an order to fill the air pores formed during the dehydration.

The most important molecular sieve effects are shown by the dehydrated crystalline zeolites. These dehydrated crystal are internal by regularly spaced channels of uniform molecular dimensions in which the adsorption can occur. Depending on the size of these intra crystal voids, molecules may be readily adsorbed, slowly adsorbed or completely excluded\(^{15-17}\).

The first analysis of the crystal structure of a zeolite, analcime was reported by Taylor in 1930\(^{18}\). In the same year, Pauling proposed structures for the framework of natrolite, as well as for the related framework structures of sodalite, scapolite and cancrinite\(^{19}\). Additional investigation of the structure of fibrous zeolites was reported in 1933\(^{20}\). The early X-ray and neutrons investigation using, the sites of the hydrogen, which are all linked to framework oxygens, which are nearly in the same plane with the water molecules, as also occurs in natrolite\(^{21}\). The structure of zeolite showed increasing destruction of the crystal framework during dehydration. Rinne\(^{22}\) included all phenomena associated with the dehydration of zeolites in the definition of crystallographic chemical destruction and explained with it all the changes in the composition of the crystal which are possible without destruction of the structure of the crystal it self while water is removed from the structure and a “skeleton” i.e. the silicate framework is preserved in the dehydrated modification as a metaphase. The
destruction in this definition is therefore a special case characterized by crystallographic properties of the residual framework.

1.2) **ZEOLITE OCCURRENCES**

Zeolites form at present or formed in the past in various sediments or rocks under varying physical and chemical environments. As a result of the geothermal or chemical gradient, zeolites commonly occur in a vertically or laterally zonal arrangement which is usually mappable as zeolite zones.

In Sedimentary Rocks- Zeolites are among the most common secondary silicate minerals that occur in sedimentary rocks. These are crystalline, and are limited to seven species, analcime, chabazite, clinoptilolite, erionite, heulandite, mordenite and phosphorite.

In Igneous and Metamorphic Rocks- The most common and perhaps best known occurrence is in the fracture and cavities of igneous rocks, particularly volcanic rocks. Most of the large and attractive zeolite specimens, in museum collections have been obtained from igneous rocks.

Genetic classification of occurrence has been attempted by some worker e.g. Coombs, Hey, Iijima and Utada, Iijima, Sheppard, Gottardi and Obradovic and Mumpton. Much work in the field and laboratory has explicitly proved that temperature is an important factor to control zeolite formation. Another significant factor is the chemistry of pore water in which zeolites participate.

1.3) **CLASSIFICATION OF ZEOLITES**

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 structures with uniform bonding.

2) Lamellar-type structures with aluminosilicate sheets weakly bonded to one another, and

3) Fibre-like structures with weakly cross-linked aluminosilicate chain units. This type classification is shown in table-1.
<table>
<thead>
<tr>
<th>IUPAC Code species</th>
<th>Structure type</th>
<th>Topological symmetry</th>
<th>Type species</th>
<th>Symmetry of the type</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDI</td>
<td>All chains at the Same level</td>
<td>P42₁m</td>
<td>Edingtonite</td>
<td>P42₁m or P2₁2₁2₁</td>
</tr>
<tr>
<td>THO</td>
<td>The chains are at two level and form planes, in which the level is constant</td>
<td>Pmma</td>
<td>Thomsonite</td>
<td>Pcnn</td>
</tr>
<tr>
<td>NAT</td>
<td>The chains are at four levels around screw tetrads</td>
<td>I4₁/amd</td>
<td>Natrolite</td>
<td>Fdd2</td>
</tr>
</tbody>
</table>

It should be reiterated that all zeolites are framework aluminosilicates and all of the zeolite structures are three-dimensional. Framework structure of zeolite may be classified in several ways. Meier⁴¹, Fischer⁴², Smith⁴³ and Breck⁴⁴ have classified zeolite structure.

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 Al-Si distribution is neglected. For example, the two simplest units are the ring of four tetrahedra (4-ring) and six tetrahedra (6-ring). These subunits have been called secondary building units (SBU) by Meier⁴¹ (The primary units are of course the SiO₄ and AlO₄ tetrahedra).

The following are the seven groups based on structural configurations (Table-2).

<table>
<thead>
<tr>
<th>Group</th>
<th>Secondary Building Unit (SBU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Single 4-ring, S 4 R</td>
</tr>
<tr>
<td>2.</td>
<td>Single 6-ring, S 6 R</td>
</tr>
<tr>
<td>3.</td>
<td>Double 4-ring, D 4 R</td>
</tr>
<tr>
<td>4.</td>
<td>Double 6-ring D 6 R</td>
</tr>
<tr>
<td>5.</td>
<td>Complex 4-1, T5O10 unit</td>
</tr>
<tr>
<td>6.</td>
<td>Complex 5-1, T8O16 unit</td>
</tr>
<tr>
<td>7.</td>
<td>Complex 4-4-1, T10O20 unit</td>
</tr>
</tbody>
</table>
Meier classified zeolite according to secondary building units (figure-1a). Instead a new terminology has been coined for some of the secondary building units, since the new designations are felt to have more interpretative significance.

Some of the larger cages capable of housing more cation and water molecules are illustrated in figure-1b. There are designated as tertiary building units, T.B.U⁴⁵-⁴⁷.

A structural classification scheme of molecular sieve zeolites has been drawn up on the basis of T.B.U. in table-3.

Three distinct groups can be recognized.

1) Chain group - example- Mordenite group, Natrolite group,
2) Transition group - Erionite and Chabazite
3) Polyhedral group - Faujasite group, ZK-S.

