Chapter - I

INTRODUCTION
INTRODUCTION

Ion exchange, from the day of its discovery has added a shining spark in the field of analytical chemistry. It is widely used in inorganic, organic and biochemical separations. In laboratories ion exchangers are being used as an important tool to solve new problems. Rapid and accurate determination of the constituents of a sample or contaminants of alloys with multicomponents, pharmaceuticals, biological substances and fission products of radioactive elements has become possible by the use of ion exchangers. The use of ion exchangers on large scale may provide mankind with pure water and may be useful for the concentration and extraction of important metals and raw materials which are becoming more and more difficult to produce.

The ion exchange materials have found a number of important analytical applications. The analytical applications of ion exchange continues to increase at an exponential rate. Ion exchange has found its application in :-

1. Water pollution control (purification of water)
2. Removal of interfering ions
3. Recovery of precious metals
4. Water softening
5. Preparation of deionized water
6. Separation of metal ions
7. Determination of total salt content of a solution
8. Separation of organic and biologically important substances
9. Concentration of trace constituents
10. Specific spot tests
11. Location of end point in titrations
12. Gas chromatography, electrophoresis and solid state separations
13. Preparation of ion selective electrodes, and
14. Preparation of ion exchanger fuel cells.

The most important application of ion exchangers is purification of water. The water pollution is increasing at alarming rate due to increase in industrialization and urbanization. Ion exchange technology is useful in removing the toxic species, when present in ionic form. The great simplicity of the technique makes ion exchange very attractive and an inexpensive tool. Purification on large scale can be made by passing the sample solution through the ion exchanger bed which takes up certain materials in preference to others.

The removal of interfering ions by replacement with an innocuous ion is another application of ion exchange. This technique can also be utilized for the recovery of useful elements in traces from dilute solution. By this technique, elements present in ionic form are exchanged by an equivalent amount of counter ion present in exchanger and subsequently eluted from the exchanger by suitable electrolytic reagents. Thus, trace amount of an ion is isolated from a
large volume of aqueous solution into a small volume of the eluent. This is an important step in determination of trace metals in water or in recovery of precious metals. This technique has also been used for the isolation and identification of the new trans-uranic elements (1,2) and for the isotopes enrichment (3,4).

Ion exchange being a separation technique finds its use in water analysis to concentrate the trace quantities and separate one substance from another. Ion exchange is advantageous for the separation of metal ions with similar properties for which specific methods are not available. Ion exchangers have been used to separate rare earth elements (5-7) now-a-days. Taylor and Urey have performed partial separation of lithium isotopes (8). Ion exchange columns now provide pure rare earth compounds on commercial scale. It has also been used for the separation of organic and biologically important substances such as aminoacids (9,10), nucleic acids (11), proteins (12), alcohols (13), carbohydrates and their derivatives (14), glycols (15), ethers (16), phenols (17), amines (18) and hydrocarbons (19) have been separated on ion exchange columns.

Ion exchangers are useful in gas chromatography, solid state separations, electrophoresis, location of end point in titrations etc. Papers impregnated with ion exchangers are used for paper chromatographic separations.

Ion exchange has established itself as one of the most powerful
techniques in the field of water analysis thus proving its worth in water pollution control.

Gans (20) recognized the practical utility of the ion exchange phenomenon for water softening using natural and synthetic zeolites and clays. In 1931 Kullgren (21) observed that sulphite cellulose works as an ion exchangers for the determination of copper. An interesting discovery began in 1935, when Adams and Holmes discovered that crushed phonograph records exhibit ion exchange properties. This led them to the synthesis of organic ion exchange resins (22) which exhibited an improved properties over the previously known ion exchangers. These organic ion exchangers have been used both in laboratory and on industrial scale for separations, recoveries of metals, purification of water, concentration of electrolytes and elucidating the mechanism of many chemical reactions (23).

