INTRODUCTION

Ion-exchange is a process in which reversible exchange of ions takes place between a solid phase and solution without affecting the solid structure. Ion-exchangers are usually solid materials but liquid ion-exchangers immiscible with water are also known to-day.

The discovery of ion-exchange property concerned with "base exchange" in minerals is reported by two English Chemists, Thomson and Way (1,2) in the year 1950. They observed that when a soil sample is treated with ammonium salt solution, ammonia is taken up by the soil releasing an equivalent amount of Calcium.

\[ \text{Cax}_2 \text{ solid} + 2 \text{NH}_4^+ \text{ solution} = 2 \text{NH}_4X \text{ solid} + \text{Ca}^{2+} \text{ Solution} \]

where \( \text{Cax}_2 \) represents the soil sample.

Several hypothesis have been proposed to explain the phenomenon of base exchange in soil(3). One of this is that humus and humic acids are present in the soils with high organic matters. The organic matters on decaying produce a large number of ill defined organic species, which possess hydroxyl and Carboxyl groups and can function as ion-exchange groups in the same way as in phenolic and Carboxylic acid resins.

The first synthetic ion-exchangers prepared by Gans and other co-workers (4) were amorphous sodium aluminosilicates containing exchangeable sodium ion. They were mainly used for water softening and in sugar industry. When hard water is passed through the exchanger bed, sodium ion is replaced by Calcium and magnesium ion. Since the process is reversible, the exchanger can be regenerated by treatment with strong sodium Chloride Solution.
During the period 1900-1950 the following workers made valuable contributions on both natural and synthetic inorganic ion-exchangers: Weignier, Ganssen, Rothmund, Kornfeld, Guntherschulze, Ramann, Spengel, Gedoroiz, Tandeloo, Mattson and Hissing(5). Two principal types(6) of permutits were distinguished viz. the fusion permutits and gel permutits. Fusion permutits were prepared by fusing together a mixture of soda, potash, Kaolin and felspar. The second variety was prepared by controlled addition of alkali to acid solutions of aluminium sulphate and sodium silicate, when a gelatinous precipitate was produced. Hydrothermal crystallisation of solution of alkali alumina and silica at elevated temperature was used as another method for synthesis of Crystalline Zeolites. The relationship between ion-exchange and crystal structure was first understood by the works of pauling(7,8) and Bragg(9) on crystal structures of mica and clay.

In 1935 Adams and Holmer (10) observed that certain synthetic organic resins were capable of exchanging ions. They prepared high capacity sulphonlc acid resin as cation-exchanger and poly-amine type resin as anion-exchanger. Later extremely stable and versatile ion-exchange resins were synthesised from styrene and acrylies by D.Alelio(11). In the period 1925-1950, the development on the study of the organic ion-exchange resins expanded rapidly in contrast with the study of inorganic ion-exchanger. Although the organic resins have versatile applications, they have limitations too by break down in aqueous solution at high temperature and in the presence of ionising...
radiations. The inorganic ion-exchangers are free from these limitations and thus revive interest during the last two decades. They are superior to organic resins for their selectivity towards some ions.

The research and development in the field of inorganic ion-exchanger is expanding at a very fast rate. Only five pages were devoted to inorganic ion-exchanger in the book "Ion Exchange" written by Helfferich (12) in the year 1962. Only two years later a comprehensive monograph "Inorganic Ion-Exchanger" was published by Amphlett(6).

It was followed by publications of several important review articles, by Churms (13), Materova (14), Alberti(16,16,17), Rees (18,19), Qureshi (20, 21), Fuller(22), Inczedy (23), Freund and Marcilly (24), Vesely and Pekarak (25,26), Clearfied et.al(27), Abe(28) and De and Sen(29) etc.

The inorganic ion-exchange materials may be classified into –

(A) Natural ion-exchangers – Which include clay minerals, Zeolites and

(B) Synthetic ion-exchangers – Which include –

1. Hydrated oxides of metals.
2. Acidic salts of polyvalent metals.
3. Basic salts of polyvalent metals.
4. Insoluble salts of heteropolyacids.
5. Insoluble ferrocyanides.
6. Synthetic alumino-silicates and
7. Other substances with weak ion-exchange property, e.g. synthetic apatites, sulphides, sulphates etc.
A: NATURAL ION-EXCHANGERS:

1. Clay Minerals:

The clay minerals are made up of a complex series of aluminosilicate structures and of basic types.

Alumino silicates are composed of two dimensional layers, containing aluminate and silicate tetrahedra (30). Free hydroxyl groups are normally present at the edges and corners. The ion-exchange capacity of clays can be explained from their above structure. Clay minerals may be divided into the following groups shown in Table - I(6).

<table>
<thead>
<tr>
<th>Type</th>
<th>Mineral</th>
<th>Cation-exchange capacity (meq./g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite group</td>
<td>Kaolinite</td>
<td>0.02 - 0.10</td>
</tr>
<tr>
<td>Illite group</td>
<td>Muscovite</td>
<td>0.105</td>
</tr>
<tr>
<td></td>
<td>Illite</td>
<td>0.13 - 0.42</td>
</tr>
<tr>
<td>Fibrous clays</td>
<td>Attapulgite</td>
<td>0.18 - 0.22</td>
</tr>
<tr>
<td>Montmorillonite group</td>
<td>Montronite</td>
<td>0.57 - 0.64</td>
</tr>
<tr>
<td></td>
<td>Saponite</td>
<td>0.69 - 0.81</td>
</tr>
<tr>
<td></td>
<td>Montmorillonite</td>
<td>0.80 - 1.5</td>
</tr>
<tr>
<td>Micaceous group</td>
<td>Biotite</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>Vermiculite</td>
<td>1.0 - 1.5</td>
</tr>
</tbody>
</table>

Kaolinite, the simplest type of clay, can be represented with the basic formula Si₄Al₄O₁₀(OH)₂. The free hydroxyl ions
exchange with anions whereas the hydrogen ions exchange with cations. The exchange is nonstoichiometric. The saturation capacity which depends upon the chemical composition of the clay and for cation, decreases in the sequence montmorillonite > illite > kaolinite. The selectivity of the clay minerals increases as hydrated ionic radii of metal ions decreasing.

e.g Li⁺ < Na⁺ < K⁺ < Rb⁺ < Cs⁺.

2. Zeolites :-

Zeolites, popularly known as molecular sieves, are a group of hydrated crystalline aluminosilicates. They are built up of a tetrahedral grouping of $\text{AlO}_4^{5-}$ and $\text{SiO}_4^{4-}$ in such a way that corners, edges and faces of the tetrahedra are shared to give condensed structures. The existence of fibrous, lamellar or rigid three dimentional net work structure of Zeolites depends on bonding. Zeolite have been extensively investigated for ion-exchange properties (31, 32).