The distinguishing features of the first designated as chain group is the presence of systems of chains dominated by a characteristic S.B.U.

Channels permeating through molecular sieve zeolites have been used as a second criterion for the classification scheme formulated in table-3 and dimensions of the crystallographic free aperture of the channels have been cited from the literature⁴⁸.

1.4) STRUCTURE OF ZEOLITE ⇒

Pauling⁴⁹ developed the current concept of zeolite structures in 1930. Modern tools such as X-ray crystallography, infrared spectroscopy, nuclear magnetic resonance have been used to compile an atlas of zeolite structure⁵⁰,⁵¹ embracing both natural and synthetic types.⁵²

There are two types of structures, one provides an internal pore system comprising interconnected cage like voids; the second provides a system of uniform channels which in some instances, are one dimensional and in other intersect three dimensional channel system. The preferred types are three-dimensional channels to provide rapid and intra crystalline diffusion in adsorption and catalytic applications.

All silicate minerals can be regarded as constructed of SiO₄ tetrahedra, which may be separate or share 1, 2 or 3 oxygen atoms in the structure⁵³-⁵⁵. A wide variety of
FIGURE 1. (a) The primary building units (PBU) and the secondary building units (SBU) of zeolite structures. (b) Some tertiary building units (TBU) of zeolite structures.
### Table 3  CLASSIFICATION OF MOLECULAR SIEVE ZEOLITES (Based on T.B.U.)


<table>
<thead>
<tr>
<th>Type</th>
<th>S.B.U.</th>
<th>T.B.U.$^a$</th>
<th>Name of Zeolite</th>
<th>Minimum No. T-linkages of functional channel opening rings</th>
<th>Free$^{**}$ aperture of main channels in Å</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Natural (found in nature)</td>
<td>Synthetic$^b$/ whether synthesized</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Philipsite W</td>
<td>8</td>
<td>3.3</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>YUGAWARITE Yes</td>
<td>8</td>
<td>4.2x4.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.1x3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHAIN</td>
<td></td>
<td></td>
<td>Natrolite Yes</td>
<td>8</td>
<td>2.6x3.9</td>
</tr>
<tr>
<td>D4-1R</td>
<td></td>
<td></td>
<td>Scolecite Yes</td>
<td>8</td>
<td>2.6x3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mesolite Yes</td>
<td>8</td>
<td>2.6x3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Thomsonite Yes</td>
<td>8</td>
<td>2.6x3.9</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Edingtonite Yes</td>
<td>8</td>
<td>3.5x3.9</td>
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<td></td>
<td></td>
<td></td>
<td>3.5x3.9</td>
<td></td>
<td></td>
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<tr>
<td>S5 R-1</td>
<td></td>
<td></td>
<td>Mordenite Zeolon</td>
<td>12</td>
<td>6.7x7.0</td>
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<tr>
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<td></td>
<td></td>
<td>Dachiordite No</td>
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<td>3.7x6.7</td>
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<td>Ferrierite Yes</td>
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<td>4.3x5.5</td>
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<td></td>
<td>No ZSM-5</td>
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<td></td>
<td></td>
<td>No Silicalite</td>
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<td>5.2x5.8</td>
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<tr>
<td>D4 D5 -1R</td>
<td></td>
<td></td>
<td>Stilbite No</td>
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<td>4.1x6.2</td>
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<thead>
<tr>
<th>Transition</th>
<th>S 6R</th>
<th>ε_1</th>
<th></th>
<th>Mazzite</th>
<th>Omega</th>
<th></th>
<th>12</th>
<th>7.5</th>
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</thead>
<tbody>
<tr>
<td>S6 R_1</td>
<td>ε_1 ε_1</td>
<td>Offretite</td>
<td>T**</td>
<td>8</td>
<td>12</td>
<td>3.6x5.2</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>D6 R</td>
<td>ε_1 ε_3</td>
<td>Erionite</td>
<td>T**</td>
<td>8</td>
<td></td>
<td>3.6x5.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ε_4</td>
<td>Levynite</td>
<td>Yes</td>
<td>8</td>
<td></td>
<td>3.2x5.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D6 R</td>
<td>ε</td>
<td>No</td>
<td>L</td>
<td>12</td>
<td>7.1</td>
<td>3.7x3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ε_2</td>
<td>Chabazite</td>
<td>R</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyhedra</td>
<td>D4 R</td>
<td>α β</td>
<td>No</td>
<td>A</td>
<td>8</td>
<td>4.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D6 R</td>
<td>β</td>
<td>Faujasite</td>
<td>X,Y</td>
<td>12</td>
<td>7.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>α γ</td>
<td>No</td>
<td>ZK-5</td>
<td>8</td>
<td>3.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D8 R</td>
<td>α γ</td>
<td>Paulingite</td>
<td>No</td>
<td>8</td>
<td>3.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>α</td>
<td>No</td>
<td>Rho</td>
<td>8</td>
<td>3.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Tertiary building unit
- Most commonly used synthetic designations.
- &epsilon;_1 - Gmelinite cage,
- &epsilon;_2 - Chabazite cage,
- &epsilon;_3 - Erionite cage,
- &epsilon;_4 - Levynite cage
- Intergrowth of Offretite type and Erionite type phases.
- "Crystallographic free diameter"
metal ions can be incorporated in these structures, either replacing silicon in the structure or as separate cations in gaps in the structure. In zeolites all the SiO$_4$ tetrahedra are linked only via single oxygen atoms (i.e. corner sharing rather than side or face sharing) and aluminium is essentially the only metal atom which can readily replace silicon in the framework.