The application of organic ion exchangers also suffers from certain limitations i.e. they decompose at elevated temperatures in aqueous systems and under the influence of ionizing radiations. This led to a revived interest in inorganic based exchangers. Apart from their far improved temperature resistance and complete immunity to ionizing radiation the inorganic ion exchangers possess a rigid molecular framework. This stiffness of structure leads to enhanced selectivity for the separation of ions on the basis of their pore size. They can also be used as ionic or molecular sieves. Being resistant to
high temperatures they can be satisfactorily used in reactor technology. Inorganic ion exchangers selectivity have also been utilized for the preparation of ion selective electrodes which have now become an important tool for solving various analytical problems.

Systematic and fundamental studies on inorganic ion exchangers commenced in 1943 with the discovery of insoluble compound, Zirconium phosphate, and its application to the separation of Uranium and Plutonium from fission products (24). The earlier work through 1964 has been excellently summarized in a monograph of Amphlett (25) entitled "Inorganic ion exchangers", which has become a classic and has stimulated impetus for subsequent research in the field. Representative type of inorganic ion exchangers have been reviewed by Ito and Abe (26). A set of reviews by Pekarek and Vesely (27,28), summarizes relevant work done till 1970. The theoretical aspects of ion exchange in the inorganic ion exchangers have been described by Marinsky (29) who has described pioneering work in this field. Marinsky (30) and Walton (31) have edited the reviews on the applications of inorganic ion exchangers. The synthesis and applications of inorganic ion exchangers have been reviewed by Walton (32-36), Clearfield (37), Qureshi and Varshney (38).

The utility of the ion exchange materials can be developed on the basis of following studies:

1. Distribution of counter ions between the exchanger and solution phases.
2. Thermodynamics
3. Kinetics and
4. Analytical applications.

The incorporation of bi or polydentate ligands on the ion exchanger matrix gives a new class of exchangers, known as chelate ion exchangers. A number of chelating ion exchangers have been synthesised to encourage the applications of ion exchange to a broader range of separation and for the recovery of certain metal ions selectivity. The chelating ion exchangers may provide a convenient technique for the analytical concentrations of many of the more interesting trace elements from natural waters and collection of toxic elements from industrial waste water. The selectivity of the most complexing agents predominantly depends on their ability to form chelates with certain metal ions.

Thermodynamics is an appropriate means of describing the theoretical behaviour of sorption ion exchange equilibria. The attempts have been made to correlate the activities with some measurable quantities, with the thermodynamic equations. The earliest approaches were based on semiempirical or empirical equations to fit in the experimental results. Probably the first quantitative formulation of ion exchange equilibria was made by Gans (39). For this purpose he used the law of mass action in its simplest form, without involving the concept of activity coefficient. This concept was extended
by Kielland (40). The formula did not involve the concept of activity coefficient. Gaines and Thomas (41) gave a general treatment using an expression for the calculation of thermodynamic equilibrium constant which is a suitable choice for this purpose. However, Gregor was able to relate selectivity to hydrated ionic volumes in his semi-quantitative model. Rigid structure, negligible swelling pressure and a differential selectivity have made the study simple on inorganic exchangers. The thermodynamic studies of alkali metals on ferric antimonate (42,43), niobium arsenate (44), zirconium triethylamine (45), thorium tetracyclohexylamine (46) were made in our laboratories.

Solid-liquid interactions which can be measured in terms of sorption have always been of interest for many workers because of the diversity of the phenomena involved and immense application in chemistry and related sciences.

Adsorption is one of the most fascinating areas of chemistry. Since, the molecules on the surface have a different environment from those in the bulk of the material, hence, surface energy is different from the energy of the bulk.

