CHAPTER-1
INTRODUCTION

Heteropoly compounds are the ionic solids having high molecular weight belonging to the family of polyoxometalates and composed of a compact skeleton of metal-oxygen octahedral anions as the basic structural unit surrounding a central atom. The octahedra are connected together giving an extremely stable and firm framework of the heteropolyanions. The cations may be hydrogen or any other metal ions. HPA’s represent a class of acid made up of a particular combination of hydrogen and oxygen with specific metals and non-metals.

A large number of structures, incorporating several metal atoms are known for molybdenum, tungsten, vanadium and niobium heteropolyanions\(^1\-\^2\). Numerous elements are playing active role as addenda atom or central metal atom as compiled in the table 1.1

<table>
<thead>
<tr>
<th>Addenda Atom</th>
<th>Central Metal Atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>W, Mo, Cr, V</td>
<td>Si, P, Al, As</td>
</tr>
</tbody>
</table>

A heteropoly compound must be having:

- Metal atom such as tungsten, molybdenum, chromium or vanadium, generally from d-block termed the addenda atom;
- Oxygen;
- Element generally from the p-block of the periodic table such as silicon, phosphorus, aluminium or arsenic etc. termed the hetero atom.

The metal addenda atoms and oxygen atoms form a cluster with the hetero-atom inside bonded via oxygen atoms.

1.1 HISTORY

Berzelius\(^3\) in 1826, first time introduced the ammonium 12-molybdophosphate \([(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})]\). Marginac in 1862, gave the precise analytical composition of tungstosilicic acid and their salts. Then, Werner’s coordination theory was introduced to derive the composition of heteropolyacid anions. After that Miolati and Pizzighelii hypothesis was adopted and a major break was given by Rosenheim. According to MR theory, heteropolyacids are having a central hetero metal atom which coordinates with \(\text{MO}_4^{2-}\) and \(\text{M}_2\text{O}_7^{2-}\) units. Pauling proposed the structure for the 12:1 complex and proposed formula for tungs tosilicic acid as \(\text{H}_4[\text{SiO}_4\text{W}_{12}\text{(OH)}_{36}]\) in accordance with its basicity. Then, Keggins used X-ray technique and resolved the structure of
H$_3$[PW$_{12}$O$_{40}$].5H$_2$O and the structure was confirmed by Bradley and Illiny Worths investigations based on powder photographs. Although voluminous research work has been done in this field but still a large number of concepts are to be discovered, like detailed mechanism of numerous syntheses etc, thus giving a broad spectrum to attract the researchers in this direction.

Table 1.1: Elements acting as central atoms or heteroatoms in heteropoly compounds

<table>
<thead>
<tr>
<th>Atoms participating in the formation of Heteropoly compounds</th>
<th>Periodic Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>I</td>
</tr>
<tr>
<td>Be$^{+2}$, B$^{+3}$, N$^{+5}$</td>
<td>II</td>
</tr>
<tr>
<td>Al$^{+3}$, Si$^{+4}$, P$^{+5}$, P$^{+3}$, S$^{+4}$</td>
<td>III</td>
</tr>
<tr>
<td>Ti$^{+4}$, V$^{+4}$, V$^{+5}$, Cr$^{+3}$, Mn$^{+2}$, Mn$^{+4}$, Fe$^{+3}$, Co$^{+2}$, Co$^{+3}$, Ni$^{+2}$, Ni$^{+4}$, Cu$^{+2}$, Zn$^{+2}$, Ga$^{+3}$, Ge$^{+4}$, As$^{+5}$, Se$^{+4}$</td>
<td>IV</td>
</tr>
<tr>
<td>Zr$^{+4}$, Mo$^{+4}$, Rh$^{+3}$, Ag$^+$, Sn$^{+4}$, Sb$^{+3}$, Sb$^{+5}$, Sb$^{+5}$, I$^{-7}$</td>
<td>V</td>
</tr>
<tr>
<td>Cs$^{+5}$, Hf$^{+3}$, Ce$^{+4}$, Ce$^{+3}$, W$^{+5}$, Pt$^{+4}$, Pt$^{+4}$, Hg$^{+2}$, Bi$^{+3}$, Te$^{+4}$, Te$^{+6}$, Tl$^{+3}$, Th$^{+4}$</td>
<td>VI &amp; VII</td>
</tr>
</tbody>
</table>