Replacement of tetravalent silicon in the zeolite framework structure by trivalent aluminium requires a negative charge on the aluminium atom. Thus the framework has a net negative charge which is compensated by the cations in the zeolite pores-

![Diagram of zeolite framework](image)

**Pore framework**

In most zeolite structures, the primary structural units, the tetrahedra, are assembled into secondary building units which may be simple polyhedra such as cubes, hexagonal prisms, or octahedral. The final structure framework consists of assemblies of the secondary building units. Breck$^{56}$ illustrated several models. W.M.Meier and D.H.Olson$^{57}$ showed the stereoscopic drawings of the entire zeolite groups (figure-2)

**STRUCTURE OF NATURAL ZEOLITES** - The structure of the natural zeolites has been investigated by W.L.Bragg and his co-workers and by members of British Museum of Natural History, particularly M.Hey$^{58}$.

Natural zeolites are formed over much of the earth's surface including the sea bottom. They consist of a rigid framework formed by aluminium, silicon and oxygen atoms, honeycombed by corridors in which sodium ions are located. These ions have some freedom of motion and when hard water flows over zeolite grain some of the sodium ions run out of the corridors in to the solution and are replaced by ions of Ca and Mg.
FIGURE 2. (a-d) METHODS FOR REPRESENTING SiO$_4$ AND AlO$_4$ TETRAHEDRA BY MEANS OF BALL AND STICK MODEL, SOLID TETRAHEDRON, SKELETAL TETRAHEDRON AND SPACE FILLING OF PACKED SPHERES. (e) LINKING OF FOUR TETRAHEDRA IN A FOUR MEMBERED RING (f) SECONDARY BUILDING UNIT CALLED THE TRUNCATED OCTAHEDRON AS REPRESENTED BY A SOLID MODEL LEFT, AND BALL AND STICK MODEL, RIGHT.
Naturally occurring silicates contain in addition to silica and oxygen, various other elements. The most important of this is aluminium which is present in most widespread silicate in two forms (a) either as a cation aluminium silicate, (b) or as part of an anion.

Since the atom of aluminium has less valence electron than the atom of silicon the number of free negative valences of the tetrahedron may increase to five negative valences of the tetrahedron may increase to five $\text{AlO}_4^-$: When the structure is displayed by negative charge of the complex anion increase by one in each tetrahedra leading to an increase in the total cation charge. This can be illustrated by comparing the composition of quartz $\text{Si}_4\text{O}_8$ and albite $\text{Na(Al}_3\text{Si}_3\text{O}_8)$. The substitution of aluminium for one atom of silicon leads to the incorporation of equivalent amount of cations.

A three-dimensional lattice forms the crystal framework in most of the complex silicates. Although silicate ions contain their structure in contrast to the typical ionic the silicate or aluminosilicate framework with its primary covalent bonds determines crystal lattice structure. This explains the high melting point and involatility. It also explains the ease with which in some silicates the metal ions are exchanged for other ions. For example, several naturally occurring zeolites and artificial silicates upon interaction with aqueous salt solutions particularly exchange their cations from the solution. A necessary condition for such exchange is that the dimensions of the two ions do not differ greatly. For example sodium ions $\text{Na}^+$ (radius 1.05Å) are easily replaced by $\text{Ca}^{2+}$ ion (radius 0.95Å) in the ratio 2:1, while the crystal, as a whole remains neutral.

Three books cover the composition and properties of natural zeolites (Breck, 1974⁵⁹; Rabo, 1976⁶⁰; Barrer, 1982). Vaughan¹ reviewed the properties of major natural zeolites. G.Gottardi and E.Galli described in detail occurrence, physical and chemical properties of natural zeolites. Munson and Sheppard surveyed properties along with occurrence of natural zeolites. In 1984 Gottardi再次 reviewed the crystal chemistry of natural zeolites after 1983. H.Minato investigated thermal properties, gas adsorption capacities and some other characteristics of some HCl treated natural
zeolites for the purpose of their utilization. E.M. Flanigen\textsuperscript{66} has described the contribution of D.W. Breck to zeolite chemistry. His many accomplishments included characterization methods, crystal growth, and determination of physicochemical and structural properties of zeolites.

The recent rapid escalation in the prices of raw materials place natural zeolites in an improving price/performance position, compared to synthetic materials. The same consideration also stimulates the search for alternative raw materials for manufactured products, and in this regard natural zeolites and zeolite tuff seem to offer some potential as a silica-alumina source for the manufacture of synthetic zeolites. In some cases one zeolite (clinoptilollite) has been used as a raw material for the synthesis of another zeolite (faujasite).

The structure, composition, physical and chemical properties of the natural zeolite natrolite belonging to the same family will be discussed here in more detail. **NATROLITE**- Natrolite group (Natrolite, Mesolite and Scolecite) is an important member of the chain group.\textsuperscript{67} Natrolite was identified as an independent species by Klaproth\textsuperscript{69}(1803) who proposed the name natrolite. The ideal composition of natrolite is Na\textsubscript{2}Al\textsubscript{2}Si\textsubscript{3}O\textsubscript{10}. 2H\textsubscript{2}O; the substitution of Na by Ca is less than 0.5 Ca per unit cell, higher values for Ca and K have also been reported by Hey\textsuperscript{(1932)}\textsuperscript{69} and Foster\textsuperscript{(1965)}\textsuperscript{70}. Harada et al. \textsuperscript{(1967)}\textsuperscript{71} and Harada and Nakao \textsuperscript{(1969)}\textsuperscript{72} have reported Natrolite samples with 0.8 Mg per unit cell.

