chapter

8

V. imp

CHEMISTRY OF METALS IN AQUEOUS SYSTEMS

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8.1 INTRODUCTION

The behavior of metals in environmental systems is a topic of ongoing interest and concern. Historically, the use of metals has been closely linked with industrialization and development. As a result, the natural biogeochemical cycling of many metals has been greatly accelerated, exposing some organisms or entire ecosystems to unhealthy, and at times lethal, levels of these chemicals.

There is no universally accepted definition distinguishing metals from nonmetals. Any definition of metals includes those elements that are refined, used in commerce, and referred to colloquially as such (e.g., Cu, Fe, Ag), but virtually all elements in the third and lower rows of the periodic table (sodium and all elements with atomic numbers larger than that of sodium) other than the halogens and noble gases share some properties that could be ascribed to metals. In this chapter, we consider what *metallic behavior* is in terms of the reactions that some elements undergo in aquatic environments.

One key characteristic of metals in aquatic systems is their ability to exist as either dissolved or solid species and to combine with numerous other species. That is, whereas virtually all the acetate in an aquatic system is likely to be present as either acetate ion or acetic acid, copper might be present as a constituent in dozens of different dissolved species. The speciation of metals has a profound effect on their physical and chemical behavior, their bioavailability, and their toxicity. The primary goal of this chapter is to provide a context for predicting and interpreting that speciation.

8.2 SPECIATION OF DISSOLVED METALS

8.2.1 COMPLEXATION WITH H_2O OR OH^-

As noted in previous chapters, even though water molecules are electrically neutral, their charges are not distributed symmetrically. Rather, they are dipoles, with a small amount of positive charge residing near the hydrogen atoms and a balancing negative charge (associated with unshared pairs of electrons) on the other side of the oxygen atom from the hydrogen atoms. Water molecules surrounding a (positively charged) metal ion orient themselves with the unshared electrons adjacent to the metal. Some of the negative charge in these orbitals is shared with the metal ion, forming a bond that might range from very weak to very strong.

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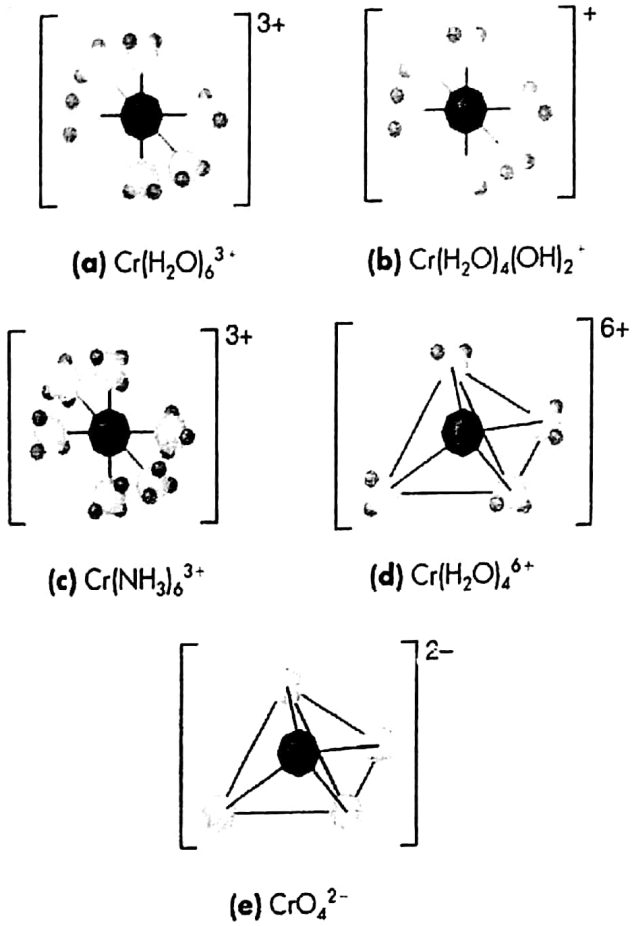

Figure 8.1 Chromium can exist in both a trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) oxidation state. **(a)** A fully hydrated Cr^{3+} ion, i.e., a $Cr(H_2O)_6^{3+}$ complex. **(b)** A $Cr(H_2O)_4(OH)_2^{+}$ complex, i.e., a species similar to that in (a), except that one H^+ ion has been lost by each of two of the waters of hydration. **(c)** A Cr^{3+} ion in which all six waters of hydration have been replaced by ammonia molecules, forming the complex $Cr(NH_3)_6^{3+}$. **(d)** A fully hydrated $Cr(H_2O)_4^{6+}$ ion in a tetrahedral complex. This ion is theoretically plausible, but it is so acidic that it is never found in aqueous solutions. **(e)** A fully deprotonated chromate ion (CrO_4^{2-}), which is the dominant form of Cr(VI) in neutral or alkaline solutions.