1.2 NOMENCLATURE

Traditional method consists of suffxing the names of the central atoms to the words -date or -dic acid, for example; tungstomolybdate or tungstophosphate. The number of atoms of the central element denoted by Greek prefixes eg. dodecatungstophosphate. According to International Union of Pure and Applied Chemistry nomenclature names of heteropolyanions begins with Arabic numerals designating the simplest ratio of molybdenum or phosphoros atoms to the central atom and then followed by the prefix molybdo or phospho by the name of the simple anion which contains the central atom in the corresponding oxidation state. Roman numerals may also be used to represent oxidation state of the central atom. Heteropoly compounds need a more adequate system of nomenclature which should include the structure, degree of polymerization and oxidation state of the central atom. Keeping in view of above properties, an advanced system of nomenclature extended IUPAC nomenclature, where the oxidation state of the central atoms is expressed by a Roman numeral in parentheses. The prefix molybdo or
vanado designates the peripheral atoms and the italicized prefix pent, hex, oct etc., allocated to the stereochemistry concerning the peripheral and the central atoms. Arabic numerals designate the respective ratio of the number of peripheral and the central atoms. The charge of the anion is indicated by a superscript Arabic numeral at the end of the name. The Greek letter is used to assign bridging between central atoms as shown in table 1.2.

### Table 1.2: IUPAC and trivial Nomenclature in HPA

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Formula</th>
<th>Proposed Names</th>
<th>IUPAC Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Na$<em>3$[PMo$</em>{12}$O$_{40}$]</td>
<td>Sodium12-oct- molybdotet-phosphate(V)</td>
<td>Trisodium dodecamolybdophosphate(V)</td>
</tr>
<tr>
<td>2.</td>
<td>Zr[PW$<em>{12}$O$</em>{40}$]</td>
<td>Zirconium12-oct-tungstotet-phosphate (V)</td>
<td>Zirconium dodecatungstophosphate (V)</td>
</tr>
</tbody>
</table>

### 1.3 METHODS OF SYNTHESIS

The properties of inorganic ion exchanger are greatly affected by the preparatory conditions such as concentration of the metal, ageing time, temperature and pH etc. Keeping in view of the above aspects, different conditions yield the product of different characteristics. Following are the methods used for the synthesis of heteropolyacid salts:

- Electrodialysis
- Ion exchange
- Etherate
- Precipitation.

But the most widely used methods are ion exchange and precipitation whereas all other methods are having certain limitations.

**Etherate method** needs a strongly acidified aqueous solution of the heteropolyanion with diethyl ether. In spite of too many efforts, this method does not yield pure heteropolyacid salts, however we get a mixture of various structures of HPA’s. Moreover, this technique is expensive, time consuming, require dangerous chemicals, produces large amount of harmful wastes and quantitatively also not suitable.
The synthesis of the heteropoly compounds via electrodialysis is rather more complicated since it requires the electrodialysis of a mixture of its ingredients and then the mixture is subjected to thermal treatment for many hours and then further followed by dialysis to obtain the desired product. Inspite of plentiful of dilemmas, Maksimov et al applied electrodialysis to synthesise iso and heteropoly acids of various structures in highly concentrated aqueous solutions⁴.

Matkovic et al investigation demonstrates that the “ion exchange” methodology is suitable for the synthesis of phosphotungstic and molybdic acids in a high yield⁵. In general, ion exchange methodology is superior method as it yields pure and non-degraded acids. Matkovic experiments indicated that the use of an organic media greatly favors the ion exchange since a lower amount of resin is required than in aqueous media. Wijesekera et al patented the synthesis of phospho-molybdic Wells-Dawson-type polyoxometallates through an ion exchange methodology in aqueous media⁶.

1.4 STRUCTURE ELUCIDATION OF HETEROPOLY COMPOUNDS

Structural characterization of ion exchangers can be completed by spectroscopic studies, XRD and thermal analysis.