The structures of these fibrous zeolites were first determined in detail by Taylor and Jackson.\textsuperscript{73} They determined that in natrolite structure, each Na\textsuperscript{+} ion has as nearest neighbours four framework oxygens and two H\textsubscript{2}O molecules.

The structure of natrolite consists of silicon and aluminium tetrahedra linked to form chains in ‘C’ direction (the vertical crystallographic axis). The structure has topological symmetry I\textsubscript{4}\textsubscript{1}/amd , the actual framework with symmetry I\textsubscript{4}d\textsubscript{1} is characterized by a rotation of the chains by an angle \( \Psi \). Shared apical oxygen atoms link Chains tetrahedrally. The lower SiO\textsubscript{4} tetrahedra of one chain are linked to the apical AlO\textsubscript{4} tetrahedra of neighbouring chains. The fibrous nature of the natrolite is explained by the relatively few bonds, linking chain laterally as compared with bonds.
within the chains (figure 3a,b). All the different ways of assembling the chains of fibrous zeolite have been described by Alberti and Gottardi\textsuperscript{74} and by Smith\textsuperscript{75}.

There are four side linkages in each repeat unit of the chain. The lower at 3/8 C, from the lowest node at (0/8 C) and two higher at 5/8 C, from the lowest node of the repeat unit as references for the height in the chain. A second chain may be connected to the first so that both have the same height or the second is 2/8 C, higher or lower (figure 4a,b and 5a,b, c, d).

In natrolite Torrie et al\textsuperscript{76} have reviewed the position of the hydrogen (1964), the water molecules is linked by bent hydrogen bonds to two framework oxygens, making an O-O(W)-O of 134°; the hydrogens lie in the plane of the three mentioned oxygens, the H-O-H angle being regularly 108°.

The structure of natrolite was refined by Alberti and Vezzalini (1981)\textsuperscript{77}, by Peacor (1973)\textsuperscript{78} and by Hesse (1983)\textsuperscript{79}. Every (Si,Al)O\textsubscript{4} tetrahedron has each of its oxygens shared with another tetrahedron, but the linkages of tetrahedra to form chains in the Z direction are the most prominent. The repeating unit in each chain occupies about 6.6Å and consists of five tetrahedral (figure 6a). Four of these form a ring with vertices pointing alternately upwards and downwards. The free oxygens O\textsubscript{1} and O\textsubscript{2} of the ring are used in forming lateral linkages to neighbouring chains of tetrahedra, and in terms of the 8Z repeat distance they are at height 3/8 and 5/8 respectively. As shown in figure (6a,b), two tetrahedra in each group of five contain aluminium atoms and the other three contain silicons. The various members of the natrolite group of zeolites differ from one another in the way in which the chain units are arranged side by side. The fibrous nature of the natrolite and its well developed cleavage along \{110\} and \{111\} are explained by the existence of relatively few bonds linking chains laterally as compared to those within the chain-like units of the structure.

Smith et al. also determined, using X-ray and neutron, the sites at the hydrogen which are all linked to framework oxygens, which are nearly in the same plane with the water molecules, as also occurs in natrolite.

The reversible dehydration and cation exchange properties of natrolite are consistent with the wide channels in the structure which house the water molecules
FIGURE 3. (a) THE STRUCTURE OF NATROLITE PROJECTED ALONG C; THE SYMMETRY IS LOWERED TO Fdd2 BY THE (Si,Al)-ORDERING; 21 ONLY ARE SHOWN; BLACK DOTS = Na, WHITE CIRCLES = H₂O.

FIGURE 3. (b) THE STRUCTURE OF DEHYDRATED NATROLITE PROJECTED ALONG C, WITH Ψ = 35°; 21 ONLY ARE SHOWN; BLACK DOTS = Na.

FIGURE 3. (c) THE STRUCTURE OF SCOLECITE PROJECTED ALONG C, SYMMETRY Fdd1; BLACK DOTS = Ca, WHITE CIRCLES = H₂O (1 AND 2), DOUBLE CIRCLES = H₂O(3). THE ARROWS SHOW THE Ca → H₂O(3) VECTORS.
FIGURE 4. THE REPEAT-UNIT OF THE CHAIN OF FIBROUS ZEOLITES.
(a) CLINOGRAPHIC VIEW AND DISTANCE ALONG C BETWEEN NODES;
(b) ORTHOGRAPHIC VIEW ALONG c, AND HEIGHT ABOVE THE (001) PLANE AS MULTIPLES OF c/8.
FIGURE 5. THE CHAINS OF THE FIBROUS ZEOLITES.
(a) CLINOGRAPHIC VIEW; THE STRIPED TETRAHEDRA ARE OCCUPIED BY
Al, THE WHITE ONES BY Si.
(b) ORTHOGRAPHIC VIEW ALONG c, THE (Si,Al)-ORDER BEING SHOWN AS
IN (a).
(c) THE FRAMEWORK OF NATROLITE PROJECTED ALONG c IN ITS MOST
SYMMETRIC ARRANGEMENTS, WITH $\psi = 0^\circ$; AMONG THE SYMMETRY
ELEMENTS, $4_1$ ONLY ARE SHOWN; NUMBERS GIVE THE HEIGHT OF
CENTRAL TETRAHEDRON AS MULTIPLES OF $c/8$.
(d) THE FRAMEWORK OF NATROLITE PROJECTED ALONG c WITH ROTATION
$\psi = 24^\circ$ OF THE CHAINS; $2_1$ ONLY ARE SHOWN; THIS STRUCTURE
HAS BEEN PROPOSED FOR TETRANATROLITE, ALTHOUGH WITHOUT AN
EXPERIMENTAL PROOF; THE POSITIONS OF Na AND H$_2$O ARE NOT
KNOWN, BUT ARE PROBABLY SIMILAR TO THOSE OF NATROLITE.
FIGURE 6. (a) THE ALUMINOSILICATE CHAIN OF TETRAHEDRA COMMON TO THE STRUCTURES OF THE NATROLITE GROUP OF ZEOLITES. CHAINS ARE LINKED TO ONE ANOTHER LATERALLY VIA OXYGEN ATOMS $O_1$ AND $O_2$ WHICH ARE AT HEIGHTS $3/8$ AND $3/5$ OF THE $c$ REPEAT DISTANCE RESPECTIVELY.
(b) THE CHAIN VIEWED ALONG THE $z$ DIRECTION.
(c) SYSTEMATIC REPRESENTATION OF THE OUTLINE OF THE CHAIN: THE NUMBERS 3 AND 5 INDICATE HEIGHTS AT WHICH NEIGHBOURING ARE JOINED.
and large cations. The cations have definite sites with in the channels and can move along them without breaking the silicate framework\textsuperscript{80}.