B> SYNTHETIC ION-EXCHANGERS:

1. Hydrated oxide of metals:-

It is now well known that alumina, ferric oxide, silica gel, etc. have adsorption property. The sorption of cations and anions by them is presumably by ion-exchange.

This cation and anion exchange property depends on the basicity of the metal atom of the oxide and on the strength of metal oxygen bond relative to that of oxygen-hydrogen bond and on the pH of the solution (25). These exchangers are mostly amphoteric in nature. The following two mechanisms represent the exchange reactions.
MOH = M⁺ + OH⁻  
MOH = MO⁻ + H⁺  

The first is favoured in acidic solution when the oxide can function as anion exchanger. The second is favoured in alkaline medium when the oxide can act as a cation exchanger. There is a transition from anion to cation exchanger with the increase of pH and vice versa e.g.

\[
\text{Al(OH)}_2^+ + \text{OH}^- = \text{Al(OH)}_3^- = \text{AlO(OH)}_2^- + \text{H}^+
\]

**HYDRATED OXIDES OF BIVALENT METALS**:

Hydrated beryllium oxide of composition Be O, 1.7 H₂O has both cation and anion exchange properties (33, 34). The selectivity order for alkali metals are Li⁺ < Na⁺ < K⁺ < Cs⁺. Hydrated magnesium oxide exhibits anion-exchange property. Mixed Oxide, Mg(OH)₂ and Fe(OH)₃ has been studied (35). Mixed Oxide, Zn(OH)₂, Al(OH)₃ was used to remove the contamination of 35g and 32p from waste solution (37). Mixed Oxide ZrO₂(SeO) (OH) 2H₂O has been reported to have cation exchange capacity (36).

**HYDRATED OXIDES OF TERTVALENT METALS**:

The cation and anion exchange properties of both hydrated oxides of iron (37,38-50) and aluminium (37,42,51-57) have been studied extensively. The adsorption of Cs⁺, Na⁺, K⁺ and Ag⁺ in hydrated ferric oxide shows ion-exchange property (37,38,39) but the adsorption of anion follows the Freundlich adsorption law (37,38-40). Ion-exchange capacity of Fe(OH)₃ decreases with the age (50).
HYDRATED OXIDES OF TETRAVALENT METALS:

Hydrated silica (58-83), hydrated stannic oxide (51, 84-96), hydrated titanium dioxide (103-113) hydrated thorium oxide (103), hydrated Zirconium oxide (114-124), hydrated manganese di-oxide (125-135), hydrated cerium di-oxide (136-139) were prepared by various methods and have good ion-exchange property.

2. ACIDIC SALTS OF POLYVALENT METALS:

Inorganic ion-exchangers of this type were widely studied. These salts act as cation-exchangers. The well studied metals are tin(IV), Cerium (IV), Titanium, Zirconium, Thorium, Chromium(III), Iron(III), Bismuth(III), Aluminium(III), Niobium(V), Tantalum(V) and Uranium(VI) etc. and the anions are phosphate, arsenate, antimonate, molybdate, tungstate, vanadate, tellurate and silicate etc.

TIN(IV) BASED ION EXCHANGER:

Stannic phosphate (140-156), amorphous stannic arsenate (141, 151-163), stannic antimonate were prepared by different methods and have the cation-exchange capacity (164-171). Stannic molybdate prepared by mixing ammonium molybdate solution with stannic chloride solution (159, 172-174) and stannic tungstate prepared by mixing sodium tungstate and stannic chloride solution (149, 172-175) are also reported to have ion-exchange property.

Stannic selenite was prepared from Sodium selenite and stannic chloride solution (176-178).
CERIUM BASED ION-EXCHANGER :-

Cerium (IV) phosphate was synthesised by mixing the ceric salt solution with phosphoric acid under different conditions (179-200). Ceric phospho sulphate (198), a new exchanger is selective for Silver. Crystalline cerium arsenate was prepared by refluxing arsenic acid with ceric sulphate (195, 198, 201, 202). Ceric antimonate (203) was prepared from ceric ammonium sulphate solution and potassium pyroantimonate solution. Ceric molybdate (204,205) has also ion-exchange property. Ceric Tungstate (206) was prepared by mixing ceric ammonium sulphate with Sodium tungstate solution.

TITANIUM BASED ION-EXCHANGER :-

Both amorphous (207-210) and crystalline (154, 227, 211-217) variety of titanium phosphate have been synthesised under different conditions. The amorphous variety with exchange property has also been reported(218).

Amorphous titanium arsenate (219,220) was prepared by mixing titanium chloride solution with sodium arsenate solution.

Titanium antimonate (221-225) was reported from titanium chloride solution either by mixing with antimony pentachloride at controlled pH or with potassium pyroantimonate solution(225).

Titanium molybdate (222, 226-228) and titanium tungstate (229-236) were prepared by mixing acidic solution of titanium (IV) with sodium molybdate and sodium tungstate solution respectively. Titanium vanadate prepared by Qureshi et.al.(2:4-237) is thermally stable. Titanium selenite was prepared from titanium (IV). solution and sodium selenite solution (234).
Among the acidic salts of polyvalent metals zirconium phosphate (154, 237-269) has been investigated intensively.

The structure and composition of Zirconium phosphate vary according to the mode of synthesis. Paterson (244) has described a material in which the ratio \((\text{PO}_4/\text{Zr} = 2)\) corresponds to diphosphate zirconic acid (245). Baestle and Plesmaker (246) prepared zirconium phosphate in which the ratio \((\text{PO}_4/\text{Zr} = 2.1)\) but possess different structure. Detailed ion-exchange mechanism for crystalline Zirconium phosphate has been discussed (248, 249). Beryllium can be separated from other element using crystalline Zirconium phosphate ion exchanger (264). Zirconium pyrophosphate, hyopophosphate, seleno-phosphate (270-276) and sulphosalicylophosphate (277-279) also act as ion-exchangers.

Both amorphous and crystalline Zirconium arsenates (280-283) both amorphous and crystalline Zirconium antimonate (284-288) were reported. Zirconium molybdate (269-289) and zirconium tungstate (289, 290-299) were prepared by mixing zirconium salt solution with ammonium salt solution with ammonium molybdate and sodium tungstate solution respectively.

**THORIUM BASED ION-EXCHANGER** :-

Crystalline thorium phosphate (303, 304, 305, 306) was prepared by mixing thorium nitrate solution with phosphoric acid at 80°C by Dey and Choudhury (305, 306).