Depending on the size of the metal ion, four to eight oriented water molecules may surround it. Since these water molecules are weakly (or not so weakly) bonded to the metal ion, the water plus the metal can be thought of as a single entity, and a reasonable representation of the metal in solution would be $Me(OH_2)_x^{n+}$, where $4 \leq x \leq 8$ (Figure 8.1a). The group of water molecules immediately surrounding the metal is called the **inner hydration sphere** or **inner coordination sphere.** As is described subsequently in the chapter, a variety of other molecules can replace the water molecules in the hydration spheres. All such molecules are called **ligands**, and the entire cluster is called a **metal-ligand complex** or simply a **complex.** A few inorganic ligands of importance and some metals to which they bind are listed in Table 8.1.

The exchange of water molecules in the hydration sphere with other molecules (either water molecules from bulk solution or different ligands) is generally quite fast, so that the formation of complexes proceeds rapidly and can be considered to reach equilibrium within seconds in most cases. However, in a few

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Table 8.1 Some important inorganic ligands and the metals to which they bind

Ligand	Metals	Environment
H_2O	All	Any aquatic system
OH^-	Virtually all	Any aquatic system
F^-	Fe^{3+}, Al^{3+}	Some natural systems; industrial systems where HF is used to treat metal surfaces
Cl^-	Cu^{2+}, Cu^+, Pb^{2+}, Cd^{2+}	Estuaries, seawater; corrosion of metals
CN^-	Fe^{3+}, Fe^{2+}, Cu^+, Cu^{2+}, Ni^{2+}, Ag^+	Metal plating
NH_3	Cu^+, Cu^{2+}, Cd^{2+}, Ni^{2+}	Metal finishing
$S_2O_3^{2-}$	Ag^+	Photofinishing
$P_2O_7^{4-}$, $P_3O_{10}^{5-}$	Ca^{2+}, Mn^{2+}, Fe^{3+}	Detergents, corrosion inhibitors

cases (especially for more highly charged metals), the waters of hydration exchange slowly, and equilibration with ligands in solution might take much longer. For instance, the characteristic residence time of water in the hydration sphere of Cr^{3+} ranges from several seconds to several days, depending on the solution pH.

The number of water molecules or other ligand groups to which the metal binds is referred to as the metal's **coordination number.** Depending on the strength and extent of the electric field generated by the metal ion, a second sphere of water molecules (an **outer hydration sphere**) may also be bonded to the complex. In general, the smaller and more highly charged the central metal ion is, the more strongly it is able to bond to and orient water molecules around it, and the larger the complex becomes. Hydrated metal ions are often referred to as **free metal ions** or **uncomplexed ions** even though, in a formal sense, they are complexed with water molecules.

The ionic charge on a metal is called its **oxidation number** or **oxidation state.** Many metal ions can exist in stable forms in two or more oxidation states (e.g., Fe^{2+} or Fe^{3+}, Cr^{3+} or Cr^{6+}). In such cases, it is common to refer to all the species in which the metal has a given charge by that charge (e.g., divalent or trivalent iron; trivalent or hexavalent chromium). The same concept is often represented by writing the charge on the metal ion (not the complex) in Roman numerals after the metal's name [e.g., Fe(II) or Fe(III); Cr(III) or Cr(VI)]. Cr species in the trivalent and hexavalent oxidation states are shown in Figure 8.1. The significance of the different charges is discussed in Chapter 9, which deals with oxidation-reduction reactions.

The attraction of the unshared electron pairs on water molecules in the inner hydration sphere to the metal ion causes electrons to be withdrawn from the water's O—H orbitals, weakening those bonds. As a result, the H^+ ions that are part of the water molecules in the hydration sphere surrounding a metal ion are more easily dissociated than those on water molecules in bulk solution, causing metal ions to act as acids. Although the actual reaction taking place is best

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represented as:

$$Me(OH_2)_x^{n+} \leftrightarrow Me(OH_2)_{x-1}(OH)^{n-1} + H^+ \quad (8.1)$$

the reaction is most often abbreviated in one of the two following forms:

$$Me^{n+} + H_2O \leftrightarrow MeOH^{n-1} + H^+ \qquad K_{(8.2)} \quad (8.2)$$

$$Me^{n+} + OH^- \leftrightarrow MeOH^{n-1} \qquad K_{(8.3)} \quad (8.3)$$

Regardless of how the reaction is written, the net effect is replacement of a water molecule by a hydroxide ion as one of the ligands in the inner hydration sphere (Figure 8.1b). The equilibrium constant written for a reaction in which a metal-ligand complex forms is called a **stability constant** or **formation constant.** In the above reactions, the stability constant $K_{(8.2)}$ is also the acidity constant K_a for a reaction in which the free metal ion Me^{n+} is the acid and $Me(OH)^{n-1}$ is the conjugate base; similarly, $K_{(8.3)}$ is the inverse of a basicity constant.