1.5) **DEHYDRATION CONDITION**

Natrolite, Scolecite and Mesolite have the same type of framework topology but exhibit different behaviour upon dehydration. Thermal analysis shows that natrolite dehydrates rapidly with in a single temperature range. This is concluded and confirmed by X-ray study that there is only one type of water molecule in natrolite respectively\textsuperscript{81}.

For natrolite dehydrated at 350\degree C, $\Psi$ increases to 35\degree, and Na\textsuperscript{+} migrates to a site nearly in the port between channels, namely not far from the site occupied by water in hydrated natrolite; besides the strong chain rotation around C, the tetrahedra are also rotated around an axis normal to C, so allowing a shortening of C in comparison with the hydrated natrolite so that cell volume is 20\% smaller. Its structure has been determined by Alberti and Vezzalini\textsuperscript{82}(1983).

The characteristic thermal dehydration behaviour of zeolite is evidenced by the dehydration curves and differential thermal analysis. Dehydration produces a change in the local charge balance, the Na\textsuperscript{+} ions tend to move towards the framework oxygen atoms which previously were linked by hydrogen bonds to water molecules. This results in shrinkage of the natrolite framework.

Johnson et al.\textsuperscript{83} were able to verify the fact by the calorimetric measurements that the entropy of the water molecules in natrolite and scolecite is similar to that of ice. As far as the chemistry of these zeolites is concerned, they are distinguished by a low Si/Al ratio. Metaphase formation during dehydration is determined and characterized by the measurements of the expansion shrinkage reaction. According to Pecsi-Donath\textsuperscript{84-86}, there may be an interval of up to 100K between the releasing of the water and the formation of dehydrated metaphase. In the case of natrolite the first dehydration stage at 285\degree produces metanatrolite-I and second dehydration at 510\degree corresponding to the metanatrolite-II. $\beta$-metanatrolite (metanatrolite-II) becomes amorphous at 775\degree C. Rehydration is always possible so long as crystallinity is maintained. The DTA curve of natrolite has been determined by Koizumi\textsuperscript{87}. 
Physical and Optical Properties of Natrolite\textsuperscript{38,39}

A. Crystallographic data:

(1) Symmetry
(2) Space group
(3) Unit cell constant
(4) Density
(5) Unit cell volume
(6) Habit
(7) Cleavage
(8) Hardness

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Fdd2</td>
</tr>
<tr>
<td>Unit cell constant</td>
<td>a =18.30Å, b =18.63Å, c =6.60Å</td>
</tr>
<tr>
<td>Density</td>
<td>2.23 g/cc</td>
</tr>
<tr>
<td>Unit cell volume</td>
<td>2250 Å(^3)</td>
</tr>
<tr>
<td>Habit</td>
<td>Long prismatic crystal fibre.</td>
</tr>
<tr>
<td>Cleavage</td>
<td>Parallel to the length of crystal</td>
</tr>
<tr>
<td>Hardness</td>
<td>5-5.5</td>
</tr>
</tbody>
</table>

B. Optical properties:

(1) \(\alpha\) 
(2) \(\beta\) 
(3) \(\gamma\) 

\[
\begin{align*}
\alpha & = 1.479 (1) \\
\beta & = 1.481 (1) \\
\gamma & = 1.491 (1)
\end{align*}
\]

C. Structural properties:

(1) Framework: Stereo
(2) SBU
(3) Channel system
(4) Hydrated-
(5) Dehydrated-

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Framework: Stereo</td>
<td>Crosslinked chains of 4-1 units. Al and Si atom are ordered.</td>
</tr>
<tr>
<td>SBU</td>
<td>Unit of 4-1 void volume: 0.23 cc/c.c, ([\text{Al}_2\text{Si}<em>3\text{O}</em>{10}]) framework density: 1.76 g/cc</td>
</tr>
<tr>
<td>Channel system</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>Hydrated-</td>
<td>8-ring 2.6 x 3.9Å</td>
</tr>
<tr>
<td>Cation locations:</td>
<td>Coordinated with $2\text{H}_2\text{O}$ and 4 framework O atom</td>
</tr>
<tr>
<td>Dehydrated-</td>
<td>Unknown</td>
</tr>
<tr>
<td>Free apertures:</td>
<td>Unknown</td>
</tr>
<tr>
<td>Cation location:</td>
<td>Unknown</td>
</tr>
<tr>
<td>Effects of dehydration:</td>
<td>Framework shrinks due to rotation of chain.</td>
</tr>
<tr>
<td>Location of $\text{H}_2\text{O}$ molecules:</td>
<td>In channels coordinated to oxygen in framework and sodium ion.</td>
</tr>
</tbody>
</table>
DEALUMINATION - The dealuminated material exhibits specific properties such as improved thermal stability and catalytic properties\textsuperscript{90-92} which can be related only to changes in framework composition.