1.4.1 SPECTROSCOPIC STUDIES

Infrared spectroscopy: Infrared spectroscopy (vibrational spectroscopy) is a simple and reliable technique widely used in inorganic/organic chemistry in research and industry. It is used in quality control, dynamic measurement and monitoring applications. Vibrational spectroscopy (IR spectra) is an extensively used tool in polyoxometalate chemistry mainly for structure elucidation and to identify M-O bonds in the polymeric backbone of the ion exchanger. There are four types of metal-oxygen linkages present in the most elaborated structure (XM₁₂O₄₀):

- X-O-M, long and weak bond (4 internal oxygens connecting X-M),
- M-O-M (12 edge sharing oxygen connecting M’s),
- M-O-M (12 corner sharing oxygen) and
- M-O, having almost double bond character (12 terminal oxygen bonding to M atom).
The region of interest for Keggin type heteropoly compounds is from 1100-600 cm\(^{-1}\) designating the absorptions due to metal-oxygen stretching vibrations. The stretching frequencies in lacunary heteropolyanions are different than those of Keggin structure\(^7\). Lacunary compounds \((\text{XM}_{11}\text{O}_{39})^\text{n}\) have a defected structure in which one metal atom and its terminal oxygen atoms are mislaid. These anions have a central cavity surrounded by five oxygen atoms and thus, they perform as pentadentate ligands.

**Scanning Electron Microscopy & Energy Dispersive Spectroscopy (SEM & EDS):** SEM and EDS are the analytical techniques used for the elemental analysis or chemical characterization of a sample with a high magnification images at high resolution combined with the ability to generate localised chemical information. It is based on the principle of interaction of the electrons of the atoms with a beam of electrons in a raster scan pattern that make up the sample producing signals containing information about the sample's surface topography, composition and other properties such as electrical conductivity. A typical EDS spectrum is portrayed as a plot of x-ray counts vs. energy peaks representing the various elements present in the sample. Its characterization capability is due to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum\(^8\).

**1.4.2 X-RAY DIFFRACTION TECHNIQUE**

X-ray diffraction is the most reliable and advanced technique used to determine the crystallinity of the ion exchange materials and the composition on an atomic scale. The technique involves nondestructive methodology and yields crystal structure information relatively easy in an atmospheric environment. XRD analysis involves the methodology by which multiple beams of X-ray create a three dimensional picture of the density of electrons of any crystalline structure. The wavelength of X-rays is of approximately same order of magnitude as equivalent to the interatomic or intermolecular distance between atoms in crystalline materials and therefore, crystals act as diffraction gratings for X-rays. In X-ray diffraction work, we normally distinguish between single crystal and polycrystalline or powder applications.

**1.4.3 THERMAL ANALYSIS**

TGA, DTA and DTG measurements give an idea about
(i) Quantitative measurement of mass change in materials associated with transition and thermal degradation.

(ii) Number and nature of water molecules present in the HPA.

(iii) Thermal stability characteristics of the exchanger material.

TGA is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature variation in a controlled atmosphere. TGA records the change in mass due to dehydration, decomposition and oxidation of a sample with time and temperature. The results of thermogravimetric analysis gave the evidence for the presence of two types of water molecules in heteropoly compounds i.e. “water of crystallisation” and “constitutional water molecules”. The total loss of crystallisation of water usually occurs at temperatures 170-200°C.

1.5 UNIQUE FEATURES OF HETEROPOLY COMPOUNDS

1.5.1 STRUCTURE AND MOLECULAR WEIGHT

Heteropolyacid salts have a complex cage like structure and very high molecular weight. They are multifunctional and their chemical composition can be altered very easily.

1.5.2 SOLUBILITY

They are insoluble in non-polar solvent. But the heteropoly salts of small cations are soluble in water. Solubility of the heteropoly compounds in water must be attributed to very low lattice energy and solvation of cations. Solubility is governed by packing considerations in the crystals.

1.5.3 HYDRATION

The crystalline as well as amorphous both salts confirmed the presence of great number of water molecules forming hydrated complex. They melt in their own water of hydration between 40°C to 100°C. In dry air, they begin to lose water molecules.
1.5.4 ACIDIC BEHAVIOUR

They are strong bronsted acids. Therefore, act as strong oxidizing agents and can be very readily changed to fairly stable reduced form and these reduced species are called “heteropoly blues”. Structure, composition of heteropolyanions, extent of hydration, type of support, thermal treatment, etc. govern the acidic and related properties of the HPA’s. Solid heteropoly compounds are pure bronsted acids.

1.5.5 COLOUR

Most of the HPA’s are white. But existence of coloured compounds can not be denied.

1.5.6 STABILITY

They exhibit the structural mobility. All heteropolyacid and their salts decomposed in strongly basic solutions. The final degradation products of these compounds are simple oxometalates ions. Thermal stability is also quite high. The decomposition at high temperatures causes loss of water molecules, consequently modification in acidity also. Heteropolyacids are generally used as solid acid catalysts for vapour phase reactions at high temperatures.