Many metal ions can act as multiprotic acids, releasing protons from water molecules in the inner hydration sphere until they are surrounded by OH^- ions instead of H_2O molecules. In some cases, the remaining protons are bonded very tightly to the oxygen atoms and are essentially non-releasable; in others, the protons that are part of the OH^- ligands in the inner hydration sphere can be released, leaving the metal ion bonded to one or more oxide (O^{2-}) ions. For instance, $Fe(OH)_6^{3-}$ is a stable species that can act as a base [forming its conjugate acid, $Fe(OH)_5^{2-}$, in the process] but not as an acid. On the other hand, As^{3+}, Se^{4+}, and Cr^{6+} can cause surrounding water molecules to deprotonate completely, to form AsO_3^{3-}, SeO_3^{2-}, and CrO_4^{2-} ions, respectively (Figure 8.1d).

For most metals, no more than four acid/base species are of practical significance. Thus, although species of the form $Cr(OH_2)_3(OH)^{5+}$ are theoretically plausible, they are so acidic as to be unimportant in all systems of interest; rather, when one is considering hydrolyzed forms of hexavalent Cr, only $CrO_2(OH)_2^{\circ}$, $CrO_3(OH)^-$, and CrO_4^{2-} are considered (Figure 8.1e). [The first two of these three Cr(VI)-containing species are chromic acid and bichromate ion, commonly written as H_2CrO_4 and $HCrO_4^-$, respectively.] In the case of Cr(VI) and most other metals that bind so strongly to water that the water molecule releases both its hydrogen ions, the Me—O^{2-} bonds are too strong to be broken under normal conditions. In such cases, rather than Me^{n+} and O^{2-} being considered to form a complex, they are considered to form a stable molecule, sometimes referred to as a *metal oxyanion.*

Just as the equilibrium constants for deprotonation of an acid (K_a) and for release of a gas from solution (H) are given special designations for convenience, conventions have been adopted for representing the stability constants of metal-ligand complexes. The designations can be summarized as follows:

K_i: Equilibrium constant for a reaction between two dissolved species, adding *one* ligand to a complex with $i - 1$ ligands, to form a complex with i ligands.

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β_i: Equilibrium constant for a reaction between an uncomplexed ion (i.e., an aquo-complexed ion) and i ligands to form a complex of the type MeL_i.

β_{ij}: Equilibrium constant for a reaction between MeL_i and $j - i$ ligands to form a complex of the type MeL_j.

$*K_i$ or $*\beta_i$: Same as K_i or β_i, except that the reaction is written with the ligand in a protonated form, usually requiring inclusion of H^+ on the product side.

Reactions for the formation of several hydroxo complexes of cadmium are shown below, along with the conventional way of representing their stability constants.

$$Cd^{2+} + OH^- \leftrightarrow CdOH^+ \qquad \log K_1 = 3.92 \qquad (8.4)$$

$$CdOH^+ + OH^- \leftrightarrow Cd(OH)_2^{\circ} \qquad \log K_2 = 3.73 \qquad (8.5)$$

$$Cd(OH)_2^{\circ} + OH^- \leftrightarrow Cd(OH)_3^- \qquad \log K_3 = 1.05 \qquad (8.6)$$

$$Cd(OH)_3^- + OH^- \leftrightarrow Cd(OH)_4^{2-} \qquad \log K_4 = -0.05 \qquad (8.7)$$

$$Cd^{2+} + 2OH^- \leftrightarrow Cd(OH)_2^{\circ} \qquad \log \beta_2 = 7.65 \qquad (8.8)$$

$$Cd^{2+} + 4OH^- \leftrightarrow Cd(OH)_4^{2-} \qquad \log \beta_4 = 8.65 \qquad (8.9)$$

$$CdOH^+ + H_2O \leftrightarrow Cd(OH)_2^{\circ} + H^+ \qquad \log *K_2 = -10.27 \qquad (8.10)$$

$$Cd^{2+} + 3H_2O \leftrightarrow Cd(OH)_3^- + 3H^+ \qquad \log *\beta_3 = -33.3 \qquad (8.11)$$

If there is any chance of confusion about which ligand is being considered, its identity can be added to the subscript; e.g., K_1 might be written as $K_{OH,1}$.

