Chapter 4

Chemical Properties of Soils

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Abstract

Soil is a complex system comprising of inorganic and organic constituents, air, water, microorganisms and plant roots. Soil develops from parent material through pedogenic processes which involves different physico-chemical reactions. Once the soil is developed, its different bio-geo-chemical properties are originated which greatly influence soil’s capacity to support plant growth and perform various environmental and ecological functions. These bio-geo-chemical properties of soils controls different reactions in soils which control adsorption-desorption, dissolution-precipitation and oxidation-reduction of different elements including essential plant nutrients in soil. Chemical properties of soils are the most important owing to their overwhelming role in chemical processes. Soil colloid is the most active fraction of the soil which controls all these chemical properties. Soil colloid may be of organic or inorganic nature but inorganic colloid dominates in most of the soils. Soil colloids carry negative charge which may be permanent or variable depending upon its mode of development. Inorganic colloids include layer silicates, oxides of iron and aluminum, allophones/amorphous clays. Chemical properties of soils include soil reaction, ion exchange, base saturation percentage, buffering capacity and soil reduct potential. Conventionally, type and nature of soil colloid, origin of charges on soil colloids and soil chemical properties are dealt with Soil Chemistry. However, with

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increasing environmental issues, soil chemistry has now very multi-farious applications ranging from chemical properties controlling nutrient availability to the plants, to different environmental issues. In this chapter, soil colloid and its types, charge development, different chemical properties of soils and their application in agriculture and environmental studies have been discussed.

**Keywords:** Colloidal Particles, Charge Development, Soil Reaction, Diffuse Double Layer

### 4.1. Introduction

Soil is a porous media having multi-components which include solids, liquids and gases. Soil is developed from parent material (rocks) through various pedogenic processes occurring at the land surface. These pedogenic processes are derived from biological, geological and hydrological phenomena. Although, the soil is developed from the rocks and minerals but biogeochemical properties of the soil are different from those of parent material. Among different properties of soils, chemical properties are very important because these control solubility and bioavailability of different chemical compounds in soils. This implies the importance of chemical properties of the soil which establish strong relationship between soils and agricultural productivity by influencing bioavailability of nutrients to the plants. Chemical properties of soils are greatly influenced by the nature of parent material and different soil forming processes occurring during soil formation. Soil colloidal particles (clay and humus) are chemically the most active fraction of the soils that contribute to soil chemical properties. Soil colloidal particles are the sites for chemical reactions occurring in the soils. Several types of clay colloids are present in soil and most of clay colloids have layered structures (layer silicate clays). These particles carry net negative charge which could be of permanent or variable nature depending upon mode of charge development. In addition to these aspects, soil liquid phase (soil solution) is very important which is seat of all chemical reactions occurring in the soil. Soil solution contains dissolved ions, substances and oxygen which ultimately provide nourishment to the plants through water movement, dissolution, dissociation, oxidation-reduction, availability of the nutrients to the plants.

Soil chemistry is the branch of Soil Science that deals with bio-geo-chemical processes occurring in soils and their effect on the solubility, mobility, distribution, and chemical forms of essential plant nutrients and contaminants in soils. Better understanding all these processes would help to predict the fate and toxicity of elements in soils and their economical remediation through different strategies for sustainable environment and agriculture, nutrient retention and their release and ultimately availability to plants. Traditionally, soil chemistry focuses on chemical and biochemical reactions governing nutrient phyto-availability, organic and inorganic fertilization and their environmental consequences particularly related with nitrogen and phosphorus fertilization. But, recently focus of soil chemistry has shifted from its traditional role in agriculture to its emerging role in environmental quality of soil and water resources. Understanding the reactions and bio-geo-chemical processes of nutrients, potential pollutants and contaminants in soils will
enable a more accurate prediction of fate and toxicity of contaminants, and development of remediation strategies.

4.2. Chemical Principles

Mole is the basic unit used to indicate the amount of chemical substance and is abbreviated as mol. It is associated with chemical formula of the substance and contains $6.02 \times 10^{23}$ (Avogadro number) chemical entities (atoms, molecules or ions). The millimole (mmol) is $1/1000^{th}$ of mole and is used to measure the smaller amounts of chemical substances. Molar mass (also known as molecular weight) is the mass of 1 mole of that substance and is calculated by summing up atomic masses of all the atoms appearing in the chemical formula of a substance. For example, one mole of water ($H_2O$) contains $6.02 \times 10^{23}$ molecules which is equal to 18 g (2 g atoms of H and 16 g for one atom of oxygen). Similarly, one mole of Hydrogen gas ($H_2$) contains $6.02 \times 10^{23}$ H atoms which is equal to 2 g. Molarity (Molar concentration) is the unit of concentration and is defined as number of moles of a substance dissolved per liter of the solution (Skoog et al. 2006) and is abbreviated as $M$. For example, one molar solution (1 $M$) of Na means one mole of Na (23 g) dissolved in one liter of solution. Molality is the number of moles of a substance dissolved per kilogram of solvent. Molality depends upon the volume of solvent which changes with temperature and pressure and thus molality also changes but molarity remains constant. Mole fraction is the ratio of the number of moles of substance in solution with total number of moles of all constituent substances of that solution including number of moles of water in case of aqueous solution (Tan 2011, Skoog et al. 2006). Gram Equivalent (Equivalent weight) is the amount of a substance that can combine with or displace one gram of hydrogen (equal to Avogadro number of charges). Normality is the number of gram equivalent of solute dissolved per liter of the solution and it is abbreviated as $N$. Equivalents can be easily used to indicate concentration of ions or nutrients due to stoichiometric nature of exchange reactions and can be obtained by dividing molecular weight with valency of that ion (Tan 2011). Equivalents have been replaced with mole of ion charge. For example, one mole of Ca$^{2+}$ equals 40 grams of Ca$^{2+}$ while mole of ion charge would contain 20 grams of Ca$^{2+}$. Another unit of concentration is mg L$^{-1}$ or mg kg$^{-1}$ which is used to express very low concentration and previously was termed as parts per million (ppm).

4.3. Soil Colloids

Clay and organic particles which are so small that they tend to remain suspended in standing water are called soil colloidal particles (soil colloids). The soil’s colloidal system is made up of the clay particles and highly decomposed organic matter or humus. The colloidal particles are also referred as micelles (microcells) (Weil and Brady 2016).
4.3.1. **Properties of Soil Colloids**

The colloids are chemically the most active fraction of soil and have distinct properties which are explained below.

4.3.1.1. **Extremely small size**

Colloids have extremely small size of about 1 µm and these cannot be seen with an ordinary (light) microscope. Colloidal particles can be seen only with the help of an electron microscope. Some soil scientists consider 2 µm as upper limit of size for colloidal particles to coincide with definition of clay particles (Weil and Brady 2016).

4.3.1.2. **Surface area**

The surface area and particle size are inversely related with each other. If the size of the particle is smaller, the surface area of the particle would be greater and vice versa. Due to extremely small size, colloids have large surface area which is more than 1000 times compared to the same mass of sand particles. Some silicate clays also possess large internal surface area due to plate like structure in addition to external surface area. The total surface area of soil colloid ranges between 10 m$^2$ g$^{-1}$ for clays with only external exposed surface to 800 m$^2$ g$^{-1}$ for those clays having internal surface exposed.

