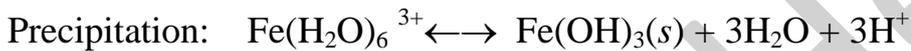
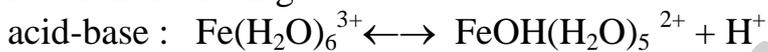


## Metals in Water

### Calcium and other metals in water :

Metal ions in water, commonly denoted  $M^{n+}$ , exist in numerous forms. A metal ion,  $Ca^{2+}$  for example, cannot exist as a separate entity in water. In order to secure the highest stability of their outer electron shells, metal ions in water are bonded, or coordinated, to other species. These may be water molecules or other stronger bases (electron-donor partners) that might be present. Therefore, metal ions in water solution are present in forms such as the hydrated metal cation  $M(H_2O)_x^{n+}$

Metal ions in aqueous solution seek to reach a state of maximum stability through chemical reactions including :



And oxidation-reduction reactions:



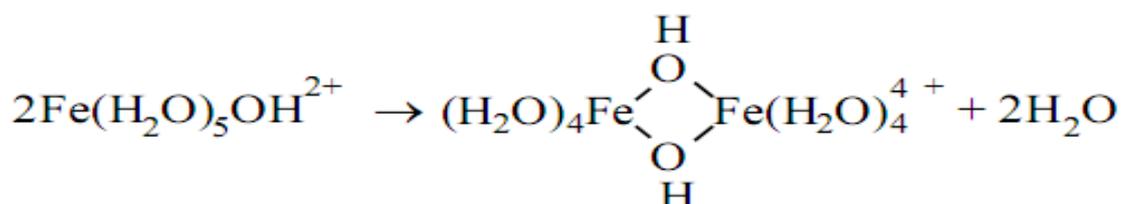
These all provide means through which metal ions in water are transformed to more stable forms. Because of reactions such as these and the formation of dimeric species, such as  $Fe_2(OH)_2^{4+}$ , the concentration of simple hydrated  $Fe(H_2O)_6^{3+}$  ion in water is vanishingly small; the same holds true for many other hydrated metal ions dissolved in water.

### Hydrated metal ions as acids:

Hydrated metal ions, particularly those with a charge of +3 or more, tend to lose  $H^+$  ion from the water molecules bound to them in aqueous solution, and fit the definition of Brønsted acids, according to which acids are  $H^+$  donors and bases are  $H^+$  acceptors. The acidity of a metal ion increases with charge and decreases with increasing radius. As shown by the reaction,



Hydroxide,  $OH^-$ , bonded to a metal ion, may function as a bridging group to join two or more metals together as shown by the following dehydration-dimerization process:



Generally, divalent metal ions do not lose a hydrogen ion at pH values below 6, whereas monovalent metal ions such as  $\text{Na}^+$  do not act as acids at all, and exist in water solution as simple hydrated ions.

Among the metals other than iron(III) forming polymeric species with  $\text{OH}^-$  as a bridging group are Al(III), Be(II), Bi(III), Ce(IV), Co(III), Cu(II), Ga(III), Mo(V), Pb(II), Sc(II), Sn(IV), and U(VI). Additional hydrogen ions may be lost from water molecules bonded to the dimers, furnishing  $\text{OH}^-$  groups for further bonding and leading to the formation of polymeric hydrolytic species. If the process continues, colloidal hydroxyl polymers are formed and, finally, precipitates are produced. This process is thought to be the general one by which hydrated iron(III) oxide,  $\text{Fe}_2\text{O}_3 \cdot x(\text{H}_2\text{O})$ , (also called ferric hydroxide,  $\text{Fe}(\text{OH})_3$ ), is precipitated from solutions containing iron(III).

## Calcium in Water

Of the cations found in most fresh-water systems, calcium generally has the highest concentration. The chemistry of calcium is simpler than that of the transition metal ions found in water. Calcium is a key element in many geochemical processes, and minerals constitute the primary sources of calcium ion in waters. Among the primary contributing minerals are gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; Anhydrite,  $\text{CaSO}_4$ ; dolomite,  $\text{CaMg}(\text{CO}_3)_2$ ; and calcite and aragonite, which are different mineral forms of  $\text{CaCO}_3$ .