1.5.7 MULTIFUNCTIONALITY

Partial exchange of protons which are loosely bonded with other cations can alter both the structural features as well as catalytic properties. They behave as cation exchanger due to the presence of exchangeable protons contained in the structural hydroxyl groups. HPAs possess appropriate redox properties, which can be redesigned by varying the chemical composition of heteropolyanion.

1.5.8 CATALYSIS

They can function as homogeneous as well as heterogeneous catalysts for the organic syntheses. Their use gives environmentally benign results.

1.6 INORGANIC ION-EXCHANGERS

The key component of a sensor is the ionophore or electroactive component which imparts the selectivity and enables the sensor to respond selectively to a particular
analyte. These inorganic compounds in the form of ion exchange materials have found extensive applications in analytical chemistry as well as in industrial chemistry in view of their elegant characteristics such as insoluble matrix, stoichiometric exchange, good selectivity, specificity and applicability to column operations. Synthetic inorganic ion exchangers are useful in the separation of radioactive materials and other analytical applications can also be achieved even at elevated temperatures. Organic resins are not suitable for such applications, as they will exhibit severe decline in ion exchange capacity as well as selectivity on exposure to radiations, owing to physical degradation at both the molecular and macroscopic level. Besides, the above limitations, degradation also accounted at high temperatures. Inorganic ion exchangers can be implanted in an inert binder material like PVC or epoxy resin for membrane fabrication and the glass transition temperature ($T_g$) of the polymer defines the compatibility as a sensing membrane. If a polymer is having high $T_g$ value, then inorganic ion exchangers exhibit high selectivity for specific ions resulting much larger separation than those exhibited by organic resins. Rigid structure and no appreciable dimensional change during ion exchange reactions, leads to specific and unusual selectivities. Hydrous oxides incorporated with anions such as phosphates, vanadates, molybdates and antimonates produced excellent ion exchangers.

Inorganic ion exchangers were first classified by Vesely and Pekarek in 1972. In 1988, Clearfield classified ion exchangers with significant ion exchange capacity into 14 categories. Again in 1995, Clearfield classified ion exchangers into three categories based on their structures:

**1.6.1 HYDROUS OXIDES**

This class principally contains hydrous oxides of zirconium and tin. These hydrous oxides have also been referred to as framework hydrates as explained by England et al.

**1.6.2 LAYERED ION-EXCHANGERS**

These ion exchangers are either oxides or phosphates of group 4 and 14 or layered double hydroxides. In group 4 and 14, phosphates are the most extensively studied exchangers of this class.
1.6.3 EXCHANGERS WITH TUNNEL STRUCTURES

Exchangers with tunnel structure were first reported by Clearfield\textsuperscript{20}. Clearfield and Stynes did the pioneer work in the field of inorganic ion exchanger by crystallizing zirconium phosphate\textsuperscript{21}. Ammonium phosphotungstate and ammonium molybdophosphate were probably the foremost heteropoly compounds, which have been studied as ion exchangers\textsuperscript{22}.

1.7 CHARACTERIZATION OF ION-EXCHANGER

An ion exchanger is characterized by the parameters like:

1.7.1 ION-EXCHANGE CAPACITY

The ion exchange capacity conveys about the number of ionogenic groups contained per gram of the exchanger material, when the material is completely converted to H\textsuperscript{+} form, which is devoid of sorbed solutes and solvents. It can be expressed as the quantity of ions that can be swapped by a specific volume of the resin. The characteristic constant obtained in this way is called scientific weight capacity and is expressed in units of milli-equivalents per gram (meq/g). Equivalents refer to the equivalent weight (E\textsubscript{W}) of the substance expressed in grams or meq in milligrams (mg).

Ion exchange capacity of a material is determined for its characterization as an ion exchanger. The ion exchange capacity can be estimated very easily by means of column operation methodology. However, most of the synthetic inorganic ion exchangers behave as weak ion exchangers and therefore, their direct titration is not practicable, where H\textsuperscript{+} ions of the exchanger are replaced by cations of a neutral salt and then, the equilibrium ion exchange capacity is determined by pH titration.