4.3.1.3. **Charged particle**

Colloid is a charged particle which may carry negative or positive charge on its internal or external surfaces. Most of the soil colloids carry negative charge with exceptions of highly acidic conditions where colloid may carry positive charge. Mode of origin of charge on soil colloids can vary among different types of colloids and some time prevailing chemical conditions e.g. pH could also influence charge. It attracts ions of an opposite charge towards its surface i.e., the negatively charged surfaces of a soil colloid attract cations (positively charged ions).

4.3.2. **Types of soil colloids**

Soil colloids are classified into organic (e.g., humus) and inorganic colloids (e.g., clay). Inorganic colloids are further classified into different groups based on their composition, structure and properties. The colloids present in soils are classified into four major classes: 1) crystalline silicate clays; 2) non-crystalline silicate clays; 3) iron and aluminium oxides; and 4) organic colloids (humus).

4.3.2.1. **Crystalline silicate clays (Phyllosilicates)**

Crystalline silicate clays are the dominant type of soil colloids present in most of the soils except the soils belonging to Andisols, Oxisols and Histosols. These clays have crystalline structure with an orderly internal arrangement. Crystalline structure of silicate clays consists of series of layers which are stacked on each other like the pages of a book. These layers are made up of sheets of silicon, aluminum, magnesium, and/or iron atoms surrounded by oxygen and hydroxy1 groups. In silicate clays, Silicon (Si$^{4+}$) tetrahedron and Aluminium (Al$^{3+}$) octahedron are basic structural units. Tetrahedron consists of a Si$^{4+}$ atom (as a central cation) surrounded by 4 oxygen atoms (as ligands) leading to the formation of structure having 4 sides.
Numerous tetrahedra (plural of tetrahedron) are linked together horizontally to form a silica tetrahedral sheet. Octahedron is composed of Al$^{3+}$ (as central cation) surround by six oxygen or hydroxyl ions (as ligands) resulting in the formation of structure having 8 sides (Fig. 4.1).

**Fig. 4.1** Silicon tetrahedron and aluminium octahedron

Various octahedra link together horizontally to form an octahedral sheet. The tetrahedral (silica) and octahedral alumina sheets are bound together by shared oxygen atoms to form different layers (Fig. 4.2). The specific nature and combination of these sheets in the layers vary from one type of silicate clay to another and largely control the physical and chemical properties of silicate clays.

**Fig. 4.2** The basic molecular and structural components of layer silicate clays
Based on number and arrangement of tetrahedral and octahedral sheets in the crystal units, silicate clays are classified into three different groups.

**i. 1:1 type silicate clays**

These are silicate clays in which one silica tetrahedral sheet is attached with one alumina octahedral sheet. Both types of sheets are tightly bound with each other due to shared oxygen atoms between two layers (Fig. 4.3). Oxygen is shared between two layers in such a way that that one apical oxygen of tetrahedron also serves as basal oxygen of upper-lying octahedral sheet. Alternating octahedral and tetrahedral sheets are stacked on each other in such a way that exposed hydroxyl atoms of one layer are adjacent to exposed oxygen atoms of the other layer. This type of arrangement leads to the formation of hydrogen bond between two layers which results in non-expansion of these silicate clays. Due to this, 1:1 type of silicate clays has low surface area thus leading to very low surface charge and low cation exchange capacity. This type of silicate clays includes kaolinite, halloysite, dickite, etc.

![Fig.4.3 Kaolinite](image)

**ii. 2:1 Type silicate clays**

In this type of silicate clays, one octahedral sheet is sandwiched between two tetrahedral sheets. The 2:1 type silicate clays are differentiated based on kinds and amounts of isomorphic substitution in tetrahedral and octahedral sheets. Isomorphic substitution leads to development of permanent charge (explained in section 3.4.1). The charge per unit formula balanced by cations other than the cations in crystal lattice is called as layer charge. Amount of layer charge determines the types and strength of interlayer bonds and thus plays important role in rendering expansion or non-expansion of silicate clays. If the layer charge is more, stronger will be the bond...
between layers and vice versa. Layer silicates are sometime differentiated based on
eightahedral positions occupied by cations. When two of three octahedral positions are
occupied by trivalent cations, the mineral is called as \textit{dioctahedral} but when all three
positions are occupied by divalent cations, then mineral is called as \textit{trioctahedral}
(Bohn et al. 2002). These types of silicate clays are further divided into expanding
and non-expanding type of silicate clays.

Smectite (montmorillonite is a common member of this group) is an important group
of expanding silicate clays. Expansion of such clays occurs due to the addition of
water to interlayer space (Fig. 4.4). In contrast to kaolinite, top and bottom planes of
adjacent sheets consist of exposed oxygen atoms and thus leading to weak oxygen-
oxygen bond giving characteristic expansion property to these silicate clays. Due to
expansion, C-spacing of these silicate clays varies between 9.6-21.4 Å Exchangeable
cations and associated water molecules are strongly attracted towards interlayer
spaces and thus layers separate apart from each other due to pushing water molecule
in the interlayer space. Due to expansion of interlayer space, internal surfaces are
exposed leading to very high specific surface area of these silicate clays. High surface
area (600-800 m$^2$ g$^{-1}$) and high layer charge lead to high cation exchange capacity of
montmorillonite which ranges between 80-120 cmol$\_c$ kg$^{-1}$. Expansion of these
silicate clays due to interlayer water molecule gives very high plasticity, stickiness
and cohesion to these clays. These clays make soils very hard on drying and very
sticky and slippery on wetting thus causing cultivation of these soils very difficult.
Such soils develop wide cracks on drying which make these soils undesirable for
construction activities. Vermiculites is another group of silicate clays which are also
classified as expanding type but their expansion is considered intermediate between
kaolinite and smectite which ranges between 14-15 Å. Their expansion is larger than
kaolinite but much lesser than smectites. This property is since unlike smectite group,
these silicate clays contain strongly adsorbed water molecules, Al-hydroxy ions and
cations such as magnesium which serve as bridge between two layers rather than
simply separating apart.

Micas are major non-expanding 2:1 type silicate clays and are primary minerals in
the soils. Among the micas, biotite and muscovite are commonly found in sand and
silt fraction while illite and glauconite are found in clay fraction (Fig. 4.5). The main
source of charge in micas is substitution of Al$^{3+}$ in about 20% of the Si$^{4+}$ sites in
tetrahedral sheets and thus leads to development of strong negative charge even more
than vermiculites. Due to strong negative charge, cations particularly K$^+$ is strongly
attracted towards interlayer spaces and strongly bind the adjacent layers due to
formation of strong bond O-K-O. This type of interlayer bonding restricts expansion
of mica type clays. Despite having high layer charge, micas have very low CEC (20-
40 cmol$\_c$ kg$^{-1}$ and surface area (70-120 m$^2$ kg$^{-1}$). Behavior of these silicate clays is
similar to kaolinite in terms of plasticity, stickiness and adsorption capacity for water
and cations.
iii. **2:1:1 Type silicate clays**

In this type of silicate clays, one additional magnesium dominated trioctahedral sheet (brucite) is sandwiched between two adjacent 2:1 type layers and thus termed as 2:1:1 type silicate clays (Fig. 4.6). These are non-expanding silicate clays due to presence of magnesium-dominated trioctahedral sheet (which serves as a cation) between two 2:1 type layers. Colloidal properties of chlorites are almost similar to those of fine-grained micas. This type of silicate clay has cation exchange capacity of 10-40 cmol$_c$ kg$^{-1}$ and surface area 70-150 m$^2$ g$^{-1}$. Such type of silicate clays is common in sedimentary rocks.