**OTHER ACIDIC SALTS** :-

Some other insoluble polyvalent metal salts have been synthesised. They exhibit the exchange property. Chromium
phosphate (307-312), Chromium triopolyphosphate (313-316), Chromium hydroxide, arsenate, molybdate, antimonate, tungstate (317) and tellurate (318), ferric phosphate (319, 320) have ion-exchange property.

3. **BASIC SALTS OF POLYVALENT METAL** :-

Basic salts of polyvalent metal have also ion-exchange property.

**BASIC LEAD SULPHATE** :-

Amorphous basic lead sulphate (319, 321) was prepared from lead nitrate, sodium sulphate or ammonium sulphate and ammonium hydroxide solution under different conditions. It has both cation and anion exchange property (319, 321).

**BASIC LEAD CHROMATE** :-

Amorphous basic lead chromate (320) was prepared by different conditions and has its cation exchange capacity (317).

**BASIC TANTALUM SULPHATE** :-

It was synthesised and reported to have cation exchange capacity (322).

**INSOLUBLE SALTS OF HETEROPOLY ACIDS** :-

First systematic study on the ion-exchange property of ammonium phospho molybdate (323-331) was published by Griffiths, Buchwald and Thistlethwaite. The general formula is $\text{H}_m\text{XY}_{12}\text{O}_{40}\text{mH}_2\text{O}$ ($m = 3.5$), where $X$ is boron, silicon, phosphorous, arsenic, germanium and selenium etc. and $Y$ is molybdenum, tungsten, Vanadium etc.
5. **INSOLUBLE FEROCYANIDE:**

The cation exchange property of insoluble ferrocyanides of a large number of metals e.g. Zn, Cu, Ni, Cr, Co, Sn, Fe, Mn, Ti, Zr, Ce, Mo, W etc. have been reported. The general method of preparation of these exchangers is mixing of metal solutions with ferrocyanic acid, potassium ferrocyanide or Sodium ferrocyanide solution. The limiting composition $M_{2}^{II}[Fe(CN)_{6}]$, $M_{2}^{I}M_{3}^{II}Fe(CN)_{6}$ and $M_{2}^{I}M_{3}^{II}Fe(CN)_{6}2$ with various amount of water of crystallisation were reported for ferrocyanide of bivalent metals (6, 26, 332-335).

**SYNTHETIC ALUMINO SILICATE:**

Synthetic alumino silicates represent a great family of inorganic ion-exchanger. On the basis of the structure they may be divided into three groups: amorphous, two dimensional layered aluminosilicate and silicate with rigid three dimensional structure (6, 26, 331, 337-340).

6. **OTHER SUBSTANCE WITH WEAK ION EXCHANGE CAPACITY:**

Many synthetic apatites were reported to have ion-exchange property. Apatite may be represented as $M_{10}(XO_{4})_{6}Y$ where $M$ = Ca, Sr, Ba, Cd, and Pb, $X$ = P, As, V, Cr, Mn, Si and Ge, $Y$ = F$_{2}$, Cl$_{2}$, (OH)$_{2}$ and CO$_{3}^{2-}$(26). The following insoluble sulphides Ag$_{2}$S, FeS, Cds, Pbs, Nis, AS$_{2}$S$_{3}$ have been reported with exchange properties (26).
REVIEW WORK
REVIEW WORK ON SYNTHETIC INORGANIC ION-EXCHANGERS BASED ON HYDROUS OXIDES, ACIDIC AND BASIC SALTS OF POLYVALENT METALS.

This review work done upto January, 1994 on Synthetic inorganic ion-exchangers based on hydrous oxides, acidic and basic salts of polyvalent metals are represented in Table - II.
### TABLE II

**REVIEW WORKS ON SYNTHETIC INORGANIC ION-EXCHANGERS**

#### A. Hydrous Oxides of Metals:

<table>
<thead>
<tr>
<th>Exchanger</th>
<th>Nature/Composition</th>
<th>Selectivity/Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ferric</td>
<td>Micro Crystalline;</td>
<td>H &gt; Fe &gt; Al &gt; Pb &gt; Ag &gt; Al &gt; Fe &gt; H</td>
</tr>
<tr>
<td>hydroxide</td>
<td>Amphoteric;</td>
<td>Cu &gt; Zn &gt; Cd &gt; Mn</td>
</tr>
<tr>
<td></td>
<td>Granular;</td>
<td>Separations:</td>
</tr>
<tr>
<td></td>
<td>Fe₂O₃, H₂O</td>
<td>⁹⁹Mo-⁹⁹Tc; ¹³²Tc-¹³²I,</td>
</tr>
<tr>
<td></td>
<td>Cation exchange</td>
<td>¹³⁷Cs-²²Na</td>
</tr>
<tr>
<td></td>
<td>capacity=1.52meq/g</td>
<td>from waste water.</td>
</tr>
<tr>
<td></td>
<td>Anion Exchange</td>
<td>Na-Mg-Al-; Zn-Cd;</td>
</tr>
<tr>
<td></td>
<td>capacity=2.54meq/g</td>
<td>Zn-Cu, Ni-Cd;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tl(I)-Pb; Tl(I)-Cd;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu(II)-alkali metals;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sc-Ti-V; Ru(III)-¹³¹I;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>³⁵S-³²P;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mo(VI)-Sea water;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu-Cd.</td>
</tr>
<tr>
<td>2. Aluminum</td>
<td>Crystalline;</td>
<td>Cl &gt; Br &gt; I</td>
</tr>
<tr>
<td>Oxide Powder;</td>
<td>Amphoteric.</td>
<td>Li &gt; Na &gt; K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Separation:-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cl-Br-I; ⁹⁰Mo-⁹⁹mTc;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>³⁵S-³²P;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO₂-SO₄²⁻-S₂O₃²⁻;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>⁹⁰Y-⁹⁰Sn;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>²³⁸U-²³⁴Th;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr(III)-Cr(VI);</td>
</tr>
</tbody>
</table>