Calcium ion, along with magnesium and sometimes iron(II) ion, accounts for **water hardness**. The most common manifestation of water hardness is the curdy precipitate formed by soap in hard water. *Temporary hardness* is due to the presence of calcium and bicarbonate ions in water and may be eliminated by boiling the water:

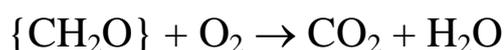


Increased temperature may force this reaction to the right by evolving  $\text{CO}_2$  gas, and a white precipitate of calcium carbonate may form in boiling water having temporary hardness.

Water containing a high level of carbon dioxide readily dissolves calcium from its carbonate minerals:



When this reaction is reversed and  $\text{CO}_2$  is lost from the water, calcium carbonate deposits are formed. The concentration of  $\text{CO}_2$  in water determines the extent of dissolution of calcium carbonate. The carbon dioxide that water may gain by equilibration with the atmosphere is not sufficient to account for the levels of calcium dissolved in natural waters, especially groundwaters. Rather, the respiration of microorganisms degrading organic matter in water, sediments, and soil, accounts for the very high levels of  $\text{CO}_2$  and  $\text{HCO}_3^-$  observed in water and is very important in aquatic chemical processes and geochemical transformations.



## Dissolved Carbon Dioxide and Calcium Carbonate Minerals

The equilibrium between dissolved carbon dioxide and calcium carbonate minerals is important in determining several natural water chemistry parameters such as alkalinity, pH, and dissolved calcium concentration (Figure 1). For fresh water, the typical figures quoted for the concentrations of both  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  are :

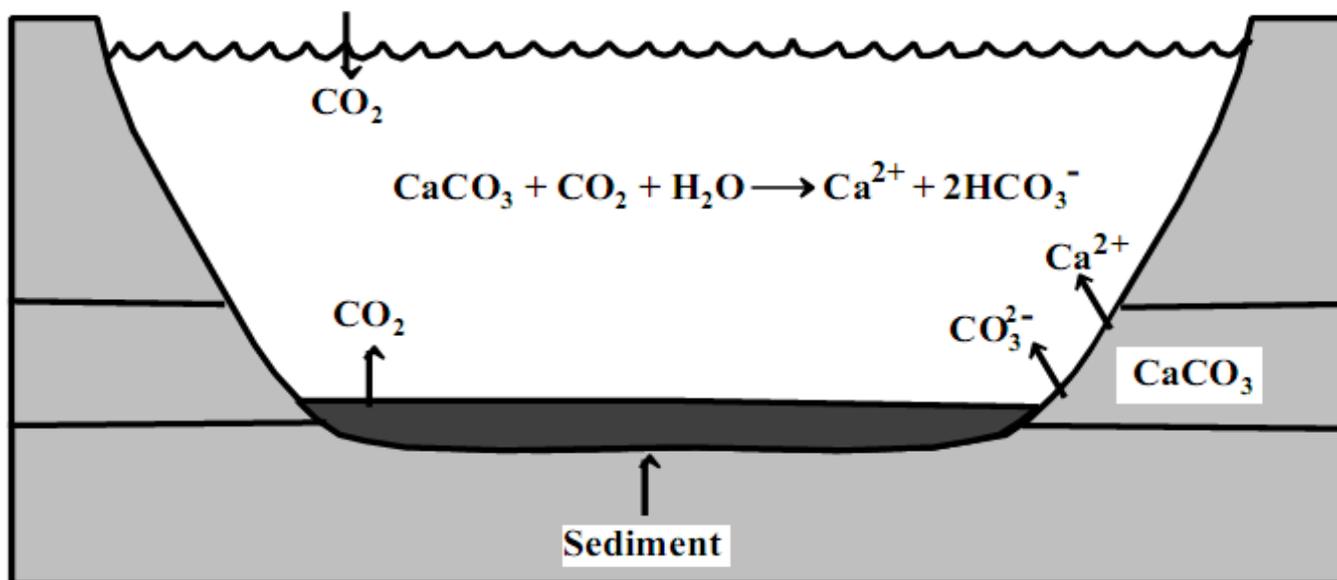


Fig.(1): Carbon dioxide-calcium carbonate equilibria.

pH was increased due to algal uptake of  $\text{CO}_2$  which cause deviations from these values.