4.3.2.2. **Non-crystalline silicate clays**

In soils, there are significant quantities of colloidal matter that is not sufficiently ordered to be detected by X-ray Diffraction due to the lack of three-dimensional crystalline structure. These are more difficult to study than those minerals which have well-defined crystalline structure. These clays consist of tightly bonded silicon, aluminum and oxygen atoms but these clays lack ordered structures. These are formed from volcanic ash and are dominantly found in Andisols. These clays carry both positive and negative charges which are pH dependent. These minerals possess plasticity when wet and have very low degree of stickiness. These minerals have extremely high adsorption capacity for phosphate and other anions particularly under acidic conditions. These clays include allophane and imogolite. Allophanes have high CEC (10-150 cmol$_c$ kg$^{-1}$) which is highly variable due to presence of pH dependent charges on these minerals.
4.3.2.3. **Iron and aluminum oxide/hydroxide**

These clays are present in a variety of soils but predominantly in the soils of warm and humid regions (highly weathered acid soils, i.e., Ultisols and Oxisols). These minerals have iron and aluminum atoms coordinated with oxygen atoms but Al is dominantly associated with $H^+$ ions to make hydroxide. Some of these minerals like gibbsite ($Al$-oxide) and goethite ($Fe$-oxide) occur as crystalline sheets while other oxide minerals are non-crystalline and occur as amorphous coatings on soil particles. They have relatively low plasticity and stickiness and carry slightly negative to moderately positive charge depending upon the soil pH. Although, generally these minerals are termed as oxides for simplicity but these are hydroxides and oxyhydroxides due to the presence of hydrogen ions. Examples of these minerals include limonite ($FeO_x.H_2O$), goethite ($FeOOH$), hematite ($Fe_2O_3$), magnetite ($Fe_3O_4$), gibbsite ($Al_2O_3.3H_2O$), boehmite ($AlOOH$) and alumina ($Al_2O_3$).

4.3.2.4. **Organic soil colloids (humus)**

This type of colloids is important in all types of the soils due to its very small size, large surface area and high CEC. These colloids are not well structured and are composed of carbon, hydrogen, oxygen and nitrogen rather than aluminum, silicon.
and oxygen like the silicate clays. These colloids have no stickiness/plasticity and have very high water holding capacity. Due to non-cohesiveness, soils rich in organic colloids have low soil strength and are not suitable for engineering constructions like roads and buildings. The organic colloidal particles vary in size but they may be at least as small as the silicate clay particles. The humus colloids are amorphous and are not stable like clay and possess high CEC. These colloids carry both positive and negative charges but negative charge is dominant and pH dependent which is very high in neutral to alkaline soils. The humus colloid has functional groups containing covalently bonded hydrogen which dissociates with the increase in pH to produce negative charges on the humus colloid. These functional groups include enolic (-COH = CH), carboxylic (-COOH), phenolic (-C₆H₅OH) and amide (NH =).

![Fig. 4.6 Structure of 2:1:1 type silicate clay](image)

**4.3.3. Role of clays in agriculture and environment quality**

Clays greatly influence soil physical, chemical and biological properties. As discussed in previous sections, clays differ in surface area, surface charge density, shrinkage and expansion. Their role in agricultural productivity, environmental quality and engineering activities is dependent on these properties. For example, soils rich in 1:1 type silicate clays have high adsorption capacity for P due to ligand exchange of phosphate anion (PO₄³⁻) with functional groups OH⁻ present on the exposed broken edges of these clays. Similarly, soils rich in 2:1 type silicate clays, like mica, have more K availability as compared to other soils as mica is the primary source of K in soils and provides K on sustainable basis due to weathering. Generally, soils having clay minerals with high CEC and more surface area, are termed as fertile
soils as such soils have high water-holding and nutrient holding capacities and less nutrient losses through leaching. In addition to the role of silicate clays in agricultural productivity, environmental quality is also greatly influenced by their presence in the soils. Soil clays control the movement of contaminants in the soils due to presence of negative charges on their surface. Most of the pollutants are cations and, thus, are attracted strongly by clays when present in soils and consequently prevent their movement and availability to plants. Clays play crucial role in purification of groundwater as most of the pollutants present in percolating water are retained by clays. Engineering activities are greatly affected by the type of soil clays as soil provides base to all type of engineering activities. Soil physical properties, like plasticity, cohesion, shrinkage-swelling and dispersion-flocculation, are important for engineering activities. Soils which are rich in swelling type of clays are not suitable for heavy engineering constructions like dams, buildings and highway constructions. Differential swelling/shrinkage of clays cause cracks in the buildings, roads and dams. However, swelling type of clay can be effectively used in environmental studies. Swelling types of clays are used to seal the ponds, sewage lagoons, industrial waste lagoons and landfills (Weil and Brady 2016) and prevent leaching/seepage from these constructions. A layer of smectite on the bottom or sides of constructions prevents the movement of water and contaminants due to swelling on wetting.

### 4.4. Development of Negative Charges

Soil reactivity depends upon surface area and surface charge. Surface area of the soil is inversely proportional to its particle size. Most of the surface area of the soils is due to presence of colloidal particles (< 2 µm) like clay and humus which are also charged particles and sources of charges for soils. In the soils, charges are originated through two major phenomena viz. isomorphic substitution and ionization of surface functional groups and thus give rise to permanent and variable or pH-dependent charges, respectively.

#### 4.4.1. Isomorphic substitution

Isomorphic substitution is the replacement of central ion with another ion of similar size but having different charge in the crystal lattice of silicate clays during growth of crystals leading to the development of positive or negative charge depending upon the valence of substituting ions in the central position of octahedral or tetrahedral coordination (Fig. 4.7). This type of charge remains unchanged after its development and thus is termed as Permanent Charge. Net negative charge will be developed if higher valent cation (e.g., Al$^{3+}$) is replaced with lower valent cation (e.g., Mg$^{2+}$). This type of substitution is common in Al-dominated dioctahedral sheets of smectite, vermiculite, and chlorite. While in some other case, Si$^{4+}$ is replaced by Al$^{3+}$ in tetrahedral sheets of fine grained mica, vermiculite and some time in smectites. Positive charge will appear if lower valence cation (Mg$^{2+}$) is replaced by higher valence cation (Al$^{3+}$) in trioctahedral hydroxide sheet present in the interlayer spaces of chlorite. Isomorphic substitution is the major source of negative charges for 2:1
and 2:1:1 type silicate clays but is of minor importance for 1:1 type silicate clay (Bohn et al. 2002).