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13
<table>
<thead>
<tr>
<th>Exchanger</th>
<th>Nature/Composition</th>
<th>Selectivity/Separation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(VI)-W(VI):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(VI)-Re(VII),</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{132}$I-$^{132}$Tc</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Hydrous Gel;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>Amorphous;</td>
<td>Ba $\sim$ Sr $&lt;$ Mg $&lt;$ Be;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cation-exchanger.</td>
<td>In $&lt;$ Ga $&lt;$ Al;</td>
<td>58-83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>La $&lt;$ Cd(III) $&lt;$ Nd $&lt;$ Gd</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tb $&lt;$ Y $&lt;$ Er $&lt;$ Tm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yb $&lt;$ Lu $&lt;$ Sc.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Separation:</td>
<td>Na-Rb-Ca-Fr</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tl-Bi; Zn and Pd</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>From various cations;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Th-U; Ni-Cu;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu from waste water;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al, Fe(III) from</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sr, Cu, Zn, Co, Ni;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Co(II) from Cu, Ni,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn, Cd, Ag from Fe,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni, Cu etc; Mn(II)-Cu-Zn.</td>
<td></td>
</tr>
<tr>
<td>4. Stanic</td>
<td>Dried gel,</td>
<td>Cu $&gt;$ Zn $&gt;$ Co$&gt;$Fe(II)$&gt;$Ni $&gt;$</td>
<td>51</td>
</tr>
<tr>
<td>Oxide</td>
<td>Amphoteric,</td>
<td>Mn(II) $&gt;$ PO$_4^{3-}$ $&gt;$ C$_2$O$_4^{2-}$ $&gt;$</td>
<td>84-101</td>
</tr>
<tr>
<td></td>
<td>Cation-exchanger</td>
<td>SO$_4^{2-}$ $&gt;$ Cr$_2$O$_7^{2-}$ $&gt;$ MnO$_4^-$.</td>
<td></td>
</tr>
<tr>
<td>Exchanger</td>
<td>Nature/Composition</td>
<td>Selectivity/Separation</td>
<td>Reference</td>
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<tr>
<td>-----------</td>
<td>--------------------</td>
<td>------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Separations:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn-Zn; Mn-Ca; Co-Fe(III);</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr(VI)-Mn(VII); Sc-Te;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tc-Mo; Li from alkali metals;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na-Cs; Cs-Be; Cu from Zn,Co, Fe(III), Mn, Ni, Cr(VI).</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>U(VI) from Th(VI); Radio active F from Fluorosilicates.</td>
<td></td>
</tr>
<tr>
<td>5. Titanium Amorphous Oxide</td>
<td>Cation-exchanger</td>
<td>Na &lt; K &lt; Rb &lt; Cs;</td>
<td>102-113</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn &gt; Cu &gt; Ni &gt; Co;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ba &gt; Sr &gt; Ca.</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Separations:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>137Cs-133Ba;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>137Cs-89Sr;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ca-Pr; CrO$_4$$^{2-}$-PO$_4$$^{3-}$, Cs</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>and Sr from Sea water.</td>
<td></td>
</tr>
<tr>
<td>6. Thorium Amorphous glassy Oxide</td>
<td>Solid, Amphoteric Cation-Exchanger</td>
<td>Mn &lt; Co &lt; Zn &lt; Cr&lt; Hg &lt;</td>
<td>102,103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ag; Cs &gt; Rb &gt; Na;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu &gt; Ni &gt; Co.</td>
<td></td>
</tr>
<tr>
<td>7. Zirconium Oxide Amphoteric, Granular, Cation-exchanger Anion-exchanger</td>
<td></td>
<td>Li &gt; Na &gt; K</td>
<td>114-124</td>
</tr>
<tr>
<td>Exchanger/Acceptor</td>
<td>Nature/Composition</td>
<td>Selectivity/Separation</td>
<td>Reference</td>
</tr>
<tr>
<td>--------------------</td>
<td>--------------------</td>
<td>-------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>B. Mangen- cation-exchanger</td>
<td>Crystalline dioxide</td>
<td>Na-K-Cs; Tc-Mo; 140Ba-140La; 51Cr from chrome iron alloy; 115Cd-115In; Co-Ni; Ag from Fe, Co, Zn; 95Zr-95Nb. Trace amount of Ca²⁺ and Sr²⁺ from K⁺; Rb⁺; Sr from Fe, In, Bi and Pb.</td>
<td>125-135</td>
</tr>
<tr>
<td>9. Cerium Crystalline</td>
<td>CeO₂⁻</td>
<td>Cu from Mg, Zn, Ca, Co(II), Mn(II).</td>
<td>136-139</td>
</tr>
</tbody>
</table>

Table - II contd.

8. Mangen- Cation-exchanger | Crystalline dioxide | 223Ra-223Fr; 212Pb-212Bi; W(VI), Mo(VI) and Rb(VI) from each other. | 16 |
### B. Acidic and basic salts of polyvalent metals.