Various methods have been used to dealuminate the framework zeolites while still maintaining much of the crystallinity of the sample. The dealumination of clinoptilolite and erionite with mineral acid was reported in 1960\textsuperscript{93}.

Kerr\textsuperscript{94} reported that the 25% aluminium of calcined zeolite in tetrahedral position were converted to cationic form which could be removed from the structure by ion exchanged with 0.1N NaOH.

\[
\begin{align*}
\text{Si} & \quad \text{Si} \\
| & \quad | \\
O & \quad O \\
| & \quad | \\
\text{Si - O - Al - O - Si} & + \text{H}_2\text{O} \rightarrow \text{Si - OH} - \text{H} - \text{O - Si} + \text{Al(OH)}_3 \\
| & \quad | \\
O & \quad O \\
| & \quad | \\
\text{Si} & \quad \text{Si} \\
\end{align*}
\]

Hydrolysis of framework aluminium

It was reported that sodium form so obtained by this treatment is more stable than original sodium zeolite. Dealumination of a zeolite improves its catalytic activities\textsuperscript{95}.

1.6) CATION EXCHANGE PROPERTY OF ZEOLITE –

The ability of cations in zeolites to exchange with other cations in aqueous solution was first reported in 1858; since then the base exchange properties of the zeolite have been studied, from the time of H.E.Eichhorn\textsuperscript{96}.

Development of synthetic aluminosilicate as commercial ion-exchangers (permutites) took place in early 20\textsuperscript{th} century. According to Gain and Thomas the
exchanger is assumed to be consisting of a solid aluminosilicate backbone, possessing a fixed number of cation exchange sites, capable of absorbing water but not anion from the surrounding\textsuperscript{97}.

Ion-exchange behaviour of zeolites is considerably more complex than those of clay minerals, their rigid three dimensional framework does not allow appreciable swelling to occur, either during absorption process or during ion-exchange\textsuperscript{98,99}.

The size of the channels in the zeolites and the clays is such, that the intracrystalline water is occluded readily. Consequently the cations are mobile. Therefore, zeolites are able to participate in exchange reactions as well as clays. And if this water is removed there is drastic decrease in the rate of exchange\textsuperscript{100-104}. The isomorphous replacement of silicon atoms by aluminium within the zeolite lattice gives rise to a net negative charge on the framework. This negative charge is partially delocalised over the zeolite framework. These pockets of charge may be effective as adsorption centres or as catalytically active sites\textsuperscript{105,106}.

The net negative charge on the lattice is electroneutralised by the zeolite, occluding cations within the molecular sized channels and cages which comprise their structure. The same behaviour has been shown by the layer or sheet silicates with occluded cations within their structure to counter balance the anionic charges on the layers\textsuperscript{107,108}. The cations must be mobile within the lattice to ensure the minerals have ion-exchange properties\textsuperscript{109}.

The cation-exchange behavior of zeolites depends upon the following factors.

(1) The nature of the cation species, the cation size, both anhydrous and hydrated, and cation charge\textsuperscript{110-118}.

(2) The temperature.

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

(4) The anion species associated with the cation in solution\textsuperscript{119}.

(5) The structural characteristics of the particular zeolite.

(6) The nature of the solvent\textsuperscript{120-122} (it may be aqueous or organic solvents).

Most of the zeolites do not undergo any appreciable dimensional change with ion exchange\textsuperscript{123}. 

Ion Exchange Theory - The treatment of ion exchange reaction in zeolites by different investigators seems to be somewhat confused because a uniform system of nomenclature has not generally been employed\textsuperscript{124}. The ion exchange process may be represented by the following equation:

$$Z_A^Z B^Z (t) + Z_B^Z A^S (s) \leftrightarrow Z_A^Z B^Z (s) + Z_B^Z A^S (t)$$

\textit{Equation (i)}

where $Z_A$, $Z_B$ are the charges of the exchanged cations A and B. The subscripts $Z$ and $S$ refer to the zeolite and solution respectively\textsuperscript{125}.

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

$$A_s = \frac{Z_A^Z M_A^Z Y_A^Z}{Z_A^Z M_A^Z Y_A^Z + Z_B^Z M_B^Z Y_B^Z} = \frac{Z_A Z_s^Z}{Z_A M_s^Z + Z_B M_B^Z}$$

\textit{Equation (ii)}

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

where $M_A^Z$ and $M_B^Z$ are the molalities of the ions A and B respectively in the equilibrium solution. Also $(A_2 + B_2) = 1$ and $(A_s + B_s) = 1$.

The preference of the zeolite for one of the two ions is expressed by the separation factor-

$$\alpha_B^A = \frac{A_s B_s}{B_s A_s}$$

\textit{Equation (iii)}

If ion A is preferred $\alpha_B^A$ is greater than unity. The separation factor $\alpha_B^A$ 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 condition 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 most cases the diffusion of the ions through the zeolite particle is the rate determining factor\textsuperscript{126}. Other factors which are of importance from an analytical point of view are that the rates of exchange increase considerably with decreasing particle size\textsuperscript{127-129} and increasing temperature\textsuperscript{130,131}. The rate of uptake decreases with increasing charge and volume of ions\textsuperscript{127-132}. Theoretical studies of cation-exchange kinetics have been published by several authors\textsuperscript{131-133}.