![Fig. 4.7 Isomorphic substitution Al\(^{3+}\) in octahedral coordination by Mg\(^{2+}\) leading to the development of negative charge](image)

### 4.4.2. Ionization of surface functional groups

Ionization of surface functional groups (OH\(^-\) group) from the surfaces of inorganic and organic colloids, and broken edges of silicate clays leads to the development of variable charge. These functional groups include hydroxyl (-OH), carboxyl (-COOH), phenolic (-C\(_6\)H\(_4\)OH) and amine (NH\(_2\)). This type of charge varies with pH of the soil and thus termed as pH-dependent or variable charge. Moderately acidic or neutral soils carry minor pH dependent charges. As pH increases, H\(^+\) ion from OH or COOH group dissociates leaving one negative charge unsatisfied. In some cases, removal of positively charged complex aluminum hydroxyl ions like Al(OH)_\(_2^+\) lead to the development of negative charge. At low pH, this complex ion block the negative sites on silicate clays but as the pH increase this ion react with OH\(^-\) in soil solution to form insoluble Al(OH)_3. The silica layer develops a negative charge from the oxygen ions along the edge of the crystal. Only one of the two negative charges of oxygen is combined with a silicon ion. Therefore, oxygen ions at the end of the crystal have one negative charge unsatisfied. Depending on the activity of H\(^+\) in the soil solution, either hydrogen is added to the structure (protonation) or released from the structure (deprotonation). So, this charge is called a pH-dependent charge or a variable charge. It is the main source of charge in 1:1 type layer silicates, Fe and Al oxides and hydroxides, allophone and humus. Effect of pH on the cation exchange capacity or negative charges of soil colloids is illustrated in the following equation. At the exposed crystal edges and flat external surfaces of minerals, the covalently bonded hydrogen of hydroxyls dissociates at pH level of more than 7 leaving negative charges carried by oxygen. The loosely bonded hydrogen is readily exchangeable.

\[
\text{No charge} \quad \text{Solution} \quad \text{One -ve charge}
\]

In some cases, the inorganic soil colloid may be responsible for -ve charge (high pH), no charge (intermediate pH) or +ve charge (low pH) due to fluctuation in pH as demonstrated below.
So, the primary source of variable charge is due to loss or gain of $\text{H}^+$ ions from functional groups on the surfaces of soil solids.

### 4.5. Soil Solution

The water present in soil pores is known as soil solution and it serves as interface between soil, atmosphere, biosphere and hydrosphere. Soil solution is the immediate source of nutrients for terrestrial organisms including plants. Soil solution is the most important medium by which chemical elements are transferred to life system via plant root absorption. Soil solution is not electrically neutral, and contains more cations compared to anions. This is due to the reason that net negative charge of soil colloids is balanced by excessive cations present in soil solution (Bohn et al. 2002).

Among dissolved solids present in soil solution, those which are dissociated into ions are the most important which influence different chemical reactions occurring in soil solution. Composition of soil solution is influenced by soil parent material, precipitation and dissolution of minerals in soils, density and type of vegetation and soil drainage. Addition of chemical fertilizers and organic matter and absorption of nutrients by plant have significant effect on composition of soil solution (Khattak 1996). The ions present in soil solution are the predominant and immediate source of nutrients to plants required for their growth. Continuous supply of nutrients in soil solution is ensured by different types of interactions between ions and soil particles. These interactions include weathering of soil minerals, organic matter decomposition, rainwater and irrigation water containing soluble salts and desorption of ions from soil colloid (Bohn et al. 2002). All these sources replenish nutrients in soil solution continuously. Once the ions are released into soil solution, ions are subjected to different losses. Ions present in soil solution are retained by the soil through different surface mechanisms to interact with soil particles and the soil may retain these ions thereby preventing their leaching.

#### 4.5.1. Chemistry of soil solution

Ions present in solution are seldom present in free state, rather, these ions are surrounded by water molecules or other ions. As concentration of solution increases, free movement of ions correspondingly decreases and their interaction with each other increases. In very dilute solutions, ions move freely in solutions while in case of concentrated solutions, ions and water molecules interact with each other and with other ions (Khattak 1996). Due to these interactions, the chemistry of soil solution is very complex. Water molecule, due to its bipolar nature, strongly reacts with ions present in soil solution. Ions interact with each other at longer distance (> 0.5 nm) in the diluted solution and this type of interaction is explained by the concept of chemical activity which is defined as:

\[
\alpha = \gamma M
\]
where $\alpha$ is activity, $\gamma$ is the activity co-efficient and $M$ is molarity. Under ideal conditions, when concentration approaches zero, then $\gamma$ approaches one and concentration and activity become equal. Interaction of ions in soil solution is influenced by amount of all the charges present in soil solution which is explained by ionic strength ($I$).

$$I = \frac{1}{2} \sum MZ^2$$

Where $M$ is molarity and $Z$ is charge. Effect of all ions present in soil solution on activity coefficient was explained by Debye and Huc kel in 1924 by proposing an equation

$$\log \gamma = -AZ_i^2 I^{1/2}$$

where $\gamma$ is activity co-efficient, $A$ is constant for aqueous solution at 25 °C. This equation is known as Debye-Huckel limiting law due to its application for very dilute solutions and works well up to ionic strength of 0.01 $M$. However, this equation does not work well at high concentrations and thus modified later to make this equation valid under conditions where ionic concentration approaches 0.1 $M$:

$$\log \gamma = -AZ_i^2 \left( \frac{1}{1 + BqI^{1/2}} \right)$$

Where $B = 0.33$ for aqueous solution at 25 °C and “$a$” is individual ion parameter determined experimentally. Davies further modified this equation which gives fairly good results for ion activity co-efficient over the range of ionic concentrations prevailing in soil solutions and fresh waters (Sposito 1989; Bohn et al. 2002)

$$\log \gamma = -AZ_i^2 \left( \frac{1}{1 + I^{1/2}} - 0.3 I \right)$$

Measuring ion activity is necessary to understand the availability of nutrients to the plants in soil. Ion or nutrient activity decreased in concentrated solution due to close range interaction (< 0.5 nm) that leads to the formation of Ion Pairs and Complex Ions of ions with each other (Fig. 4.8). Ions in ion pairs and complex ions lose their separate entity and behave like a single entity in soil solution (Khattak 1996; Bohn et al. 2002).