Not all the stability constants listed above are independent. For instance, β_i is related to the various K_i's by

$$\beta_n = K_1 K_2 K_3 \cdots K_n = \prod_{i=1}^{n} K_i \qquad (8.12)$$

and β_4 and $*\beta_4$ are related through the following reactions:

$$Cd^{2+} + 4OH^- \leftrightarrow Cd(OH)_4^{2-} \qquad \beta_4 \qquad (8.9)$$

$$4H_2O \leftrightarrow 4H^+ + 4OH^- \qquad K_w^4 \qquad (8.13)$$

$$Cd^{2+} + 4H_2O \leftrightarrow Cd(OH)_4^{2-} + 4H^+ \qquad *\beta_4 \qquad (8.14)$$

Thus, $*\beta_4 = \beta_4 K_w^4$ or, in general, for formation of hydroxide complexes

$$*\beta_i = \beta_i K_w^i \qquad (8.15)$$

and

$$*K_i = K_i K_w \qquad (8.16)$$

A list of stability constants written in various ways for complexation of several metals by OH^- is provided in Table 8.2.

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Table 8.2 Stability constants for complexation of metals by OH^-

	i	Log K_i	Log $^*K_i$	Log β_i	Log $^*\beta_i$
Ag^+	1	2.00	−12.00	2.00	−12.00
	2	2.00	−12.00	4.00	−24.00
Al^{3+}	1	9.01	−4.99	9.01	−4.99
	2	8.89	−5.11	17.90	−10.10
	3	8.10	−5.90	26.00	−16.00
	4	7.00	−7.00	33.00	−23.00
Ca^{2+}	1	1.40	−12.60	1.40	−12.60
Cd^{2+}	1	3.92	−10.08	3.92	−10.08
	2	3.73	−10.27	7.65	−20.35
	3	1.05	−12.95	8.70	−33.30
	4	−0.05	−14.05	8.65	−47.35
Co^{2+}	1	4.80	−9.20	4.80	−9.20
	2	4.90	−9.10	9.70	−18.30
	3	1.10	−12.90	10.80	−31.20
Cr^{3+}	1	10.00	−4.00	10.00	−4.00
	2	8.38	−5.62	18.38	−9.62
	3	6.87	−7.13	25.25	−16.75
	4	2.98	−11.02	28.23	−27.77
Cu^{2+}	1	6.00	−8.00	6.00	−8.00
	2	8.32	−5.68	14.32	−13.68
	3	0.78	−13.22	15.10	−26.90
	4	1.30	−12.70	16.40	−39.60
Fe^{2+}	1	4.50	−9.50	4.50	−9.50
	2	2.93	−11.07	7.43	−20.57
	3	3.57	−10.43	11.00	−31.00
Fe^{3+}	1	11.81	−2.19	11.81	−2.19
	2	10.52	−3.48	22.33	−5.67
	3	6.07	−7.93	28.40	−13.60
	4	6.00	−8.00	34.40	−21.60
Hg^{2+}	1	10.60	−3.40	10.60	−3.40
	2	11.30	−2.70	21.90	−6.10
	3	10.26	−3.74	32.16	−9.84
Mg^{2+}	1	2.21	−11.79	2.21	−11.79
Ni^{2+}	1	4.14	−9.86	4.14	−9.86
	2	4.86	−9.14	9.00	−19.00
	3	3.00	−11.00	12.00	−30.00
Pb^{2+}	1	6.29	−7.71	6.29	−7.71
	2	4.59	−9.41	10.88	−17.12
	3	3.06	−10.94	13.94	−28.06
	4	2.36	−11.64	16.30	−39.70
Zn^{2+}	1	5.04	−8.96	5.04	−8.96
	2	6.06	−7.94	11.10	−16.90
	3	2.50	−11.50	13.60	−28.40
	4	1.20	−12.80	14.80	−41.20

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8.2.2 LOG C–pH DIAGRAMS FOR DISSOLVED METALS

Recognizing metals as polyprotic acids, we can develop log C–pH diagrams for metals by following the same procedures we used previously for other acids. For instance, consider a system containing 10^{-4} M TOTCd. Up to four protons can be released from the waters of hydration in the free aquo Cd^{2+} complex; i.e., Cd^{2+} is a tetra-protic acid, with K_a values as follows.

$$Cd^{2+} + H_2O \leftrightarrow Cd(OH)^+ + H^+ \qquad \log K_{a1} = \log {}^*K_1 = -10.08$$

$$CdOH^+ + H_2O \leftrightarrow Cd(OH)_2^{\circ} + H^+ \qquad \log K_{a2} = \log {}^*K_2 = -10.27$$

$$Cd(OH)_2^{\circ} + H_2O \leftrightarrow Cd(OH)_3^- + H^+ \qquad \log K_{a3} = \log {}^*K_3 = -12.95$$

$$Cd(OH)_3^- + H_2O \leftrightarrow Cd(OH)_4^{2-} + H^+ \qquad \log K_{a4} = \log {}^*K_4 = -14.05$$

The constants are designated as $^*K_i$ values; other than that change of symbols, everything else is as in any other system with a tetra-protic acid. The corresponding log C–pH diagram is shown in Figure 8.2.