## Complexation and Chelation :

The properties of metals dissolved in water depend largely upon the nature of metal species dissolved in the water. Therefore, **speciation** of metals plays a crucial role in their environmental chemistry in natural waters and wastewaters. In addition to the hydrated metal ions, for example,  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  and hydroxy species such as  $\text{FeOH}(\text{H}_2\text{O})_5^{2+}$ , metals may exist in water reversibly bound to inorganic anions or to organic compounds as **metal complexes**. For example, a cyanide ion can bond to dissolved iron(II):

$\text{Fe}(\text{H}_2\text{O})_6^{2+} + \text{CN}^- \longleftrightarrow \text{FeCN}(\text{H}_2\text{O})_5^+ + \text{H}_2\text{O}$  Additional cyanide ions may bond to the iron to form  $\text{Fe}(\text{CN})_2$ ,  $\text{Fe}(\text{CN})_3^-$ ,  $\text{Fe}(\text{CN})_4^{2-}$ ,  $\text{Fe}(\text{CN})_5^{3-}$ , and  $\text{Fe}(\text{CN})_6^{4-}$ , where the water molecules still bound to the iron(II) are omitted for simplicity. This phenomenon is called **complexation**; the species that binds with the metal ion,  $\text{CN}^-$  in the example above, is called a **ligand**, and the product in which the ligand is bound with the metal ion is a **complex**, **complex ion**, or **coordination compound**. A special case of complexation in which a ligand bonds in two or more places to a metal ion is called **chelation**. In addition to being present as metal complexes, metals may occur in water as **organometallic** compounds containing carbon-to-metal bonds . The solubility, transport properties, and biological effects of such

species are often vastly different from those of the metal ions themselves. In the example above, the cyanide ion is a unidentate ligand, which means that it possesses only one site that bonds to a metal ion. Complexes of unidentate ligands are of relatively little importance in solution in natural waters. Of considerably more importance are complexes with chelating agents. A **chelating agent** has more than one atom that may be bonded to a central metal ion at one time to form a ring structure. Thus, pyrophosphate ion,  $P_2O_7^{4-}$ , bonds to two sites on a calcium ion to form a chelate.

Complex compounds of metals such as iron (in hemoglobin) and magnesium (in chlorophyll) are vital to life processes. Naturally occurring chelating agents, such as humic substances and amino acids, are found in water and soil. The high concentration of chloride ion in seawater results in the formation of some chloro complexes. Synthetic chelating agents such as sodium tripolyphosphate, sodium ethylenediaminetetraacetate (EDTA), sodium nitrilotriacetate (NTA), and sodium citrate are produced in large quantities for use in metal-plating baths, industrial water treatment, detergent formulations, and food preparation. Small quantities of these compounds enter aquatic systems through waste discharges.

### **Selectivity and Specificity in Chelation**

Some complicated chelating agents of biological origin approach almost complete specificity for certain metal ions. One example of such a chelating agent is ferrichrome, synthesized by and extracted from fungi, which forms extremely stable chelates with iron(III). It has been observed that cyanobacteria of the *Anabaena* species secrete appreciable quantities of iron-selective hydroxamate chelating agents during periods of heavy algal bloom. These photosynthetic organisms readily take up iron chelated by hydroxamate-chelated iron, whereas some competing green algae, such as *Scenedesmus*, do not. Thus, the chelating agent serves a dual function of promoting the growth of certain cyanobacteria while suppressing the growth of competing species, allowing the cyanobacteria to exist as the predominant species.

### **General Questions:**

Q1: Metal ions in aqueous solution seek to reach a state of maximum stability through chemical reactions. What are these reactions? Answer with chemical equations.

Q2: Hydroxide,  $OH^-$ , bonded to a metal ion, may function as a bridging group to join two or more metals together. Show the diagram of dehydration-dimerization process.

Q3: What are the differences between Complexation and Chelation processes.

Q4: Why is chelating agent usually added to artificial algal growth media?