![Simple diagrams of ion pair and complex ions](image-url)
In complex ions (also known as inner sphere complex), central cation is surrounded by one or more ligand. Ligand is any ion which is present in coordination sphere of central ion. In case of ion pairs (outer sphere complex), anions attached with central cation in second solvation sphere and thus weakly attached with central cation as compared to complex ion. Many of alkaline and transition metals are present in soil solution as ion pairs or complex ions. Complex ions/ion pairs are formed when attractive force between cation and anion supersede attractive forces between cations and H⁺ for ligands including water (Ghafoor et al. 2013). Formation of mono-fluoro-aluminium complex during Al³⁺ extraction from soil is the simple example of complex ion formation

\[
\text{Al} (\text{H}_2\text{O})_6^{3+} + \text{H}^+ + \text{F}^- \rightarrow \text{AlF} (\text{H}_2\text{O})_5^{2+} + \text{H}_2\text{O}
\]

The strength of association between different ions in solution is explained by different equilibrium constants. Stability constant (formation constant or binding constant) is equilibrium constant for complex ions and indicates interaction between reagents that comes together for complex ions formation. Stability constant helps to calculate concentration of complexes in soil solution and has useful application in soil chemistry, pure chemistry biological studies and medicines (Ghafoor et al. 2013). Stability constant for above mentioned complex ion can be calculated as

\[
K_{\text{AlF}^{2+}} = \frac{\text{[AlF}^{2+}]\text{[H}^+][\text{F}^-]}{\text{[Al(H}_2\text{O})_6^{3+}]}
\]

The water of hydration is ignored due to excess of water in aqueous solution. Similarly, hydrolysis (deprotonation) constant is equilibrium constant of H⁺ dissociated from water ligand attached to the central cation. Ion pairs or complex ions are soluble in soil solution but their presence decreases the activity of individual ions and influence different chemical reactions in soil solution like ion exchange, nutrient availability and nutrient leaching.

**4.6. Diffuse Double Layer**

In dry soil, ions directly reside on soil colloids and are held tightly but in wet soils, ions are not tightly held by soil colloids (Fig. 4.9). Negatively charged soil colloids attract cations from soil solution and forms distinct layers of ions containing both positive and negative charges and this layer is known as diffuse double layer (DDL). Diffuse double layer is also known as Helmholtz double layer and describes the electrical phenomenon at liquid-solid interface. Diffuse double layer theory is based on the assumptions of Gouy-Chapman which states that: 1) exchangeable cations exist as point charges; 2) colloidal surfaces are infinite and planar; and 3) charge is uniformly distributed on the surface of colloid. In DDL, cations concentration decreases with increasing distance from the surface of soil colloid and become equal to anions concentration in bulk solution (point in soil solution where colloid has no influence on dissolved ions). Two forces are responsible for counter ions in DDL: electrostatic attractive force draws in the cation towards negatively charged surface while repulsive force between anions and negatively charged surface push the anions into bulk solution and maintain electrical balance. Later, Stern proposed model to
explain the retention of ions in double layer. He proposed that some ions are strongly adsorbed by charged surface and thus not subjected to changes. This layer of ions which strongly adsorbed on charged surface is called as Stern layer while other ions form diffuse double layer of ions which diffuse away into bulk solution. Diffuse double layer has role in adsorption and desorption of ions in soil, nutrients availability and dispersion/flocculation of soil colloidal particles.

Fig. 4.9 Diffuse double layer

4.7. Ion Retention

The most important property of soils is ion retention and their ultimate slow release into soil solution to match with plant absorption. The ion retention by soils has dual function of keeping ionic concentration in soil solution at optimum level. This phenomenon keeps the ion concentration in soil solution at adequate level but not at ideal level. The quest for maximum crop yields has put pressure on soils and thus may require boosting the ionic concentration in soil solution to the desired level through fertilization. Soils retain ions through process of ion exchange. Soil chemistry mainly deals with cation exchange process while ignoring anion exchange process due to dominance of negative charge on soil particles. Ion retention by soils can be divided into two categories; weaker electrostatic retention of alkali and alkaline earth metals and strong retention of trivalent and transition metals through chemical bonding of polyvalent cations with $O^2-$ and $OH^-$ of silicate clays, hydroxides and phosphates. Retention of ions through chemical bonding is known as precipitation or strong adsorption and is influenced due to different precipitation-dissolution reactions (Bohn et al. 2002).
4.7.1. Ion exchange

As already discussed, soil colloids carry positive or negative charges which may be permanent or variable. Irrespective of nature of charges, soil colloids attract oppositely charged ions which constantly vibrate in a swarm near the colloidal surface and are held by electrostatic force of attraction. Break away ions from this swarm are replaced by those ions present in soil solution. This process of ion replacement in the swarm by other ions in soil solution is referred to as ion exchange. This is the most important property of the soil, by which soil retains and releases the ions slowly into soil solution. If soil colloids carry positive charge, then it will attract and exchange negative ions (anions) with soil solution and process would be known as anion exchange. Conversely, if soil colloid is negatively charged, it will attract and exchange positive ions (cations) with soil solution and the process will be known as cation exchange. Due to dominance of negative charges on soil, cation exchange is widely discussed while ignoring the anion exchange process.

4.7.1.1. Principles of cation exchange reactions

i. Reversibility

Cation exchange reactions are reversible and can proceed in both directions depending upon the concentration of reactants or concentration of products. Consider simplest case of cation exchange in which sodium ion (Na\(^+\)) on soil exchange complex is replaced by H\(^+\) ion in soil solution. If Na is added into the soil, then reaction will move to left and vice versa. In the following reaction “X” represents soil exchange complex

\[
NaX + H^+ \rightleftharpoons HX + Na^+
\]

ii. Stoichiometry

Cation exchange reactions are always stoichiometric in nature emphasizing the replacement of ions with each other on charge equivalence basis. For example if soil exchange complex is occupied by one Ca\(^{2+}\) ion, then two monovalent cations (Na\(^+\)) will be needed to replace adsorbed divalent cation (Ca\(^{2+}\)) from exchange complex and vice versa.

\[
CaX + 2 Na^+ \rightleftharpoons 2NaX + Ca^{2+}
\]

iii. Mass action

Cation exchange reactions are reversible reactions and their direction is controlled by law of mass action. According to law of mass action, rate and direction of reaction is determined by concentration of active ion. If concentration of active ion is increased, it would have more chances to replace the ion present on exchange complex.

\[
CaX + 2Na^+ \rightleftharpoons 2NaX + Ca^{2+}
\]

High concentration of Na in this reaction will drive the reaction in forward direction.
iv. Anion effect

During the process of cation exchange, anions are always accompanying the exchanging cations and thus can greatly influence exchange reactions. As direction of exchange reaction is dependent upon concentration of active ion and will move in the right direction if the ion released from exchange site is removed from the system through precipitation, volatilization or strong association with anion. The role of anion is very important and thus will determine the direction of reaction. For example, if $\text{H}^+$ ion from exchange site is replaced by $\text{Na}$ from $\text{NaOH}$ and end product will be $\text{H}_2\text{O}$ molecule which dissociates very weakly and thus reaction will move in right direction and exchange reaction will not be reversed. Consider another case where $\text{H}^+$ is replaced by $\text{Na}$ from $\text{NaCl}$ and end product will be $\text{HCl}$ which strongly dissociate and thus free $\text{H}^+$ will reverse exchange reaction.