Adsorption is of two types: physical and chemical called as "Physiosorption" and "Chemisorption" respectively. In physiosorption the molecules are adsorbed to a solid surface essentially by physical forces, while in chemisorption, the molecule forms the chemical bonds with the solid surface. In physiosorption there is a Vanderwaal's interaction (for instance dispersion or polar interaction) between the surface and adsorbed molecule. These are weak types of interactions
and the amount of energy released when the molecule is physically sorbed is of order of 25 KJ mol\(^{-1}\) i.e. the enthalpy of condensation. This energy can be absorbed by the vibration of the lattice and is dissipated as heat. A molecule bouncing across the surface will lose its kinetic energy and stick to the surface resulting in the rise in temperature of the system i.e. heat is evolved. In chemisorption, the molecules stick to the surface, as a result of the formation of chemical bonds, usually covalent bonds and tend to find the site that increases their coordination number with the temperature. Thus the energy of attachment is in the range of 40 to 200 KJ mol\(^{-1}\).

For a spontaneous process, \(\Delta G\) should be negative. As the species is adsorbed, there is reduction in its translational freedom. So, \(\Delta S\) is also negative. Hence, \(\Delta H\) must be negative if \(\Delta G = \Delta H - T\Delta S\) is to be negative and a negative \(\Delta H\) corresponds to the exothermic process. But sometimes the adsorbate dissociates at high temperature, thus leading to breaking of bonds and high translational mobility on the surface, in that case enthalpy is small and positive.

Plotting of adsorption isotherms is the most convenient way of studying and understanding the nature of adsorption taking place in a particular system. The isotherms are obtained by plotting the amount adsorbed against the equilibrium concentration at any instant at a particular temperature. Different models for adsorption isotherm, applicable to both gases and liquids, are available in literature. Two of
the most common models are however being discussed in brief as follows:-

1. **Langmuir Model**

   Langmuir proposed

   \[
   \frac{C_e}{X_m} = \frac{1}{K} \cdot \frac{1}{b} + \frac{1}{b} \cdot C_e
   \]

   Where \( C_e \) is the equilibrium concentration and \( X_m \) is the amount adsorbed per specified amount of adsorbent. \( K \) is the equilibrium constant and \( b \) is the amount of adsorbate required to form a monolayer. Hence a plot of \( C_e/X_m \) vs \( C_e \) should be a straight line, with a slope equal to \( 1/b \) and intercept equal to \( (1/K) \cdot (1/b) \).

2. **Freundlich Model**

   According to this model

   \[
   X_m = K \cdot C_e^{1/n}
   \]

   \[
   \ln X_m = \ln K + \frac{1}{n} \cdot \ln C_e.
   \]

   where all the terms have usual significance and \( n \) is an empirical constant, thus a plot of \( \ln X_m \) Vs \( \ln C_e \) should give a straight line with a slope equal to \( 1/n \) and intercept gives the value of \( \ln K \).

   This model deals with the multilayer adsorption of the substance on the adsorbent. Alumina, silica, cellulose and carbon are most commonly studied adsorbents. They are mainly used for the adsorption of phenols, organic acids, hydrocarbons, alcohols, dyes,
pesticides and pollutants etc. Literature survey reveals that even inorganic ion exchangers and organic synthetic resins have also been used for many adsorption studies Table 1.1.

In addition to the materials mentioned so far, a number of other types of exchangers have been developed, e.g. "electron ion exchangers" and "redox ion exchangers". The electron ion exchangers are solid oxidizing and reducing agents. They are, as a rule, resins with a cross linked hydrocarbon matrix. They contain the species such as quinone/hydroquinone, forming a redox couple which can be reversibly oxidised or reduced. They can be regenerated by a suitable reducing (or oxidising) agent after having been oxidised (or reduced) by a substrate.

Redox ion exchangers are conventional ion exchange resins containing reversible oxidation-reduction couples such as Fe³⁺/Fe²⁺, Cu²⁺/Cu or methylene blue etc (97-98). These redox couples are held by the ion exchange resins (e.g. Dowex-50, cation exchange resin) either as a counter ion or by sorption or complex formation. Duolite S-10 is a commercial redox ion exchanger.