1.7.2 SORPTION STUDIES

Distribution of an ion between exchanger phase and the solvent gives the measure of the selectivity of the exchanger for that particular ion. Distribution coefficients and consequential selectivity, helps to predict the separation of different counter ions. Batch adsorption procedure was followed to carry out the sorption studies. The selectivity may depend upon following factors:

- Donnan potential
- Sieve action
Complex formation

The Distribution coefficient (K_d) value were calculated after attainment of the equilibrium from the equation

\[ K_d = \frac{I - F}{I} - \frac{X}{0.2} \]

Where I is the initial volume of EDTA used to neutralise the metal ion, initially and F is the final volume of EDTA (after the attainment of equilibrium) used to neutralise the metal ion.

1.8 ELECTROCHEMICAL PROPERTIES OF ION-EXCHANGE MEMBRANES

According to the theory of permselectivity, properties of certain natural and artificial membranes can be explained by the existence of the easily dissociated ions that are loosely bounded to the fixed groups of the opposite charge. Above properties help inorganic membranes for their use in cells for electrolytic desalting of brackish water \(^{23}\), fuel cells and electrical storage batteries \(^{24}\). The basic theory of permselective membranes and their electrochemical properties was first developed by Teorell and then by Meyer and Sievers \(^{25-26}\). An ideal permselective membrane is difficult to produce but can be approximated by careful choice of such membrane variables like the composition and physicochemical properties.

These ion-exchange materials have the following analytical applications:

- Ion-selective electrodes.
- To locate the end point in indicator titrations.
- Ion-exchange paper chromatographic separations.
- Micro determination by ion exchange colorimetry.
- Electrophoresis.
- Purification of substances.

Separations of metal ions, catalysis and use of ion exchange membranes as ion selective electrodes are the most widely accepted applications. As inorganic ion exchangers are solid and insoluble. They can be easily incorporated into some inert polymeric matrix so as to give heterogeneous membranes.

A sensor material should possess the following qualities:

- Compatible with the matrix,
Right proportion,
Appropriate grain size (1-15nm),
Rapid ion exchange at the membrane-solution interface with low solubility product.

1.9 APPLICATION AS ION-SELECTIVE ELECTRODE

More than thousands of ion exchangers have been synthesised during the last few decades. Majority of these are amorphous in nature but crystalline form can also be synthesised after digestion and then their structure elucidation was done to elaborate their nature, composition and structure. Ion exchanger today forms one of the most important groups of chemical sensors. However, for many analytes especially for anions and heavy metal ions, considerable efforts have led to the development of selective sensors for alkali, alkaline earth and rare earth metal ions\textsuperscript{27-30}. Ruzicka et al\textsuperscript{31} were the first investigators to introduce liquid state electrode based on carbon.

Potentiometric sensors have found the most widespread practical applicability since the early 1930’s, due to their simplicity, familiarity and cost.

Types of Potentiometric Sensors
(a) Ion-selective electrodes (ISE),
(b) Field-effect transistors and
(c) Potentiometric solid state sensors with new sensing systems, namely solid contact electrodes\textsuperscript{32} (SCE).

Synthetic ion exchangers are mixed with inert binders, like SBR, epoxy resin, polystyrene or polyvinyl chloride etc. in an optimum proportion so as to provide working strength to the membrane. A large number of such electrodes have been prepared by Mittal et al\textsuperscript{33-39} and applied for the quantitative analysis of analyte samples.

1.9.1 THEORY OF POTENTIOMETRIC ION SENSORS

Ion sensors work on the principle of chemical sensing in which information is obtained about the chemical composition of a system with the help of an amplified electric signal produced by it. It involves two sequential steps: recognition and intensification. Interaction of an ion with the electrode is highly precise. The signal
(electrode) is amplified (pH meter) in order to obtain the information in an applied and authentic form. The recognition (selectivity) is based on assorted chemical interaction, while a transducer translates the magnitude of the signal into a measure of the amount of the analyte in different perceivable ways. Two types of interactions are there: (i) surface interaction where the interested species is adsorbed at the surface and (ii) bulk interaction in which the species under consideration partitions between the sample phase and the sensor.