\[
\text{HX} + \text{Na}^{2+} \text{ (from NaOH)} \rightleftharpoons \text{NaX} + \text{H}_2\text{O} \quad \text{(poorly dissociated)}
\]

\[
\text{HX} + \text{Na}^{2+} \text{ (from NaCl)} \rightleftharpoons \text{NaX} + \text{HCl} \quad \text{(strongly dissociated)}
\]

v. Valence dilution

Cations (irrespective of valence) present in soil solution are always in equilibrium with those present on soil colloids. Addition of the water into soil will disturb this equilibrium and favor the adsorption of multivalent cations compared to the monovalent cations.

vi. Cation selectivity

Cations are held by the soil colloid with different strength and thus arranged in the order of strength with which they are held by soil (lyotropic series). Generally, cations with smaller hydrated size and high charge density are strongly adsorbed and thus less likely to be exchanged. Different types of minerals present in the soil preferred particular cation for adsorption. For example, vermiculites and fine grained mica has the preference for potassium ($\text{K}^+$). Potassium is strongly attracted towards the inter layer spaces and thus fixed in interlayer spaces strongly.

vii. Complementary cations

Soil is very complex system where cation exchange does not take place between two different ions present on soil colloid and soil solution only. Soil colloid is occupied by many different cations which are in equilibrium with similar type of diverse cations in soil solution. Cations present on soil colloid affect the replacement of neighboring cation and this phenomenon is known as complementary cation effect. For example, it would be easy to replace $\text{Ca}^{2+}$ by $\text{NH}_4^+$ from $\text{Ca}^{2+}$-$\text{Al}^{3+}$ system than from $\text{Ca}^{2+}$-$\text{Na}^+$ system.

viii. Speed

Exchange reactions are very rapid and instantaneous in nature which leads to the existence of dynamic equilibrium between soil solid and solution phases. Speed of the exchange reactions is only affected by movement of ions from or to exchange complex. This is important in case of field conditions where diffusion of ions is restricted by tortuous nature of soil pores.
4.7.2. Cation exchange capacity

Cation exchange capacity (CEC) is an amount of exchangeable cations that a soil can retain and exchange with soil solution at specific pH. Previously milliequivalent per 100 g soil (me 100 g\(^{-1}\)) was used to express CEC but presently moles of charge per kg\(^{-1}\) is used to express CEC. For convenience and calculating whole number, centimoles of charge per kg\(^{-1}\) are generally used which is equivalent to me 100 g\(^{-1}\) soil.

1 me = 1 mmol_c (millimole of charge)
1 me 100 g\(^{-1}\) = 1 mmol_c 100 g\(^{-1}\)
1 me 100 g\(^{-1}\) = 10 mmol_c 1000 g\(^{-1}\) (multiply and divide by 10 on right side)
1 me 100 g\(^{-1}\) = 10 mmol_c kg\(^{-1}\) (1000 g = 1 kg)
1 me 100 g\(^{-1}\) = 1 cmol_c kg\(^{-1}\) (10 mmol_c = 1 cmol_c)

4.7.2.1. Factors affecting cation exchange

i. Soil pH

Cation exchange capacity of soils is directly related with soil pH. Cation exchange capacity of soils is the consequence of presence of negative charges on soil particles and it varies with the change in negative charge on soil particles. In soils, two types of charges are present \textit{viz.} permanent and variable charges. Permanent charges remain constant while variable charges vary with a change in soil pH (explained in section 3.4.2). As the pH increases, negative charges on soil colloids, particularly organic colloids, allophones, oxides of Fe and Al and 1:1 type silicates, increase and thus cation exchange capacity is also increased.

ii. Type of soil colloids

The type of the colloids present in soil has significant effect on CEC of the soil. As already discussed in section 3.3.1.2., 2:1 types silicate clays (expanding type) have high charge density and surface area compared to the 1:1 type silicate clays. The soils which contain 2:1 silicate clay have high CEC than those having 1:1 type silicate clays provided that total amount of clay contents is equal.

iii. Organic matter

Organic matter is a source of variable charges in soils and thus contributes in CEC. More OM in soils more would be the CEC of soils and vice versa. One percent increase in soil organic matter results in 2 cmol_c kg\(^{-1}\) increase in CEC of soil.

4.7.2.2. Significance of CEC

Cation exchange capacity is an important phenomenon in soil fertility, reclamation of salt-affected soils, alleviation of soil acidity/alkalinity, retention of pollutants and purification of percolating water. Significance of CEC is explained as below.
i. Soil fertility

Plants absorb nutrients mainly from soil solution and concentration of various nutrients in soil solution depends on the concentration of nutrients present on exchange sites. Most of the cations (Ca$^{2+}$, Mg$^{2+}$, K$^+$) which are held by soils on its exchange sites are plant nutrients, except Al$^{3+}$. Cation exchange is the process which drives cations from exchange sites into soil solution and thus plays a very important role in plant nutrition. For example, K is an important macronutrient and exchangeable K is the major and immediate source of K for plants which become easily available through the process of cation exchange. Similarly, exchangeable Ca and Mg serve as potentially available sources for plants. Cation exchange process slows down the leaching losses of some nutrients like Ca$^{2+}$, Mg$^{2+}$, K$^+$ and NH$_4^+$. After application of fertilizer, concentration of these nutrients become very high in soil and thus may be subjected to leaching losses but soils retain these nutrients due to cation exchange capacity. These nutrients are adsorbed on exchange sites and later on, are released slowly into soil solution.

ii. Correction of soil acidity

Soil acidity and alkalinity are undesirable soil conditions for plant growth and thus need to be managed properly. Under highly acidic soil conditions (i.e., pH below 5.8), exchange sites are pre-dominantly occupied by H$^+$ and Al$^{3+}$ ions which make soil conditions unfavourable for plant growth. To make the conditions suitable for plant growth, H$^+/Al^{3+}$ must be replaced from the soil’s exchange sites and rendered inactive. The excess H$^+$ and Al$^{3+}$ ions on the soil’s exchange sites are replaced with Ca$^{2+}$ ions through liming, i.e., application of lime (CaCO$_3$), increases the pH of the acid soil and pH moves towards neutrality. Rise of soil pH up to 5.8 with liming is considered adequate for the growth of most crops. Cation exchange capacity of soils helps to calculate the amount of lime required to ameliorate the soil acidity. Soils with high CEC require more lime and vice versa.

iii. Reclamation of sodic/saline-sodic soils

Sodic and saline-sodic soils are characterized by the presence of excessive amount of Na$^+$ on exchange sites which deteriorate soil physical and chemical properties. Soluble source of Ca$^{2+}$ (gypsum) is applied to reclaim the sodic/saline-sodic soils. Soluble Ca$^{2+}$ obtained due to the dissolution of gypsum in soil solution replaces Na$^+$ ions from soil’s exchange sites by mass action and thus reclaiming the sodic/saline-sodic soil. Application of gypsum to sodic and saline-sodic soils is accompanied by heavy irrigation which leaches down the desorbed Na into deeper layers of soils and improves soil physical and chemical properties.

\[
2\text{NaX} + \text{Ca}^{2+} \quad \text{(from gypsum)} \rightarrow \text{CaX} + 2\text{Na}^+ \quad \text{(leached down)}
\]

iv. Purification of percolating water

Soil colloids serve as sorbent for many pollutants present in soil and water passing through soil due to the presence of negative charges. Soils purify the percolating water by adsorbing different pollutants present in the water and this is very important in case of waste water. Waste water contains variety of organic and inorganic pollutants (Fe$^{2+}$, Cu$^{2+}$, Mn$^{2+}$, Pb$^{2+}$, Ni$^{2+}$, Cd$^{2+}$) which are adsorbed by soil while
percolating through soil. Adsorption of these pollutants by soil colloids is due to
cation exchange capacity and thus CEC plays very important role in purification of
groundwater.