<table>
<thead>
<tr>
<th>Exchanger Nature/Composition</th>
<th>Selectivity/Separation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Stannic Amorphous, Phosphate Crystalline, P/Sn= 1.25-1.50</td>
<td>Ba &gt; Sr &gt; Ca &gt; Mg; Cs &gt; Rb &gt; K &gt; Na; Cs &gt; Zr &gt; Nb &gt; Y; Cs(III) &gt; Sr &lt; Ru; Separations: K-Rb; Na-Cs; K-Cs; K-Na; 89Sr-144Cs; 137Cs-144Cs; 90Sr-90Y; Zr from other metals; Ni from Fe(III); Al, Zn, Cs, Ag; Al(III)-Pd(II)-Pt(VI); 28 cations from each other.</td>
<td>140-156</td>
</tr>
<tr>
<td>2. Stannic Amorphous, Arsenate Crystalline Sn/As = 1.8</td>
<td>Cu-Pb; Cu-Fe(III), Fe(III)-Pb, Fe(II)-Cu; Fe(II)-Fe(III); Sr-Ba; Mg-Ba; Ca-Ba; Co-Fe(III); Al-Fe(III); Mn-Fe(III); Ca-Fe(III); Ni-Fe(III); Al-In; Mg-Al; Pb-Zn or Mn; Cs from alkali metals.</td>
<td>141; 151-163</td>
</tr>
<tr>
<td>3. Stannic Amorphous Antimonate Sb/Sn=1:4 to 2:1</td>
<td>Cs &gt; Rb &gt; K &gt; Na &gt; Li Separations: Rare earths, actinide</td>
<td>164-171</td>
</tr>
<tr>
<td>Exchanger</td>
<td>Nature/Composition</td>
<td>Selectivity/Separation</td>
</tr>
<tr>
<td>-----------------</td>
<td>--------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>4. Stannic</td>
<td>Amorphous molybdate</td>
<td>Fe(III) from Al, Mg, Ni, Mn, Ce(III) from Pr$^{3+}$, Nd$^{3+}$; Pb from other metals; Em-Tm; Eu(III)-Dy(III); Fe(II)-Cu; Fe(II)-UO$_2$(II); Mg(II)-Ag(I)-V(IV); Cs-Pb; Ba-Sr; Co-Ni; Mo(VI)-V(VI); Ti(V)-V(V); Th(IV)-Tm(III)-Lu(III); In-Al; Ti-Zr; Hf-Ti; Dy-Lu-Gd; Th-Y-Gd; Fe(III)-Al; Mn(II)-Fe(III); Be-Al-Ga.</td>
</tr>
<tr>
<td>5. Stannic</td>
<td>Semi Transparent Tungstate Granular</td>
<td>Co &gt; Be &gt; Pb &gt; Ni &gt; Cu; Mn, Sr &gt; Mg &gt; Cd &gt; Zn</td>
</tr>
<tr>
<td></td>
<td>Sn/Mo=1:1</td>
<td>Separations: As(III)-Sb(III); As(III)-Bi; Zr-Th; Zn-Mn-Ni; Ag-Cu-Au(III); Ca-Ba.</td>
</tr>
<tr>
<td>Exchanger</td>
<td>Nature/Composition</td>
<td>Selectivity/Separation</td>
</tr>
<tr>
<td>---------------</td>
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<td>----------------------------------------</td>
</tr>
<tr>
<td>6. Stannic</td>
<td>Amorphous</td>
<td>Fe-Pb, Sc-V, Cu from 176-178</td>
</tr>
<tr>
<td>Selenite</td>
<td>Sn/Se = 1.33</td>
<td>Fc, Ni, In; lanthanides and each other.</td>
</tr>
<tr>
<td>7. Cerium</td>
<td>Amorphous</td>
<td>Cs &gt; Rb &gt; K &gt; Na &gt; Li 179-200</td>
</tr>
<tr>
<td>Phosphate</td>
<td>P/Ce = 1.03-1.93</td>
<td>Cs &lt; Na &lt; Ag</td>
</tr>
<tr>
<td>Micro-crystalline</td>
<td>P/Ce = 1.5</td>
<td>Tl(I) &gt; Ag &gt; Ni</td>
</tr>
<tr>
<td>Fibrous</td>
<td>Crystalline</td>
<td>Li-Na-K; Ni-Ag-Tb;</td>
</tr>
<tr>
<td>Crystalline</td>
<td>Ce:P:S = 2:1:2</td>
<td>Co-Eu-Fe; Co-Eu(III)</td>
</tr>
<tr>
<td>8. Cerium</td>
<td>Crystalline</td>
<td>K &gt; Na &gt; Li at low pH 195,198</td>
</tr>
<tr>
<td>arsenate</td>
<td>As/Ce = 2.0</td>
<td>Li &gt; Na &gt; K at high pH. 201,202</td>
</tr>
<tr>
<td>Ce(HASO₄), 2H₂O</td>
<td>Separations :</td>
<td>Alkali metals and each others.</td>
</tr>
<tr>
<td>9. Cerium</td>
<td>Amorphous</td>
<td>Hg from Cd, Zn, Tl and 203</td>
</tr>
<tr>
<td>antimonate</td>
<td>Sb/Ce = 0.3-0.32</td>
<td>Pb.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Th-Zr; Al-Fe, Mn-Cu.</td>
</tr>
<tr>
<td>10. Cerium</td>
<td>Amorphous</td>
<td>Mg, Zn, Co, Cu from Pb. 204,205</td>
</tr>
<tr>
<td>Molybdate</td>
<td>Mo/Ce = 2.33-3.29</td>
<td></td>
</tr>
<tr>
<td>11. Cerium</td>
<td>Amorphous</td>
<td>Mg(II) &gt; Tl(I) &gt; Co 206</td>
</tr>
<tr>
<td>tungstate</td>
<td>Ce/WO₄ = 0.49-0.57</td>
<td>Tl(III) &gt; Ag &gt; Cs</td>
</tr>
<tr>
<td>Exchanger</td>
<td>Nature/Composition</td>
<td>Selectivity/Separation</td>
</tr>
<tr>
<td>-----------</td>
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<td>------------------------</td>
</tr>
<tr>
<td>Cu&gt; Ni; Zn&gt; Cd &gt; Mn(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12. Titanium Phosphate</td>
<td>Amorphous, P/Ti = 0.6-2.0</td>
<td>Zr and Pb from others</td>
</tr>
<tr>
<td></td>
<td>Crystalline</td>
<td>Ti(HPO₄)₂, 2H₂O</td>
</tr>
<tr>
<td>13. Titanium Arsenate</td>
<td>Amorphous</td>
<td>Pb from series of Bi-valent metals</td>
</tr>
<tr>
<td></td>
<td>Crystalline</td>
<td>Ba-Mg; Ba-Ca; Ba-Sr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K-Na; Cs-Na;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>238-Th, 227-Ac</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Codeine, Atropine, Strychnine, Quinine and Cinconine from nicotine</td>
</tr>
<tr>
<td>14. Titanium Antimonate</td>
<td>Semi-crystalline</td>
<td>Pb &gt; Ba = Ca &gt; Cd &gt; Co &gt; UO₂(II) &gt; Ca &gt; Ni &gt; Hg</td>
</tr>
<tr>
<td></td>
<td>Amorphous</td>
<td>Ni &gt; Zn; Mn &gt; Sr &gt; Hg; Ba &gt; Zn &gt; Cd &gt; Pb &gt; Sr</td>
</tr>
<tr>
<td></td>
<td>Sb/Ti = 1 - 3.6</td>
<td>Co &gt; UO₂(II) &gt; Ca &gt; Ni &gt; Hg.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Separations :-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UO(II) from Fe(III), Al, Mn, UO₂(II), Zn, Hf, Mg from Sr, Ca, Al, Mn-Al.</td>
</tr>
<tr>
<td>Exchanger</td>
<td>Nature/Composition</td>
<td>Selectivity/Separation</td>
</tr>
<tr>
<td>--------------------</td>
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<td>----------------------------------------</td>