The fraction of the total dissolved metal that is present as a given species is designated by an α, as in other acid/base systems. Thus, in the Cd system, $\alpha_{Cd^{2+}}$ is

$$\alpha_{Cd^{2+}} = \frac{[Cd^{2+}]}{TOT\,Cd} \tag{8.17}$$

Assuming that the solutes behave ideally, the total dissolved Cd concentration can be written in terms of the concentration of free Cd^{2+}, the stability constants

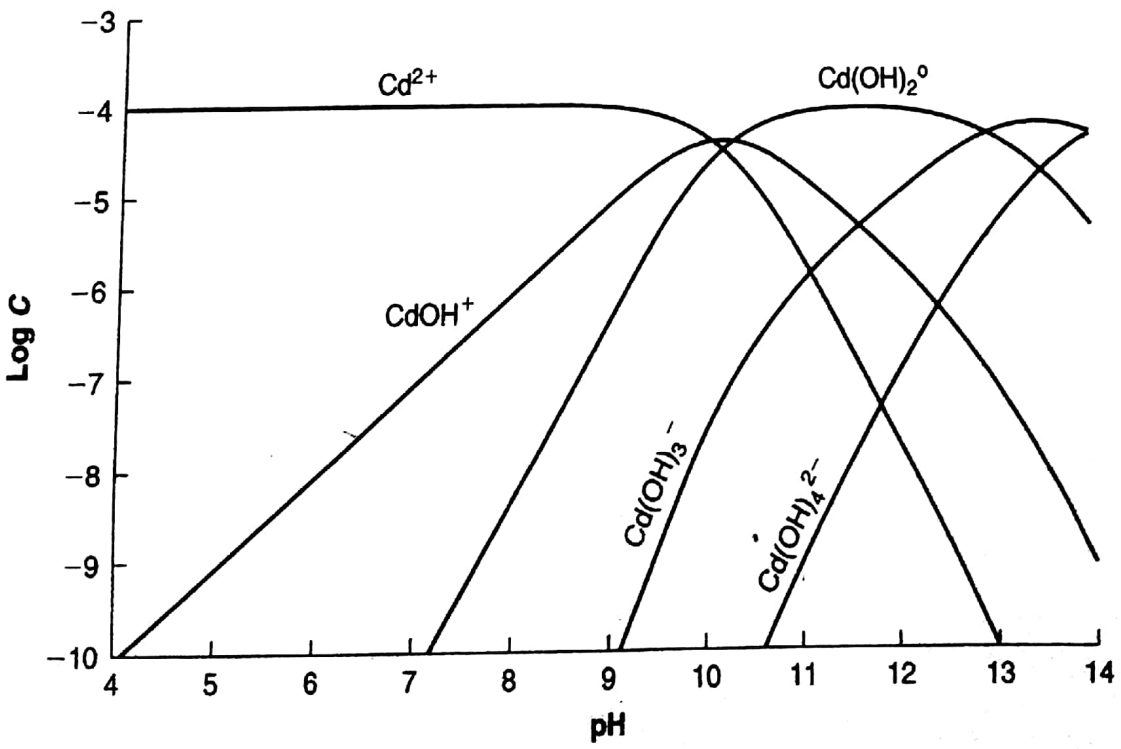

Figure 8.2 Log C–pH diagram for Cd in a system with 10^{-4} M TOTCd.

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for formation of the complexes, and the hydroxide ion activity, as follows:

$$TOTCd = \{Cd^{2+}\} + \{CdOH^{+}\} + \{Cd(OH)_2^{o}\} + \{Cd(OH)_3^{-}\} + \{Cd(OH)_4^{2-}\} \quad (8.18a)$$

$$= \{Cd^{2+}\}\left[1 + \frac{\{CdOH^{+}\}}{\{Cd^{2+}\}} + \frac{\{Cd(OH)_2^{o}\}}{\{Cd^{2+}\}} + \frac{\{Cd(OH)_3^{-}\}}{\{Cd^{2+}\}} + \frac{\{Cd(OH)_4^{2-}\}}{\{Cd^{2+}\}}\right] \quad (8.18b)$$

$$= \{Cd^{2+}\}(1 + K_1\{OH^{-}\}^1 + \beta_2\{OH^{-}\}^2 + \beta_3\{OH^{-}\}^3 + \beta_4\{OH^{-}\}^4) \quad (8.18c)$$

$$= \{Cd^{2+}\}\left(1 + \sum_{i=1}^{4}\beta_i\{OH^{-}\}^i\right) = \{Cd^{2+}\}\left(1 + \sum_{i=1}^{4}\frac{{}^{*}\beta_i}{\{H^{+}\}^i}\right) \quad (8.18d)$$