Boyd et al.\textsuperscript{127} 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\textsuperscript{128}, as well as by Kressman and Kitchener\textsuperscript{130}.

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.

**Ion-exchange kinetics and ion diffusion** - In the crystalline zeolite, ion-exchange is controlled by diffusion of the ion within the crystal structure. The extent of exchange follow in the initial step the following relationship\textsuperscript{134}.

\[
\frac{Q_t}{Q_\infty} = \frac{Q_0}{Q_\infty - Q_0} \cdot \frac{25 \sqrt{D^v}}{V \pi} = \frac{6 \sqrt{D^w}}{r \pi}
\]

where,

- \( Q_t \) and \( Q_\infty \) - amount of exchange at time \( t \) and equilibrium \( \infty \) respectively
- \( Q_0 \) - concentration of tracer ion initially present,
- \( S \) - Surface area, \( V \) - volume and \( r \) - radius of the exchanger particles.
The effective diffusion coefficient $D$ is related to the inter-diffusion of the two exchanging cations or inter change of cations A and B both of the same valence.

The effective diffusion coefficient varies with temperature according to the Arrhenius equation. For zeolite, the value of diffusion coefficient varies from $1 \times 10^{-8}$ to $10^{-13}$ cm$^2$ sec$^{-1}$. Barrer and others made detailed studies of ion-exchange kinetics and diffusion on zeolite mineral, chabazite and mordenite.$^{135-138}$

The energy barrier associated with the self-diffusion process varies from about 7 Kcal. for the univalent ions to about double that value for divalent ions.

**Thermodynamics of the ion-exchange process**

$$Z_A^{{\text{Z}^+}_{B(\text{z})}} + Z_B^{{\text{Z}^+}_{A(\text{z})}} \rightleftharpoons Z_A^{{\text{Z}^+}_{B(z)}} + Z_B^{{\text{Z}^+}_{A(z)}}$$

Represent the ion exchange process in zeolites.

The free energy of the exchange process $\Delta G^\circ$ is given by-

$$\Delta G^\circ = -RT / Z_A Z_B \log Ka \quad \text{--- (v)}$$

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

$$\Delta S^\circ = \Delta H^\circ / T \quad \text{--- (vi)}$$

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

$$d \log Ka / dt = \Delta H^\circ / RT^2 \quad \text{--- (vii)}$$

Enthalpy changes in zeolite ion-exchange reactions are generally small. The ion exchange model originally proposed by Eiseman$^{139}$ has been extended to account for the variation in ion-specificity, exhibited by zeolites.$^{140}$ Interaction of the ion with the zeolite and solution phase is considered H.S. Sherry considered the entropy change that occurs in the zeolite phase, and the corresponding difference in entropy of hydration of the ions in equilibrium solutions in the ion-exchange model given by him.$^{141}$

**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.$^{142}$ These categories of molecular sieves have been distinguished by
Barret\textsuperscript{143} according to the minimum diameter of the pores governed in principle by the framework Al-Si-O ring. These apertures range may be from 0.3nm to 1.01nm. By useful choice of the zeolite 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.

(1) \textbf{Ion Exchange Application}. The first physical chemical property of zeolites which had an application was cation exchange investigated about 100 years ago. This led to the development of synthetic amorphous aluminosilicates as commercial exchanger materials in the early 20\textsuperscript{th} century which were primarily used as water softener. Zeolite structure have unique features that lead to unusual type of cation selectivity and sieving. Cation-exchange in zeolite causes the alteration of adsorption behaviour, selectivity and catalytic activity.

(A) \textbf{Water purifying filtration materials}. The water purifying filtration materials are NaA or NaY zeolites ion-exchanged with Ag\textsuperscript{+}, Cu\textsuperscript{2+}, Mg\textsuperscript{2+}, Zn\textsuperscript{2+} and NH\textsuperscript{4+} ions\textsuperscript{144}. These materials are prepared by ion exchanging the zeolite to replace 1-20\% of Na(I) ions in the zeolite, washing, drying and filtering the ion-exchanged zeolite at 400-550\textdegree{}C, mixing with binder, lubricant and surfactant, kneading with water and granulating into (0.1-5mm) granules and baking at 600\textdegree{}C for 20 hours\textsuperscript{144}.

(B) \textbf{In Detergents}. Zeolites are widely used as a water-softener replacing sodium tri-polyphosphate [STPP] builder used as a water-softener in detergents\textsuperscript{145}. In commercial detergents, synthetic zeolites are used as an ion-exchange agent (builder) replacing the environmentally undesirable sodium tri-polyphosphate. Naturally occurring zeolites with a Ca\textsuperscript{2+} exchanging capacity are found satisfactory, but their performance is much less then their synthetic counterparts\textsuperscript{146}.

(C) \textbf{Separation of Sugars}. Mcgready and Hassid\textsuperscript{147} isolated and purified glucose-1-phosphate with the aid of ion exchange resins. These sugars are first of all converted in to borate complexes.

Similarly, disaccharides can be separated from mono-saccharides and the individual compounds of hexose and pentose mixture resolved.
(D) Analysis of Milk, Beer and Apple Juice\textsuperscript{148-150}.

(E) Isolation of radio-elements from Urine\textsuperscript{151}.