</tr>
<tr>
<td>15.Titanium molybdate</td>
<td>Amorphous Mo/Ti = 0.5-2.0</td>
<td>Pb &gt; Sr &gt; Mg; Ba &gt; Ca &gt; Cu &gt; Cd &gt; Zn</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Separations: Zn-Pb-Tl; Bi-Pb-Tl; Na from Rb, Ca; K-Cs, Ba-Ca.</td>
</tr>
<tr>
<td>16.Titanium tungsten</td>
<td>Amorphous Ti/W = 3:4</td>
<td>Ca from Sr, Mg, Ba; Na from Pb, Cs; K-Cs; Ga from Fe, Al and In; Pd(II) from 28 cations; Pt(IV) from 36 cations; Cd, Hg(II) from 30 cations; Tl from 57 cations; Sn(IV) from 40 cations; Sn(II)-Sn(IV).</td>
</tr>
<tr>
<td>17.Zirconium phosphate</td>
<td>Amorphous, Semicrystalline Crystalline P/Zr=0.5-2.0</td>
<td>Cs &gt; Rb &gt; K &gt; Na &gt; Mg &gt; Ca &gt; Sr &gt; Be Zn &gt; Cu(II) &gt; Ni &gt; Co; Ce(IV) &gt; U(VI) &gt; Cf &gt; Eu(III) &gt; Cm(III) &gt; Am(III) &gt; Ce(III). Separations: Rb-Cs; Na-K; Cm-Am; Ca-Sr-UO$_2$(II), Eu, Zr, Pu; Sr-Y-Cs;</td>
</tr>
<tr>
<td>Exchanger</td>
<td>Nature/Composition</td>
<td>Selectivity/Separation</td>
</tr>
<tr>
<td>----------------------</td>
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</tr>
<tr>
<td>18. Zirconium Poly phosphate</td>
<td></td>
<td>Ni-Co-UO$_2$(II)-Fe(III);</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd-Zn-UO$_2$(II)-Fe(III);</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UO$_2$(II)-Sr; UO$_2$(II)-Ce;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Eu from Zr, Pu, Fe, Mn, Ni, Pb, Al, Cr; Ca from Zn, Ag Cd; Pu from irradiated uranium; Uranium from fission products; Sr from radioactive waste water; $^{137}$Cs from reprocessing solution.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NH$_4^+$ from selective for 257-279 alkali metals ions H$^+$ from selective for Fe(III) Cu, Ca, Ba, Sr, Ni, Sn, and Sb(III).</td>
</tr>
<tr>
<td>19. Zirconium arsenenate</td>
<td>As/Zr=1.53-1.98</td>
<td>Cs &gt; K &gt; Na at pH 2.6 280-283 Na &gt; K &gt; Cs at pH 4.65 Separations:- Aliphatic amines quantitatively separated.</td>
</tr>
<tr>
<td>Exchanger</td>
<td>Nature/Composition</td>
<td>Selectivity/Separation</td>
</tr>
<tr>
<td>-------------</td>
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<td>------------------------</td>
</tr>
<tr>
<td>20. Zirconium Antimonate</td>
<td>Amorphous</td>
<td>Na &gt; K &gt; NH₄ &gt; Rb</td>
</tr>
<tr>
<td>21. Zirconium Tungstate</td>
<td>Zr/W=1.0-0.44</td>
<td>Cs &gt; Rb &gt; K &gt; Na &gt; Li</td>
</tr>
<tr>
<td></td>
<td>Amorphous</td>
<td>Separations: Ca-Sr; Ca-Sr; Sr-Y.</td>
</tr>
<tr>
<td>22. Zirconium Telurate</td>
<td>Zr(H₂TeO₄)₄H₂O</td>
<td>Cs &gt; Rb &gt; K &gt; Na; Ba &gt; Ca &gt; Sr.</td>
</tr>
<tr>
<td>23. Thorium Crystalline Phosphate</td>
<td>PO₄/Th=1.6-2.1</td>
<td>Cu, Mg, Mn, Zn, Cd, Co, Hg, Ca, from Pb; Zn, Cu, Co, Cd, Hg, Ni from Bi.</td>
</tr>
<tr>
<td>24. Chromium Amorphous Phosphate</td>
<td>P/Cr=0.6-1.0</td>
<td>K-Cs; Rb-Cs; Rb-Br; Mn-Fe(III); Co-Fe(III); Te-MO; Sn-In.</td>
</tr>
<tr>
<td>25. Ferric Phosphate</td>
<td>P/Fe = 2.0</td>
<td>Selective for Pb, Eu, Ga.</td>
</tr>
<tr>
<td>Exchanger</td>
<td>Nature/Composition</td>
<td>Selectivity/Separation</td>
</tr>
<tr>
<td>-----------</td>
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<td>------------------------</td>
</tr>
<tr>
<td>26. Ferric Amorphous</td>
<td>Selective for K, Na, Li.</td>
<td>315</td>
</tr>
<tr>
<td>27. Niobium Amorphous</td>
<td>Selective for rare earths.</td>
<td>316</td>
</tr>
<tr>
<td>arsenate Nb/As=1.96</td>
<td>Separations: Mg from Al, Mn; Ga form Al, Hg, Cd.</td>
<td></td>
</tr>
<tr>
<td>28. Niobium Semi-crystalline</td>
<td>Mg from Sr, Ba, Hg, Ga, Al</td>
<td>317</td>
</tr>
<tr>
<td>Antimonate</td>
<td>Fe(III), La(III), Th(IV), Mg.</td>
<td></td>
</tr>
<tr>
<td>29. Tantalum Amorphous</td>
<td>VO₂(I)–Al–Ti;</td>
<td>318</td>
</tr>
<tr>
<td>Antimonate Ta/Sb=1.3</td>
<td>VO₂(I)–Fe(III)–Ti;</td>
<td></td>
</tr>
<tr>
<td>30. Basic Lead</td>
<td>Cu(II) from Mg(II), Ca(II)</td>
<td>319, 321</td>
</tr>
<tr>
<td>Sulphate</td>
<td>Ni(II), Zn(II), Cd(II), Hg(I), Pb(II) and Th(IV).</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr(II) from Mg(II), Ca(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(I), Pb(II) and Th(IV).</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SCN⁻ from Cr(VI), PO₄³⁻, V(V), [Fe(CN)₆]⁴⁻, As(V), As(III) and IO₃⁻.</td>
<td></td>
</tr>
<tr>
<td>Exchanger Nature/Composition</td>
<td>Selectivity/Separation Reference</td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
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<td></td>
</tr>
<tr>
<td>Cr(VI) from MnO₄⁻, [Fe(CN)₆]⁴⁻, BrO₃⁻, IO₃⁻, PO₄³⁻, V(V).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe(CN)₆]³⁻, from [Fe(CN)₆]⁴⁻, IO₃⁻, PO₄³⁻, As(III), Cr(VI) and V(V).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(II) from Mg(II) Co(II), Mn(II), Zn(II) and Cd(II).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(II) from Mg(II), Co(II) Mn(II), Zn(II), Cd(II), Cu(II), Th(IV), Th(IV) from Mg(II), Co(II), Mn(II), Zn(II), Cd(II), Cu(II).</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K from Na Zn from Cd, Ti(IV), Th(IV).</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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23. Basic