The behaviour of redox ion exchangers and electron ion exchangers is similar to that of the soluble oxidation-reduction couples. The redox potential of a couple is little affected by incorporation of the couple into a resin (100,101). In its reduced form the redox ion exchanger can reduce the couples having a higher
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<td>39</td>
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standard redox potential, whereas in its oxidised form it can oxidise the couples having a lower redox potential. Standard redox potentials of some of the most common redox couples are given by Latimer (102).

The redox ion exchangers possess some advantages over dissolved oxidizing or reducing agents. The most important advantage is their insolubility and hence they can be easily separated from the solution containing a substrate being oxidised or reduced. No contamination of the solution by these exchangers occur as only electrons and protons are transferred between the exchanger and solution phases. The only possible change in solution, except for the redox reaction of the substrate, is a change in pH. Another advantage is that they can be easily regenerated after use by a suitable reducing or oxidising agent.

Redox ion exchangers and electron ion exchangers are characterized by their redox capacity, redox potential and rate of the reaction. The redox capacity is the amount of a substrate being oxidised or reduced by a specified amount of the exchanger and is expressed in terms of the milliequivalents per gram of dry resin. The reaction rate determines the time required for the redox process under a given set of conditions. The standard redox potential indicates, which substrate can be reduced or oxidised. Some important redox ion exchangers are listed in Table 1.2.
Table 1.2 : Redox Ion Exchangers And Their Redox Capacity.

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<th>Redox Capacity (meq/g)</th>
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<td>3.</td>
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<td>4.</td>
<td>Phosphonic acid type redox resin</td>
<td>-</td>
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<td>5.</td>
<td>Phosphomolybdovanadic acid</td>
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</tr>
<tr>
<td>6.</td>
<td>Tetra chlorohydroquinone</td>
<td>-</td>
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</tr>
<tr>
<td>7.</td>
<td>Tetra chloroquinone</td>
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</tr>
<tr>
<td>8.</td>
<td>p-benzoquinone melomine copolymer</td>
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<tr>
<td>9.</td>
<td>Zirconium molybdovanadate</td>
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</tr>
<tr>
<td>10.</td>
<td>Alkali and Nickel ferrocynide</td>
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<td>111</td>
</tr>
<tr>
<td>11.</td>
<td>Phospho tungstovanadic acid</td>
<td>-</td>
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</tr>
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<td>12.</td>
<td>Active carbon</td>
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</tr>
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<td>13.</td>
<td>Zeolite alumino silicate</td>
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</tr>
<tr>
<td>14.</td>
<td>Zirconium peroxide metatungstate</td>
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<tr>
<td>15.</td>
<td>Molybdenum benzoinoximate</td>
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<td>16.</td>
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<tr>
<td>17.</td>
<td>Zirconium silico molybdate</td>
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Chromatography is an analytical method based on differences in the partition coefficient of substances distributed between stationary and mobile phases, usually a great surface area and a moving fluid phase. Thin layer chromatography (TLC) together with paper chromatography comprise "planar" or "flat-bed" chromatography is the simplest of all of the widely used chromatographic methods to perform.

The history of liquid chromatography dates back to the first description of chromatography by Michael Tswett (119) in early 1900's, who separated components of plant pigments by passing their solutions through columns of solid adsorbents. Stahl (120,121), Kirchner (122) and Pelick et al. (123) have reviewed the history of TLC. TLC is a relatively new discipline and chromatography historians usually date the advent of modern TLC from 1958. The review of Pelick et al. tabulated significant early developments in TLC and provided translations of classical TLC studies by Izmailov and Schraiber and by Stahl. In 1938, Izmailov and Schraiber separated certain medicinal compounds on unbound alumina spread on glass plates. Since they applied drops of solvent to the plate containing the sample and sorbent layer, their procedure was called "drop chromatography". Meinhard and Hall in 1949 used a binder to adhere alumina to microscope slides, and these layers were used in the separation of certain inorganic ions using drop chromatography.
In the early 1950's Kirchner and colleagues (124) at the U.S. Department of Agriculture developed TLC as we know it today. They used sorbent held on glass plates with the aid of a binder and plates which were developed with conventional ascending procedures used in paper chromatography. Kirchner coined the term "Chromostrips" for his layers. Stahl introduced the term "Thin layer chromatography (TLC)" in the late 1950's. His major contributions were the standardization of materials, procedures and nomenclature and the description of selective solvent systems for resolution of important compound classes.