8.2.3 COMPLEXES WITH OTHER LIGANDS

In addition to water and hydroxide, other dissolved species can act as ligands and form soluble complexes with metal ions. In all such cases, at least a portion of the ligand molecule must have a local excess of electronic (negative) charge which it donates or shares with the metal ion, thereby forming a chemical bond. For instance, ammonia can form strong complexes with some metal ions because the nitrogen atom in an ammonia molecule has an orbital containing an unshared pair of electrons (see Figure 3.7). These electrons, which cause the nitrogen atom to carry a slight negative charge in free NH_3 molecules (much as the oxygen atom does in water molecules), can be shared with metal ions to form the Me—NH_3 bonds (Figure 8.1c). The most common *donor atoms* (i.e., atoms that can donate electronic charge to the metal) of environmental significance are O, N, and S.

If the bonds formed between a ligand and a metal ion are strong enough that the ligand replaces water in the inner hydration sphere, the reaction is referred to as **ligand exchange,** and the ligand is said to form an **inner sphere complex,** e.g.,

$$Me(H_2O)_x^{n+} + NH_3 \leftrightarrow Me(H_2O)_{x-1}(NH_3)^{n+} + H_2O \quad (8.19)$$

The above reaction is more commonly written as

$$Me^{n+} + NH_3 \leftrightarrow Me(NH_3)^{n+} \quad (8.20)$$

Yet other ligands bond to the metal ion but remain separated from it by a water molecule. These **outer sphere complexes** are relatively weak and are called **ion pairs.**

The rules for naming and using stability constants for ligands other than hydroxide are essentially identical to those listed above. For instance, for ammonia complexes of Zn^{2+}, the reactions and labels assigned to the various

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stability constants are as follows:

$$Zn^{2+} + NH_3 \leftrightarrow Zn(NH_3)^{2+} \qquad \log K_1 = 2.2 \qquad (8.21)$$

$$Zn(NH_3)^{2+} + NH_3 \leftrightarrow Zn(NH_3)_2^{2+} \qquad \log K_2 = 2.3 \qquad (8.22)$$

$$Zn(NH_3)_2^{2+} + NH_3 \leftrightarrow Zn(NH_3)_3^{2+} \qquad \log K_3 = 2.5 \qquad (8.23)$$

$$Zn(NH_3)_3^{2+} + NH_3 \leftrightarrow Zn(NH_3)_4^{2+} \qquad \log K_4 = 2.0 \qquad (8.24)$$

$$Zn^{2+} + 2NH_3 \leftrightarrow Zn(NH_3)_2^{2+} \qquad \log \beta_2 = 4.5 \qquad (8.25)$$

$$Zn^{2+} + 3NH_3 \leftrightarrow Zn(NH_3)_3^{2+} \qquad \log \beta_3 = 7.0 \qquad (8.26)$$

$$Zn^{2+} + NH_4^{+} \leftrightarrow Zn(NH_3)^{2+} + H^{+} \qquad \log {}^*K_1 = -7.0 \qquad (8.27)$$

Note that, in this case, the ligand is neutral, so all the complexes are divalent (as is the case when water is the ligand).

8.2.4 MIXED LIGAND COMPLEXES AND CHELATING AGENTS

Complexes that contain more than one type of ligand (other than water) can also form. Such complexes are called **mixed-ligand complexes.** For instance, a reaction leading to formation of a mixed, ammonia-chloro complex is as follows:

$$Me(H_2O)_x^{n+} + Cl^- + NH_3 \leftrightarrow Me(H_2O)_{x-2}(NH_3)Cl^{n-1} + 2H_2O \qquad (8.28)$$

Also, some ligands have more than one "donor" atom, in which case one ligand molecule might expel more than one water molecule from the inner hydration sphere. These ligands are called **multidentate** ligands and tend to form strong complexes. If the complexes are very strong, they are called **chelates,** and the ligands are called **chelators** or **chelating agents.** Commercially, the most important chelating agent is the tetraprotic acid EDTA (ethylene diamine tetra-acetic acid), which, in its most dissociated form, has the structure shown in Figure 8.3.