Lead Chromate

Cu(II) from Mg(II) Co(II), Mn(II), Zn(II) and Cd(II).

Fe(II) from Mg(II), Co(II) Mn(II), Zn(II), Cd(II), Cu(II), Th(IV), Th(IV) from Mg(II), Co(II), Mn(II), Zn(II), Cd(II), Cu(II).

K from Na Zn from Cd, Ti(IV), Th(IV).
THEORIES OF
ION-EXCHANGE
THEORIES OF ION-EXCHANGE

The most important theories of ion-exchange process are:

a) Crystal lattice theory;
b) Double layer theory;
c) Donnan membrane theory.

A) CRYSTAL LATTICE THEORY :-

The mechanism of ion-exchange has been developed from the modern concept of the nature of ionic solids (7-9). According to the most recent concept of the nature of ionic solids, solid may be considered to consist of constituent ions arranged in a definite manner but not as a molecule. Ion-exchange takes place at the ionic sites, not only at the surface of the exchanger but throughout its net work.

B) DOUBLE LAYER THEORY :-

Helmholtz(341), Gouy(342) and Stern(343) introduced the double layer theory for ion-exchange mechanism. This theory assumes that the double layer consists of an inner fixed layer and an external diffused and mobile layer of charges. The charged layers originate from adsorbed ions. The concentration of ions in the diffused layer depends upon the concentration and pH of the external solution.

The two theories viz. Crystal lattice theory and double layer theory are apparently similar but fundamentally the two theories are quite different. Crystal lattice theory assumes that a fixed number of exchange sites is not dependent on pH and concentration of the solution but in double layer theory, the capacity of diffused double layer is dependent on both concentration and pH of the solution.
The third theory of ion-exchange is a special case of Donnan membrane theory. According to this theory, the interface between the solid and the liquid is a membrane. There are unequal distributions of ions on the two sides of the membrane. One side of the membrane contains an electrolyte whose ions are nondiffusible through the membrane. The exchangeable ions are attached to the non-diffusible sites.

**ION-EXCHANGE EQUILIBRIUM**

**A> Cation-Exchange Equilibrium:**

When a solution containing a metal ion is brought into contact with a cation exchanger, the exchange of ions takes place between the exchanger phase(E) and the solution phase(s). The process continues till equilibrium is established.

\[
H^+X^-(\text{Exchanger}) + M^+(\text{Solution}) \rightleftharpoons M^+X^-(\text{Exchanger}) + H^+(\text{solution}) \ldots \ldots (1).
\]

Where \( H^+X^- = \text{cation exchanger and } M^+ = \text{metal ion.} \)

The equilibrium constant is given by

\[
K = \frac{a_{ME}}{a_{HE}} \cdot \frac{a_{HS}}{a_{MS}} \ldots \ldots (2)
\]

\[
= \frac{c_{ME}}{c_{HE}} \cdot \frac{Y_{ME}}{Y_{HE}} \cdot \frac{x_{HS}}{x_{MS}} \cdot \frac{Y_{HS}}{Y_{MS}} \ldots \ldots (3)
\]

Where \( c_{ME} \) and \( c_{HE} \) are the ion concentration in the exchanger phase, \( x_{HS} \) and \( x_{MS} \) are the ion concentration in the solution and \( Y \) is the activity coefficient. For practical purposes, an apparent equilibrium constant is defined by
In general, $K_a$ depends on the ratio of $\frac{C_{ME}}{C_{HE}}$ and may be considered constant within certain limits(35). In analytical chemistry the exchange affinity for different ions for the ion-exchangers plays an important role. This affinity depends on the total concentration of ions in the exchanger phase. The difference in the affinity can be correlated with activity coefficients in the exchanger phase, difference in ionic volumes and the thermodynamic osmotic pressures.

When $\frac{C_{ME}}{C_{HE}} = 1$, $K_a$ gives the measure of the relative affinity of the ions and when $K_a = 1$, the affinities of two ions will be the same.

The charges and ionic radii of the ions have some influence upon the exchange affinity, which increases with the increase in charge and decrease in radii.

B> ANION-EXCHANGE EQUILIBRIUM :-

The anion-exchange reaction is similar to that of cation-exchange process. The anion-exchange equilibrium can be expressed as $R^+X^-$(Exchanger) + $Y^-$ (Solution) = $R^+Y^-$ (Exchanger) + $X^-$ (Solution) ....(5). Where $R^+X^-$ = anion exchanger and $Y^-$ = anions to be exchanged.

The equilibrium constant can be derived similarly as in the case of cation exchange system.
DISTRIBUTION COEFFICIENT AND SEPERATION FACTOR :-

For practical purposes, the ion-exchange equilibria are best expressed in terms of elution constant (E), bed distribution coefficient (D) and overall distribution coefficient (K_d). Taking a simple case, if we consider two ion Mn^+ and H^+, competing for the exchanger, then in sufficiently dilute solutions where activity coefficients may be neglected in the exchange reaction, the equilibrium may be represented as,

\[ n^+ \text{M}^{(\text{Solution})} + n\text{HX(Exchanger)} \]
\[ \overset{\sim}{=} n\text{H}^+(\text{Solution}) + n\text{M}^+(\text{X}^-) \text{ n (Exchanger)} \ldots \ldots (6) \]

Where Mn^+ = metal ion and HX = Exchanger.

The equilibrium constant,

\[ K_H = \frac{[Mn^+] [H^+]^n}{[Mn^+] [H^+]^n} \ldots \ldots \ldots \ldots (7) \]

using the bars to represent the solid phase. If \([Mn^+] > [H^+]\) as in tracer solutions of ion Mn^+, the variation in \([H^+]\) may be neglected and we may write the distribution Coefficient of metal ion of equilibrium.

\[ K_d = \frac{[Mn^+]}{[Mn^+] [H^+]^n} = K_H \cdot \frac{[H^+]^n}{[H^+]^n} = \frac{K_1}{[H^+]^n} \ldots \ldots (8) \]

Where \(K_1 = K_H \cdot [H^+]^n\).

If the law of mass action is obeyed, a plot of \(K_d\) versus log\([H^+]\) will be a straight line of slope \(n\).

The distribution Coefficient can be determined
experimentally. It is expressed as,

$$K_d = \frac{\text{Concentration of cation in the exchanger phase}}{\text{Concentration of cation in the solution phase}}$$

$$= \frac{\text{Amount of metal ion in exchanger / Weight of exchanger}}{\text{Amount of metal ion in solution / Volume of solution}}$$

$$= \frac{\text{Amount of metal ion in exchanger}}{\text{Weight of exchanger}} \times \frac{\text{Volume of solution}}{\text{Amount of metal ion in solution}} \ldots (9)$$

In column operations, an useful quantity is the elution constant ($E$) which is expressed as $E = \frac{(d.A)}{V}$ \ldots (10).

Where $d$ is the distance in cms. of band maximum which travels when $V$ ml. of eluent is passed through a column of cross-sectional area $A$ sq. cms.