Quantitative TLC, introduced by Kirchner et al. in 1954 (124), described an elution method for direct measurement of bands separated by means of electrophoresis and was later used on paper chromatograms. Densitometry in TLC was initially reported in the mid 1960's by Dallas et al. (125) using the Joyce Loebl Chromascan and by Genest (126) and Thomas et al. (127) using the Photovolt densitometer. A symposium on quantitative TLC held in 1968 in Great Britain led to the 1st book published on this topic (128).

High performance TLC plates (129) were produced commercially in the mid-1970's and provided impetus for the improvements in practice and instrumentation that occurred in the late 1970's and 1980's and led to the methods termed "High-performance thin layer Chromatography (HPTLC)" (130) and "instrumental
HPTLC" (131), centrifugally accelerated preparative-layer chromatography (132) and forced-flow techniques in TLC (overpressured layer chromatography, OPLC) (133) were introduced in the late 1970's.

TLC is highly sensitive, selective, quantitative, rapid and automated technique for analysis of all types of samples and analytes and for preparative separations. The biennial review by Sherma (134) of advances in theory, practice and applications of TLC is indispensable.

TLC involves the concurrent processing of multiple samples and standards on an open layer developed by a mobile phase. Development is performed, usually without pressure, in a variety of modes, including simple one dimensional, multiple, circular and multidimensional. Paper chromatography, which was invented by Consden, Gordon and Martin in 1944, is fundamentally very similar to TLC, differing mainly in the nature of the stationary phase. Paper chromatography has lost favour compared to TLC because the latter is faster, more efficient and allows more versatility in the choice of stationary and mobile phases.

HPTLC layers are smaller, contain sorbent with a smaller, more uniform particle size, are thinner and are developed for a shorter distance compared to TLC layers. These factors lead to faster separations, reduced zone diffusion better separation efficiency, lower
detection limits and less solvent consumption. However, smaller sample, more exact spotting techniques are required.

Column liquid chromatography involves the elution under pressure of sequential samples in a closed, "On-line" system, with dynamic detection of solutes, usually by UV adsorption.

TLC is most versatile and flexible chromatographic method. It is rapid because precoated layers are usually used as received without preparation. Even though it is not fully automated like HPLC, TLC has the highest sample throughout, because upto 30, individual samples and standards can be applied to a single plate and separated at the same time. Modern computer-controlled scanning instruments and automated sample applicators and developers allow accuracy and precision in quantification that rival HPLC and GC. There is a wide choice of layers, developing solvents (acidic, basic, completely aqueous, aqueous organic) and detection methods. Every sample is separated on a fresh layer, so that carry over and cross contamination of samples and sorbent regeneration procedures are avoided. Mobile phase consumption is low, minimizing the costs of solvents and waste disposal because layers are normally not reused, sample preparation methods are less demanding and less pure samples can be applied. The wide choice of detection reagents leads to unsurpassed specificity in TLC, and all components in every sample including irreversibly sorbed substances, can be detected visually. There is no need to rely
on peaks drawn by a recorder or to worry about sample components possibly remaining uneluted on a column. Being an "off line" method, the various steps of the procedure are carried out independently. This allows zones to be scanned repeatedly with different parameters that are optimum for individual sample components.