EDTA can bind to a metal to form a hexadentate chelate by replacing six water molecules in the hydration sphere and forming bonds with the metal ion by electron sharing via the two nitrogen atoms and the four carboxylate groups. Thus, a single EDTA molecule can act like six individual monodentate ligands. The binding of EDTA to many metals is so strong that, under many circumstances, EDTA—Me complexes form until either the free EDTA or free metal is essentially 100% complexed. Thus, adding excess EDTA to a solution is an effective way to maintain the activity of free (i.e., uncomplexed) metal ions at extremely low levels.

In addition to applications in industry, EDTA is used extensively as a food additive, at least in part to "tie up" metal ions that might come in contact with the food and prevent them from participating in other reactions with the food. It is also used medically in the treatment of acute metal poisoning, as a way of collecting metal ions from organs and holding them in solution so that they can be excreted.

The fact that metal—ligand complexes form in a system indicates that the potential energy of the system is lower (i.e., the system is more stable) with those complexes present than if the metal and ligand remained separate. Therefore, it is

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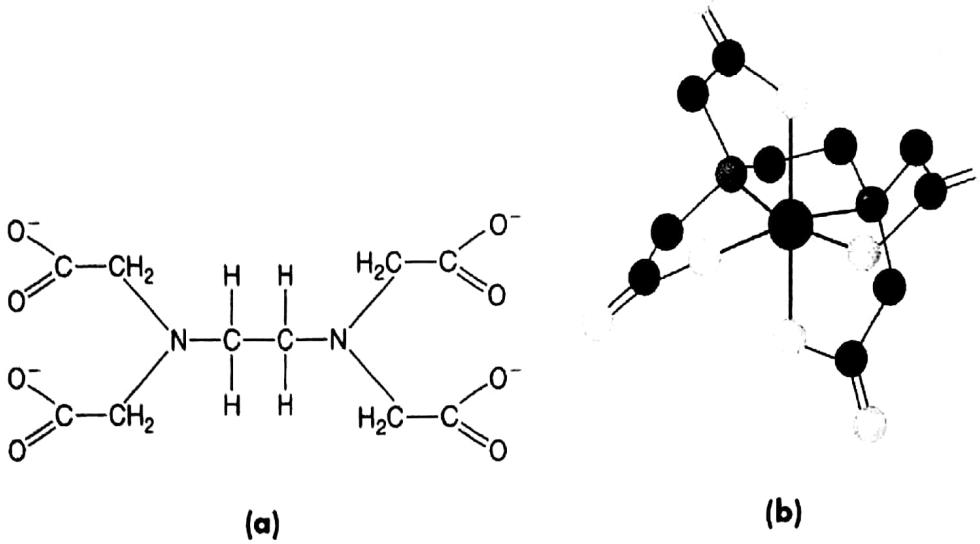

Figure 8.3 **(a)** The bond structure of the strong chelating agent EDTA, in its fully deprotonated form ($EDTA^{4-}$). **(b)** The structure of a $(Pb\text{-}EDTA)^{2-}$ chelate. In part (*b*), the stippled circle at the center is the Pb^{2+} ion, and the white, gray, and black circles are oxygen, nitrogen, and carbon atoms, respectively. Hydrogen atoms have been omitted to minimize clutter. The six bonds between the EDTA and Pb are shown in bold.

not surprising that the formation of complexes reduces the likelihood that the metal will undergo other reactions (at least from a thermodynamic perspective; the kinetics might be a different story). Mathematically, this effect is obvious from the fact that when complexes form, the concentration, activity, and molar free energy of the free metal ion decrease. The stronger the complex, the greater the reduction in free metal ion activity, so chelates can reduce metal reactivity very substantially.

One consequence of the lower reactivity of complexed metals compared to the same concentration of free metal is that complexation or chelation tends to stabilize metals in solution at the expense of metals associated with solids. For instance, complexation reduces the tendency for metals to precipitate out of solution as solids or to bind (adsorb) to the surface of solids in contact with the solution. The former fact is exploited extensively in industry, where chelating agents are used to prepare solutions with very high concentrations of metals, under conditions where most of the metal would precipitate if the chelating agent were not present. Similarly, adsorption of metals tends to diminish when they become complexed (Figure 8.4), although there are circumstances (discussed in Chapter 10) under which complexation enhances metal sorption. The same effect (lower chemical activity, and therefore lower reactivity) generally causes uptake of chelated metals by organisms to be much less efficient than uptake of free metal ions, and hence the chelated metals are less toxic, at a given total metal concentration. Stability constants for a variety of metals and ligands are listed in Table 8.3.