Potentiometric ion sensors are based on the principle of sensing the metal ion by ion selective membrane. These sensors make use of the development of an electrical potential at the surface of a solid material when it is placed in a analyte solution. Ions penetrate the boundary between two phases generating an electrochemical equilibrium, in which potentials difference between two phases are formed. The magnitude of the potential difference generated between the phases is governed by activities of the target ion in these phases and the measurement of the cell potential is made under a 'zero current' condition. Equilibrium means the transference of analyte ions from the membrane into solution is equivalent to the transfer of the same from the solution to the membrane. If the ion selective membrane separates two solutions of different ionic activities \(a_1\) and \(a_2\) and mounted membrane is permeable to only specific ion, then the potential difference \(E\) across the membrane is described by the Nernst equation:

\[
E = E^0 + \frac{RT}{z_x F} \ln \left( \frac{a_2}{a_1} \right) \tag{1.1}
\]

If activity of the target ion \(a_1\) in its respective phase is kept constant, the unknown activity \(a_\chi\) in phase 2 is related to EMF generated:

\[
E = \text{constant} + \frac{RT}{z_x F} \log \left( \frac{a_\chi}{a_1} \right) = \text{constant} + S \log_{10} (a_\chi) \tag{1.2}
\]

Where, \(S = 59.16 \div z_x \text{ mV at 298 K}\) and \(z_x = \text{charge of the analyte}\).

The potential difference can be measured between two identical reference electrodes placed in two phases. Practically, the potential difference (electromotive
force) is measured between an ion selective electrode and a reference electrode, placed in the sample solution and the observed signal is a collective measurement of potentials difference created at all solid-solid, solid-liquid and liquid-liquid interfaces.

A series of analyte ion solutions can be used to draw the response curve/calibration curve of an ion selective electrode. Plot of electromotive force versus the activity of analyte is used to find the linear range which in turn explains the activity of the target ion in any unknown solution. However, it should be specified that only at constant ionic strength, a linear relationship between the signal measured and the concentration of the analyte is maintained as the activity is directly proportional to the concentration.

Practically, there is not even a single membrane which is truly selective for a single type of ions and completely non-selective for other ions. The potential of such a membrane is not only governed by the activity of the primary (target) ion and but also by the activity of other interfering ions. The consequence of the presence of interfering species in a sample solution on the measured potential difference can be taken into consideration in the Nikolski-Eisenman formalism:

\[ E = E^0 + S \left[ \log (a_x) + (z_x/z_y) \cdot \log (K_{xy}.a_y) \right] \]

where, \( a_y \) is the activity of an interfering ion, \( z_y \) is its charge and \( K_{xy} \) represents the selectivity coefficient (determined experimentally).

### 1.9.2 CHARACTERIZATION AS ION SELECTIVE ELECTRODE

Characterization as ion selective electrode can be done with the help of following properties:

**Selectivity Coefficient:** Selectivity coefficient (\( K_{A,B_{pot}} \)) is an important parameter of ISEs as it often determines whether a reliable measurement in the sample is possible or not. Selectivity means the extent to which it can determine particular analyte in a complex mixture without any interference of any other components present in the mixture\(^{40}\). Then the term “selectivity” promoted and definition was revised as Selectivity is the
recommended term in analytical chemistry to express the extent to which a particular method can be used to determine analytes under given conditions in the presence of other components of similar behavior. Different methods of the selectivity determination can be found in the literature.

The IUPAC suggests three methods: Separate Solution Method (SSM), Fixed Interference Method (FIM) and Matched Potential Method (MPM). If the electrode exhibits non-Nernstian response, the values of $K_{A,B_{pot}}$ obtained by the SSM, FIM or MPM method depends up on the activity of the interfering ion. Gadzepko et al determined the selectivity coefficient of the membrane electrode against a number of interfering ions by using Matched Potential Method (MPM).

Ion exchangers prefer one species over another due to several causes:

- Electrostatic interaction between the charged framework and the counter ions
- Size, valency and nature of the counter ion.
- Interactions between ions and their environment.
- Sterically exclusion from the narrow pores of the ion exchanger.

All these effects may lead to preferential uptake of a species by the ion exchanger. This precise ability of the ion exchanger to distinguish between the various counter ion species is called selectivity.

**Slope:** According to the Nernst equation, slope of the linear part of the calibration curve of the electrode is

- 59.16 mV/decade at 298 K for a single charged analyte ion,
- 59.16/2 = 29.58 mV per decade for a double charged analyte ion,
- 59.16/3 = 19.72 mV per decade for a triple charged analyte ion.

However, in certain applications the value of the electrode slope is not in accordance with Nernstian equation but this deviation from Nernstian slope does not exclude its usefulness.