The beginning of inorganic chromatography may be attributed to the work of Runge on paper chromatography (135), and Beyerinck on thin layers of gelatin (136). Planar chromatography has found wide use in forensic chemistry, identification of drug samples. Since years, TLC technique has been applied in the analysis of organic and inorganic substances and for the analysis of pharmaceutical, biological and environmental samples (137). In addition to the analysis of aminoacids, bases, steroids, pesticides, toxins and inorganics, TLC and HPTLC technique is also applicable in drug formulations, pharmaceutical preparation and in analysis of Lipid.

The ion exchange property of the adsorbent plays a more prominent role than its simple adsorption behaviour. The analytical capabilities of synthetic inorganic ion exchangers as thin layer materials in TLC had been reviewed by Sherma and Fried (138). For the sake of convenience, inorganic ion exchangers are classified into four categories, and all of them find their use in TLC:

(a) Thin layer of hydrated oxide.

(b) Thin layer of insoluble metal salts of polybasic acids.
(c). Thin layer of heteropoly acid salts.

(d). Thin layer of metal ferrocyanide.

For the first time, zirconium oxide was used for the separation of metal ions by Zabin and Rollins (139). Berger et al. (140, 141) used zirconium oxide for the study of ferrocyanide, sulfocyanide and ferricyanide. Terpenes were separated on the layers of zirconium oxide by Kirchner et al. (142). Ortho-para and meta amino phenols were separated by TLC on titanium oxide layers by Grace (143). Alberti et al. (144) studied the movement of cations on the titanium phosphate layer. The movement of cations was also studied on the layers of zirconium hypophosphate and cerium phosphate by Keonig and Demiel (145) and Keonig and Gray (146) respectively. The movement of 47 metal ions on stannic arsenate layers was studied by Sherma et al. (147). Qureshi et al. (148) reported 20 binary separations of metal ions on non refluxed stannic arsenate layers. Amino acids were separated on stannic tungstate layers by Nabi et al. (149). Rawat et al. (150, 151) used zinc silicate as an adsorbent for paper chromatographic separations of phenols and amines respectively. Chromatography of some metal ions on ligand combined ion exchange papers was studied by Rawat and Chitra (152). TLC method (153) was developed for quantitative separation of Hg(II) from several metal ions on lanthanum antimonate layers. TLC behaviour of 28 phenolic compounds was studied on stannic tungstate layers (154). Tin vanadopyrophosphate layers was used for the analysis of amino acids
by HPLC method (155). Layers of lanthanum silicate were used to study the behaviour of 28 metal ions by Husain et al. (156). Zhengquan et al. (157) studied TLC application of Ce metaphosphate layer in the separation of 10 metal ions. TLC behaviour of 30 cations using Ce(III) silicate was studied by Husain et al. (158) Kawamura and co-workers (159) have analysed various alkali metals on layers of zinc ferrocyanide. Recently inorganic ion exchanger layers have been used as adsorbent for studying the behaviour of pesticides by TLC method. Qureshi et al. (160) used zirconium phosphate layer for the separation of carbamate pesticides and related compounds.

In the present work sorption equilibria of transitional metal ions [Nickel (II), Cadmium (II), Cobalt (II) and Iron (III)] on Duolite ES 467 at 20 to 50°C have been studied and various thermodynamic parameters, such as standard free energy (ΔG⁰), standard enthalpy (ΔH⁰) and standard entropy (ΔS⁰) changes are evaluated. The application of inorganic ion exchanger, stannic molybdate as an electron exchanger have been carried out by studying its redox property. A new redox exchange material has been prepared by immobilising hydrazine sulphate on Duolite ES 467. The successful reduction of certain metal ions has been studied. The application of the inorganic ion exchanger stannic oxide, have been extended to the thin layer chromatographic separations of organophosphate pesticides (chloropyrithion, methyl demeton, dimecron, dimethoate, malathion, monocrotophos, quinolphos) which are responsible for environmental pollution.
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135. F.F. Runge, Farbenchemie, III (1850).