4.8. Soil Reaction (pH)

Soil pH is defined as negative log of hydrogen ion concentration \([\text{H}^+]\) (expressed in
moles per liter) or hydrogen ion activity \((\text{H}^+)\) (Weil and Brady 2016; Ghafoor et al.
2013). Unit of pH is mole per liter if it is defined in terms of hydrogen ion
concentration but it becomes unitless if it is defined in terms of hydrogen ion activity.
Soil pH indicates the degree of soil acidity or soil alkalinity and greatly influences
soil physical, chemical and biological properties. The pH scale varies from 0 to 14
with pH 7 as the neutral point (Ghafoor et al. 2013). As pH is inversely related with
hydrogen ion concentration/activity, increasing \(\text{H}^+\) ions would decrease the soil pH
causing more acidic conditions. As pH increases from 0 to 7, soil conditions remain
acidic but between pH 7 to 14 the soil conditions are alkaline/basic (Bohn et al.
2002). Mathematically, pH can be expressed as (Khattak 1996; Ghafoor et al. 2013):

\[
\text{pH} = \log \frac{1}{\text{[H]}} = -\log(\text{H})
\]

We can derive this equation as follows

\[
\text{HOH} \rightleftharpoons \text{H}^+ + \text{OH}^-
\]

\[
\frac{[\text{H}][\text{OH}]}{[\text{HOH}]} = \text{Kw}
\]

Concentrations of \(\text{H}^+\) and \(\text{OH}^-\) are expressed in mol L\(^{-1}\) while Kw is equilibrium
constant of water which is equal to \(10^{-14}\).

One mole of \(\text{H}_2\text{O}\) is equal to 18 g at 25 °C and one liter of water is equal to 997 g.
There will be 55.93 moles in one liter of water.

\[
\text{HOH} = 55.39 \text{ mol L}^{-1}
\]

\[
[\text{H}^+] = [\text{OH}^-] = 10^{-7}
\]

Or

\[
(\text{H}^+) = (\text{OH}^-) = 10^{-7}
\]

By taking log on both sides

\[
\log (\text{H}^+) = \log (\text{OH}^-) = \log 10^{-7} \text{ or pH} = \text{pOH} = 7
\]

4.8.1. Significance of soil pH

Many of plant species and microbial populations in soils are pH sensitive. Common
field crops like alfalfa, barely, beans, sugarbeet, clover and sugar cane grow well at
pH range of 6-8 while rice, maize, tobacco, wheat, peas and peanuts grow well at pH
range of 5.5 to 7.0. However, most of forest trees grow well at the pH range of 4-7
Soil pH affects the availability of essential plant nutrients and other elements in the soil for root uptake by plants. For example, micronutrients, except for molybdenum (Mo), are more soluble in slightly acidic to moderately acidic soils, while macronutrients are more soluble at alkaline pH. Among the macronutrients, availability of P is more sensitive to pH changes. Phosphorus availability in soils is optimum in the range of pH 6.0 and 7.5. At low pH (i.e., < 6.0), P is precipitated with iron (Fe) and aluminium (Al) and at alkaline pH (i.e., > 7.5), P forms insoluble compounds with calcium (Ca). Most nutrient deficiencies can be avoided at soil pH 5.5 to 6.5, provided the soil minerals and soil organic matter contain adequate essential plant nutrients. The soil pH can also affect the types of micro- and macroorganisms present in the soil (Tisdale et al. 2006). Earthworms are usually absent from very acid soils but fungi prefer acidic conditions and bacteria prefer a neutral soil. This last point can be very important when growing peas and beans (legumes) because if the soil is too acid the rhizobium bacteria which fix nitrogen for the legumes will not be able to survive, so neither will the legumes, so that a vital part of the crop rotation may be lost. Another aspect of unfavourable soil pH affecting plant growth is through soil microorganisms inducing slime-mould which causes club root, a disease of crucifers; slime-mould thrives only in acid soils and raising the soil pH with liming can reduce or eliminate this problem.

4.9. Base Saturation Percentage

It is the amount of basic cations (Ca, Mg, Na, K) which a soil can adsorb on its surface (exchange complex) at some particular soil pH and is expressed in terms of percentage. Base saturation is positively related to soil pH because a high base saturation value would indicate that the exchange sites are dominated by basic cations. Indirectly, base saturation indicates the extent of leaching of exchangeable basic cations (Ca, Mg, K, Na) from soils. The soils of arid/semi-arid regions have high basic cation saturation as compared to soils of humid regions. Percent base saturation is calculated as:

\[
\text{Percent Base Saturation (\%) = } \frac{\text{Sum of exchangeable basic cations (Ca}^{2+}, \text{Mg}^{2+}, \text{K}^+, \text{Na}^+)/\text{CEC at a specific pH}}{\times 100}
\]

4.9.1. Significance of base saturation

Basic cation saturation percentage is considered an indicator of soil fertility. Soils having high base saturation, can easily release adsorbed cations into soils solution for plant absorption. For example, a soil with > 80% of base saturation is considered to be very fertile soil, a soil with base saturation between 50-80% is considered to be medium fertile soil and soil with base saturation of < 50% are considered to be non-fertile soil. Base saturation percentage is very important in soil classification to differentiate between mollie epipedon and umbric epipedon.
4.10. **Buffering Capacity**

Capacity of the soil to resist the change in pH on addition of acid or base is called buffering capacity of soil. In soils, soil acidity has three distinct pools, viz., active acidity, potential acidity and residual acidity. Residual acidity plays a crucial role in buffering of soil by maintaining equilibrium between these three pools of soil acidity. Potential acidity in soils maintains the equilibrium with active acidity. For example, if base is added into soil solution, this will disturb the equilibrium of $H^+$ ions in soil solution. At this stage, potential acidity will release $H^+$ ions into soil solution and this would restrict any change in pH due to disturbance of equilibrium of $H^+$. Similarly, if some acid is added into soil solution, excess $H^+$ in soil solution added due to acid would be adsorbed by potential acidity and thus any change in pH would be nullified. In soils clay and soil humus act as principal buffering agents because these both provides adsorbing sites for $H^+$.

4.10.1. **Significance of buffering capacity**

Soil buffering capacity is very important due to agricultural and environmental reasons. Drastic fluctuations in soil pH in the absence of buffering capacity would have detrimental consequences on plants, soil microorganism and aquatic ecosystem. For example, plants absorb most of the essential nutrients at pH around 6-7 but if soil pH is not buffered, pH may be very high or very low thereby interfering in the availability of plant nutrients and ultimately plant growth. Well buffered-soils prevent acidifying effect of acid rains on soils and drainage water. Buffering capacity determines the amount of amendment (sulfur or lime) required to bring the desired change in soil pH.