**Linear Range and Detection Limit:** According to IUPAC recommendations, the detection limit is defined by the cross-section of the two extrapolated linear parts of the
ion selective calibration curve. The observed detection limit is often governed by the presence of other interfering ions or impurities. Electrode calibration curve generally exhibits a linear response range between $10^{-6}$ and $10^{-1}$ M, although at a high and very low target ion activities, there are deviations from linearity. It is possible to enhance the detection limit down to $10^{-10}$ M with the help of suitable metal buffers.

**Response Time:** According to IUPAC recommendations, it was defined as the time at which the ion concentration in a solution is changed on contact with ISE and a reference electrode and it is the first instant at which the potential of the cell becomes equal to its steady-state value within 1 mV or has reached 90% of the final equilibrium value. This definition can be extended to consider the drift of the system. In this case, the second time instant is defined as the time at which the e.m.f vs. time slope becomes equal to a limiting value. Practically, it is calculated by measuring the time required to achieve 90% of the equilibrium potential from the moment of addition of metal ion solution.

**Nature of Solution:** Varying conditions such as pH and the non aqueous medium are taken into consideration.

**Lifetime:** Lifetime of a sensor refers to the time period during which the sensor can be used effectively for the determination of the analyte and it is determined by the stability of the ion exchanger material.

### 1.9.3 RARE EARTH METAL IONS

Rare earth elements have been traditionally defined as 4f block elements with atomic numbers 57-71 as well as the elements yttrium and scandium which behave chemically similar to the lanthanide elements. The electronic configuration of free atoms of most of the lanthanide series is generally accepted to be $\text{[Xe]} \, 4f^n 5d^0 6s^2$.

**Coordination:** The lanthanide ions have a high charge, which favour the formation of complexes. They are strong reducing agents. Lanthanides have high coordination number varying from 6-9 and give a variety of stereochemistry. Coordination numbers 10 and 12 occur in the larger lanthanides and small chelating ligands $\text{NO}_3^-$ and $\text{SO}_4^{2-}$. The complex
[Ce(NO$_3$)$_6$]$^{3-}$ has one of the largest, 12-coordinated geometry known among lanthanides$^{44}$. Many techniques have been applied to study the coordination chemistry of rare earth elements$^{45}$. However, the selective determination of these metal ions is complicated by virtue of similarity in their chemical properties and the fact that they all exist mostly as trivalent cations in solution$^{46}$.

**Toxicity:** Rare earth elements are extremely toxic if they tend to remain in the lungs, liver, spleen and kidneys$^{47}$. The toxicity of rare earth elements causes loss of muscle coordination, labored respiration and cardiovascular collapse. Rare earths can degrade DNA molecules and have been reported to produce tumors at the site of interaction$^{48-49}$. They can also bond with plasma proteins and accumulate in bones$^{50}$.

**Uses:** Lanthanides are generally used as catalysts in the production of glasses, superconductors, in optoelectronics applications, cathode ray tube technology and television sets. These are used in making colour TV's tubes and LED and also used for ulcer therapy and edema therapy studies$^{51-53}$. Uses of resins as artificial kidneys, bacterial adsorbents, catalysts etc. testify to the widespread applications of these materials. In laboratories, ion-exchangers are used as an aid in analytical and preparative chemistry. Ion exchangers have the distinction of being the only successful technique for their separation and selective determination from mixtures.

**1.10 APPLICATION OF HETEROPOLY COMPOUNDS AS CATALYST**

Catalysis by heteropolyacids (HPA) and related compounds is a field of growing importance, attracting attention worldwide in which many novel and exciting developments are taking place both in the area of research and technology and their compounds act as consistent candidates as green, eco-friendly and effective catalysts$^{55-57}$.

Although, there are many structural categories of HPAs, but the majority of the catalytic applications constitute the most extensively studied and important class of polyoxometalates, Keggin-type HPAs because of easy availability and chemical stability$^{58}$. The Keggin structures possess qualities such as good thermal stability, high acidity, undergo fast reversible multi-electron transfers, mobility of protons at the
electrocatalytic interfaces and high oxidising ability. Other catalysts such as Wells-Dawson and Preyssler heteropolyacids have begun to be used.\textsuperscript{2,59} The use of conventional liquid and Lewis acids such as sulphuric acid, hydrochloric acid, hydrofluoric acid, zinc chloride, aluminum trichloride and boron trifluoride are no longer considered as a reliable means for synthesis because of numerous shortcomings and therefore, there is an urgent need to eliminate the aggressive mineral acid from the acid catalysed processes.\textsuperscript{60} Global efforts are going on to replace the conventional liquid acid catalysts by the solid acid catalyst.