From the equation due to Kettle and Boyd(36) the velocity of an adsorption band moving through an adsorbent can be found under equilibrium conditions.

Thus $\frac{(d)}{t} = \frac{V}{1 + (D/1)} \ldots (11)$

Where $t$ = time

$V$ = linear flow of the reaction,

$i$ = interstitial space

and $D$ = bed distribution Coefficient which is defined as

$$D = \frac{\text{Concentration of ion per ml of bed}}{\text{Concentration of ion per ml of solution}} \ldots (12)$$

It is also known that $tV = \frac{(V/iv)}{1} \ldots (13)$

Combining eqns. (10), (11) and (13)

We have $E = 1/(i+D) \ldots (14)$.

For small values of $i$ and large values of $D$, the equation(14) can be written as $E = (1/D) \ldots (15)$. 30
It is clear from equation (15) that the elution constant is the reciprocal of bed distribution Co-efficient (D). The relation between distribution Co-efficient and bed distribution Co-efficient is given by

\[ D = p \cdot Kd \ldots(16). \]

Where \( p \) is in the density of the exchanger.

If \( E_a \) and \( E_b \) are the elution constants and \( D_a \) and \( D_b \) are bed distribution coefficients for ions 'a' and 'b' respectively, the separation factor \( S \) can be represented as

\[ S = (E_a/E_b) = (D_a/D_b) \ldots\ldots..(17). \]

The magnitude of the separation factor controls the efficiency of an ion-exchange separation, the larger the value of \( S \), the better is the separation. When the value of \( S \) is unity, the separation is not possible.

The efficiency of an eluting agent can be determined from the value of elution constant or bed distribution coefficient. The efficiency of an eluting agent will be high when the value of the elution constant is large so that small volume of eluting agent is necessary for complete stripping of the adsorbed ion from the exchanger.

**pH - Titration:**

The ion-exchange capacity indicates the number of fixed inorganic groups in milliequivalents per g. of exchanger. Cation exchangers in hydrogen form can be titrated with standard bases (5,12,344). In such a titration the ion-exchanger remains insoluble, but comes to equilibrium with the solution to which titrant is added. The pH of the supernatant solution is recorded.
The number of inorganic groups can be evaluated from such a pH -
titration curve. The pH - titration curve was first introduced
by Grickbasch(347). Let a monofunctional cation exchanger be
titrated with standard alkali solution. The ion-exchange reaction
takes place as

\[ H^+X^- + Na^+ = Na^+X^- + H^+ \]

Bars indicate exchanger phase.

The H⁺ ion released by the exchanger combines at once with the
OH⁻ ions of the base. When all H⁺ ions have been displaced from
the exchanger by Na⁺, the pH of the solution rises sharply with
further addition of alkali. The number of acid equivalent i.e.
the capacity of the exchanger can be calculated from the amount
of titrant added up to the point where steep rise in pH occurs.

Similarly the anion-exchanger in hydroxyl form can be
|  
| titrated with standard acids. In this case ion-exchange reaction
| for a mono-functional anion-exchanger may be represented as

\[ R^+OH^- + Cl^- = R^+Cl^- + OH^- \]

The capacity of the anion-exchanger can be calculated from the
amount of titrant added up to the point where steep fall in pH
occurs.

This pH titration can also be done in the presence of the
salt. The addition of salt serves to depress the Donnan effect.

GENERAL TECHNIQUES.

ION-EXCHANGE CHROMATOGRAPHY :-

There are mainly two types of operations for ion-exchange
procedure.

\[ \text{a} \] Batch operation,
b> Column operation.

a> Batch operation:

This technique is simple but inefficient. A known amount of exchanger is allowed to equilibrate with a known volume of solution containing exchangeable ions for a fixed period of time and the phase separation is made by decantation, filtration, centrifugation etc.

b> Column Operation:

This technique is extensively used for ion-exchange separations. In this technique, the test solution is allowed to run from the top of the column, packed with exchanger and the filtrate is known as effluent. The column operation consists of (I) sorption (II) washing and (III) elution.

(I) SORPTION: In this process the exchangeable ions are adsorbed by the exchanger, when the test solution is passed through the exchanger.

(II) WASHING: In this step the exchanger column is washed with water to remove any unadsorbed ions.

(III) ELUTION: A suitable eluting agent is next used to strip off the desired ion adsorbed on the exchanger bed. The eluting agent is generally an acid, alkali, salt solution or a complexing agent e.g. citric acid, E.D.T.A. etc. The elution process depends on flow rate, particle size of the exchanger, eluted composition and temperature. The nature of the elution curve can be determined from the integral elution curve or from the differential elution curve.
PAPER CHROMATOGRAPHY

Under suitable conditions papers can be impregnated with inorganic ion-exchangers. These impregnated papers can then be used for paper chromatographic work. Generally five techniques are adopted for paper chromatography. These techniques are based on different method of development (348-349).

a> ASCENDING CHROMATOGRAPHY :-

In this technique, solvent is placed at the bottom of the tank. The samples are applied above 2-4 cms. from the lower margin of the paper. The paper is inserted with its lower edge in the solvent. This method has an advantage that the solvent flow stops itself at the upper edge of the paper and the components are not washed out of the paper. This simplest method finds wide application for chromatographic work.

b> DESCENDING CHROMATOGRAPHY :-

In this method developing solvent is placed in a trough. The sheet of the paper, freely suspended over a glass rod, has its top end in the trough and the solvent moves through the paper towards the lower end. The samples are applied near the top end of the sheet. The whole system being mounted in a closed jar in which air is saturated with solvent vapour to prevent evaporation. This method is used for routine chromatography.

c> TWO DIMENSIONAL CHROMATOGRAPHY :-

This is an effective method for separations of complex mixture. A square sheet of paper is used. The test solution is applied near one corner of the paper and ascending or descending chromatography is carried out.
The paper is removed from the tank, dried and turned through 90°, and the chromatogram developed in a different solvent. After second development the paper is removed from the tank, dried and the substance located with a selective reagent.

d) RADIAL CHROMATOGRAPHY :-

The sample is placed on the paper in a ring around the centre. The solvent is introduced into the centre of the paper and flows outwards. When development is complete the substances are distributed on the chromatogram in radian rings.

e) PAPER ELECTROPHORESIS :-

This is based on differential migration of ions in a suitable buffer system under an applied electric field for an optimum period.

A pencil line is drawn perpendicular to the length of the paper. The paper is carefully moistened with the buffer solution which is placed as electrolyte and the two ends dipped into the same buffer solution. Spots of samples are applied to positions marked on the papers and potential difference is applied. The distance travelled by the ion/ions are measured after the development of the spots as usual.
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