4.11. **Point of Zero Charge**

This is pH of a soil where net charge on soil particles becomes zero. The point of zero charge is a fundamental description of a mineral surface which explains that the total concentration of surface anionic sites is equal to the total concentration of surface cationic sites. If the pH is more than PZC, the net charge on soil surface would be negative. Conversely if the pH is less than PZC, net charge on the soil surface would be positive (Appel et al. 2003).

4.12. **Soil Redox Potential ($E_h$)**

Redox potential is derived from reduction and oxidation. This indicates the capacity of some substance to accept or donate electrons. Soil redox potential represents the availability of electrons in the soil system. In redox reactions, there is simultaneous occurrence of oxidation and reduction of two substances involved in reaction where one substance is reduced while other substance is oxidized. This property of soils is related with soil aeration. In well aerated soils, oxidized states of elements dominate while in poorly aerated soils, reduced forms of elements dominate. For example, in well aerated soils, oxidized form of iron ($Fe^{3+}$) and nitrogen ($NO_3^-$) will dominate...
while in poorly aerated soil reduced form of iron (Fe$^{2+}$) and nitrogen (NH$^+_4$) will dominate.

### 4.12.1. Significance of rodex potential

Redox potential is linearly related with soil pH and pH greatly influences nutrient availability to plants. Redox potential can be used to indicate aeration status of soils. Aeration of soil can greatly influence different physical, chemical and biological properties of soils. Low redox potential indicates that soil is submerged and has deficiency of oxygen. Deficiency of oxygen in soil greatly influences root respiration, and microbial activity. At low redox potential, iron is present as Fe$^{2+}$, manganese as Mn$^{2+}$, nitrogen as NH$^+_4$ and sulfur as H$_2$S while at high redox potential these elements are present as Fe$^{3+}$, Mn$^{4+}$, NO$_3^-$ and SO$_4^{2-}$. Changes in redox potential of soil drastically changes microbial population in soils. At low redox potential, anaerobic microbes will dominate while at high redox potential, aerobic microbes will dominate.

### 4.13. Exchange Equations

Irrigation water, liming, weathering, fertilizations and acid rains disturb the equilibrium between exchangeable cations and those present in soil solution thereby necessitating the prediction of exchangeable cations in soils (Bohn et al. 2002). The relationship between exchangeable cations and those present in soil solution is predicted by different exchange equations which provide valuable information about elemental deficiencies or imbalance, movement of toxic metals and soil dispersion (Khattak 1996; Bohn et al. 2002). Most of exchange equations have limited applicability under field conditions because these equations consider simple exchange reactions between ions against actual multi-element exchange process, constant exchange capacity, simple stoichiometry and complete reversibility of reactions (Ghafoor et al. 2013; Tan 2011; Bohn et al. 2002). Simplest exchange reaction is

\[
\text{CaX} + 2\text{Na}^+ \rightleftharpoons 2\text{NaX} + \text{Ca}^{2+}
\]

Reaction co-efficient would be

\[
k = \frac{(\text{NaX})^2}{(\text{Ca}^{2+})}(\text{CaX})(\text{Na}^+)
\]

This equation is known as Kerr Equation which assumes that ionic concentration is directly proportional to ionic activities and this equation works well at low concentrations.

Another equation was proposed by a chemist Gapon in 1933 known as Gapon Equation. This equation has considerable application in soils particularly sodic/saline-sodic soils for Na-Ca exchange. This equation was based on the law of mass action and takes into ion concentration instead of ion activity. In this equation, exchanging cations are expressed on chemically equivalent basis. The Gapon equation cannot be applied satisfactorily on entire range of Na-Ca exchange, however its application is quite encouraging for range of ionic concentration suitable
Chemical Properties of Soils

for irrigated agriculture. Generally, range of Gapon constant is 0.010 to 0.015 (L mmol$^{-1}$) in agricultural soils (Bohn et al. 2002). The Gapon Equation is written as under

$$\text{Ca}^{1/2}X + \text{Na} \rightarrow \text{NaX} + (\text{Ca}^{2+})^{1/2}$$

$$k_G = [\text{NaX}] [\text{Ca}^{2+}]^{1/2} / [\text{Ca}^{1/2}X] [\text{Na}]$$

whereas concentration of exchangeable cations are in mmoles of charge per gram (or kg) and soluble cations are expressed in mmoles of charge per liter.

4.14. Chemical Equilibria in soils

Generally chemical reactions are reversible and direction of chemical reaction is determined by concentration of reacting chemicals (reactants) or concentrations of emerging products of chemical reactions (products). Equilibrium is well explained by equilibrium constant (K) which is explained by the following equation

$$\text{A} + \text{B} \leftrightarrow \text{C} + \text{D}$$

Equilibrium constant can be calculated as

$$K = \frac{[\text{C}] [\text{D}]}{[\text{A}] [\text{B}]}$$

The condition or the point at which the forward and backward reactions occur simultaneously is known as chemical equilibrium. Concept of chemical equilibria is very important in different chemical reactions occurring in soils. Chemical equilibrium in soils is influenced by different processes which are explained in Fig. 4.10.

Soil comprises of solid phase (50%) and pore space (50%) which is jointly shared by water (liquid phase $\approx 25\%$) and air (gaseous phase $\approx 25\%$). Solid phase of soil provides foundation for the living organisms and tends to remain in dynamic equilibrium with solution phase of soil. Soil solution is important as plants absorb nutrients from soil solution. Upon the absorption of specific nutrient/ion by the plants from soil solution, deficiency of specific nutrient/ions emerges in soil solution. Deficiency of nutrient/ion in soil solution triggers the removal of ions from solid phases into solution phases and this process continues till the equilibrium between two phases is achieved. Solid phase of soil comprises of crystalline and non-crystalline minerals which controls chemical equilibrium in soil. For example, if soil solution becomes supersaturated with specific nutrient/ion, that specific nutrient/ion precipitates and become the part of solid phase and thus equilibrium is immediately achieved. Contrary to this, if soil solution becomes deficient of any nutrient/ion due to absorption by the plants or any other process, nutrient/ion on solid phase immediately dissolves into soil solution till the equilibrium is achieved.
Fig. 4.10 Chemical equilibria in soils

4.15. Conclusion

Chemical properties of soils are the most important in determining fate of different ions in soils. Ion retention, ion transformation, ion adsorption-desorption, ion solubility and bioavailability and ion leaching are important processes which ultimately affect the environmental quality, its sustainability and agricultural productivity. Ion exchange is the most important phenomenon after photosynthesis through which nutrients become available to the plants from solid phase. Soil reaction further affects the availability of these nutrients to the plants by solubilizing or insolubilizing nutrient elements in soil. An understanding of chemical properties of soils enables the students to better understand all the processes concerning environmental quality and agricultural productivity.

References