1.10.1 LIMITATIONS OF CONVENTIONAL ACID CATALYST

Though, the mineral and Lewis acids are widely used in different industries for the production of quantitative yield of the products, they are having certain limitaions:

- Poses threat in handling,
- Risky disposal,
- Difficulty in regeneration due to their corrosive nature,
- Sophisticated storage,
- Highly volatile,
- Toxicity,
- Contamination of products,
- Purification by costly methods,
- Liquid acids also involve large investment for treating the effluents.

1.10.2 ADVANTAGES OF USING HETEROPOLYACIDS SALTS AS CATALYST FOR VARIOUS SYNTHESSES

Activity: Molar catalytic activity of heteropolyacid salts is thousands times greater than that of mineral acids.

Separation: Being heterogenous in nature, they can be easily recovered from the reaction mixture by simple filtration. Moreover, the exhausted catalyst can be regenerated and reused after activation or without activation, thereby making the process economically viable.
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**Reuse:** In many cases, heterogeneous catalysts can be recovered with only minor change in activity and selectivity so that they can be conveniently used in continuous flow reactions reducing the generation of waste byproducts\textsuperscript{61-63}.

**Prevention from corrosion:** Use of solid acids eliminates the corrosive action of liquid acids.

**Ecofriendly:** Use of solid (heterogeneous) catalysts in organic synthesis and in the industrial manufacturing of chemicals is important since they provide green alternatives to the homogeneous catalysts\textsuperscript{64}.

Numerous developments are being carried out in basic research as well as in fine chemistry processes\textsuperscript{65}. In recent times, inorganic solid acid catalysed organic transformations are gaining much more importance due to the proven advantage of heterogeneous catalysts. Heterogeneous catalysts are used extensively in protection or deprotection processes in organic synthesis\textsuperscript{66}. They may find wide applications in fine chemical industry such as fragrance, pharmaceutical and food\textsuperscript{67-68} etc.

**1.10.3 REACTIONS PROMOTED BY HETEROPOLYACID SALTS**

- Cyclisation & Isomerisation
- Alkylation & Dealkylation
- Hydration & Dehydration
- Esterification & Trans-esterification
- Condensation & Hydrolysis
- Oxidation & deoxidation
- Acylation
- Etherification
- Polymerisation
- Protection reactions
- Reduction and various other miscellaneous reactions involve heteropolyacid salts as catalyst.
Salts of heteropoly acids have been studied in different organic transformations under heterogeneous conditions\textsuperscript{69-70}. They play a vital role in the treatment of environmental pollutants. Keggin-type heteropolyacids show remarkable acid catalytic properties\textsuperscript{71-74} that are of practical importance as illustrated in numerous reviews\textsuperscript{75-78}. The fact that heteropolyanions undergo spontaneous adsorption (from aqueous solution) on various substrates provides a simple mechanism for modification of electrode surfaces. The applications of heterogeneous acid catalysts in place of homogeneous acid catalysts in organic synthesis is the interesting area of research in the laboratory as well as in the industrial context. Because of exclusive physicochemical properties, they have found various industrial applications, in numerous processes\textsuperscript{79-81}. The use of HPAs salt in non-polar solvents improves product selectivity and moreover, separation of HPA's salt from the reaction mixture is effortless\textsuperscript{7}.

1.10.4 ACID CATALYSIS IN HETEROPOLYACID SALTS

The catalytic property of the heteropoly compounds is associated with the strong Bronsted acidity, which is comparatively superior to the mineral acid catalysts. They are highly efficient and selective in catalytic reactions. Moreover, due to the inert nature of the anions, they do not pop in side reactions like chlorination, sulphonation and nitration as observed in mineral acids. The negative charge of the heteropolyanion spread over a much larger surface area resulting in less interaction but easy dissociation of the proton. In aqueous and non-aqueous solutions, the heteropolyacid salts consists of solvate ion-pairs $\text{H}^+ (\text{H}_2\text{O})_m \text{HPA}^n$ in which the protons are hydrated and linked to the anion as a whole and not to a specific centre in heteropolyanion. Higher the negative charge on the central sphere, larger will be its acid strength. That’s why; generally tungstophosphoric acids and its salts are most widely employed as compared to other HPA containing other metal ions. They are easy to use and no side reactions are observed with the heteropolyacid salts.
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