(F) Isolation of Amino acid\textsuperscript{152-158}.

(2) Adsorption And Diffusion Phenomenon On Zeolites- 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\textsuperscript{159}. 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. The behaviour of a given zeolite acting as adsorbate diffusion medium and molecular sieve is also regulated by the size, charge and locations of the cations present in the structure. (Adsorbing materials are called adsorbents and substances, which are adsorbed and called adsorbates).

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 associating with the adsorption of gases in zeolites shows that there are two different types of adsorption. The first type, known as Vanderwaals 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 depends on the type of cation present.

Adsorption process is widely prevalent in zeolite chemistry. This is due to regularity in the internal pore system, or voids. Void volumes of a zeolite represent a space where adsorption field exists.

Zeolites have high capacity for selective adsorption for the following reasons.

(A) Size and configuration of the molecule relate to the size and geometry of the main apertures of the zeolites structures.

(B) Zeolites adsorb molecules in particular those with a permanent dipole moment and have other selective interactions.
In dehydrated crystalline zeolites, adsorption of gases or vapours depends on equilibrium pressure, temperature and nature of gas or vapours. Adsorption process involves a decrease in free energy and enthalpy change must also be negative since the change in entropy is exothermic and heat is evolved. The heat of adsorption is derived from the Clausius Clapeyron equation. Adsorption isotherm is determined by volumetric method and by weighing the sample on a closed balance\textsuperscript{160}. In a correction for this method determination of the volume of the sample is necessary\textsuperscript{161-163}.

Different zeolites show different properties of adsorption\textsuperscript{164-168}. Certain zeolites encapsulate gases at high pressure and elevated temperatures\textsuperscript{169}.

**Diffusion of Gases in Zeolites**- The diffusion process in zeolites is the result of the findings of Walker and co-worker\textsuperscript{170}. When zeolites are used as selective adsorbents, molecular sieves and catalyst, migration of the adsorbate with the crystal is an important and some times rate controlling factor. The variation of the crystal size or adsorbent bed configuration has been shown to provide a simple test of crystalline diffusion\textsuperscript{171}. Barrer has considered the rate of diffusion of a number of gases into a given zeolite and of a single gas into a number of different cationic forms of the same material when the following results were obtained\textsuperscript{172}.

(A) For a gas, the uptake decreases as increasing the diameter of cations present in the adsorbent or by introducing water molecules or anions in to the channels decreases the channel diameter.

(B) For a given cationic form of adsorbents, the uptake decreases as the atomic or molecular diameter of the gas is increased and large molecules may be excluded altogether.

Water and other smaller molecules when diffusing in a zeolite channel are subjected to sticking on active sites and clustering around the channel located cations. Sticking is due to cation dipole interaction.

**Adsorption Kinetics**- In zeolite adsorption processes the adsorbates migrate in to the zeolite crystals. First, transport must occur between crystals contained in a compact or pellet, and second, diffusion must occur within the crystals. Diffusion co-efficient are measured by various methods, including the measurement of adsorption rates and the
determination of jump times as derived from NMR results. Factors affecting kinetics and diffusion include: channel geometry and dimensions; molecular size; shape and polarity; zeolite cation distribution and charge; temperature; adsorbate concentration; impurity molecules; the crystal surface defects. Activation energy has been determined, for the activated diffusion, the variation is given by the following equation.\(^{173}\)

\[
D' = D_0 e^{-\frac{E_A}{RT}} \quad \quad \quad \text{(viii)}
\]

Where \(E\) is the activation energy for the diffusion process. Barrer and Peterson compared the role of aperture size in zeolites\(^ {174}\). Barrer and Ibbotson have also contributed most on kinetics of adsorption reactions\(^ {175}\). Others have equally enhanced the knowledge of activation energy in regard to adsorption phenomena\(^ {176-181}\). The energy barriers indicated by the diffusion of water in a zeolite channel larger than in water in liquid states. Sticking of water on active site is due to dipole interaction\(^ {182}\).

At constant pressure the solution of the diffusion equation is-

\[
\frac{M_t}{M_\infty} = \frac{Q_t - Q_\infty}{Q_\infty - Q_o} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{\left(\frac{Dr_0^2 \pi^2 t}{r_o^2}\right)^{1/2} \exp\left(-\left(\frac{Dr_0^2 \pi^2 t}{r_o^2}\right)^{1/2}\right)}{r_o^2} \quad \quad \quad \text{(ix)}
\]

In this equation, \(Q_t\), \(Q_o\) and \(Q_\infty\) are the amounts adsorbed at time \(t\), when \(t=0\) and at equilibrium respectively. \(D\) is the diffusion co-efficient and \(r_o\) is the radius of the zeolite crystals. when \(t\) is large-

\[
\ln \frac{Q_\infty - Q_t}{Q_\infty - Q_o} = \ln \frac{6}{\pi^2} - \frac{D\pi^2 t}{r_o^2} \quad \quad \quad \text{(x)}
\]

When \(t\) is small, it tends to

\[
\frac{M_t}{M_\infty} = \frac{6}{r_o^2} \frac{(Dt)^{1/2}}{\pi} = 2A \frac{(Dt)^{1/2}}{V} \quad \quad \quad \text{(xi)}
\]

In this equation, \(A\) is the total external surface and \(V\) is the total volume of crystallites. The inter relation-ship of a critical Vander Waals dimensions of the different molecules and the free diameter of windows controlling intrusion to the
zeolite crystals with the diffusion co-efficient and energy of activation for diffusion has
been studied.\textsuperscript{183-186}

\textbf{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
poles.

(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.
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