8.2.5 METAL SPECIATION IN SYSTEMS CONTAINING COMPLEXING LIGANDS

The equilibrium speciation of metals in systems containing ligands bears a close connection to the speciation of simple acids and bases and can be

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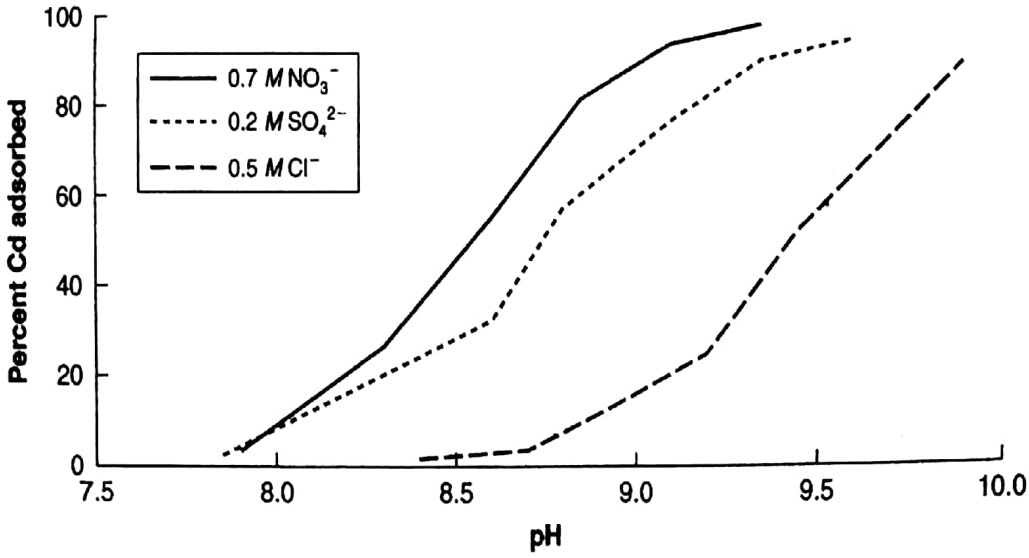

Figure 8.4 Adsorption of Cd^{2+} to $SiO_2(s)$ is diminished when Cl^- or SO_4^{2-} is added to the solution and free Cd^{2+} ions are converted to Cd-Cl or Cd-SO_4 complexes. All solutions contained 30 g/L $SiO_2(s)$ and 5×10^{-7} *M TOT*Cd and had an ionic strength of 0.7 *M*.

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represented on log *C*–log {ligand} diagrams that bear many similarities to log *C*–pH graphs. Consider, for instance, the speciation of Cd over a range of Cl^- activities in a system containing 10^{-4} *M TOT*Cd. In the preliminary analysis, we will assume that the pH is low enough that OH^- complexes of Cd^{2+} can be ignored. The stability constants for formation of Cd—Cl complexes are given below.

$$Cd^{2+} + Cl^- \leftrightarrow CdCl^+ \qquad \log K_1 = 1.98 \qquad \textbf{(8.29)}$$

$$CdCl^+ + Cl^- \leftrightarrow CdCl_2^{\circ}(aq) \qquad \log K_2 = 0.62 \qquad \textbf{(8.30)}$$

$$CdCl_2^{\circ}(aq) + Cl^- \leftrightarrow CdCl_3^- \qquad \log K_3 = -0.20 \qquad \textbf{(8.31)}$$

By writing the equilibrium expression for formation of $CdCl^+$ as $\{CdCl^+\}/\{Cd^{2+}\} = K_1\{Cl^-\}$, the relationships shown in Table 8.4 are easily derived. The table includes analogous expressions for an acid/base pair for comparison.

The only significant difference between the equations for the acid/base and metal/complex systems is that the crossover point is at pH = pK_a in the acid/base system and at pCl = $\log K_1 = -pK_1$ in the metal/complex system. This difference in sign arises because K_a is defined as the equilibrium constant for a *dissociation* reaction, whereas K_1 is defined for an *association* reaction.

Using a spreadsheet, we can determine the concentrations of all Cd species at any given value of $\{Cl^-\}$, much as we did in Chapter 3 when developing the log *C*–pH diagram for a multiprotic acid. The values in the spreadsheet, in essence, represent the simultaneous solutions to the three equilibrium-constant expressions [Equations (8.29) to (8.31)] and the mass balance on Cd. Plotting the

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Table 8.3 Stability constants for some metal—ligand complexes. Values shown correspond to log β.

	CO_3^{2-}	SO_4^{2-}	Cl^-	F^-	NH_3	PO_4^{3-}	EDTA	CN^-	HS^-
Ag^+		AgL 1.29	AgL 3.27 AgL_2 5.27 AgL_3 5.29 AgL_4 5.51	AgL 0.36			AgL 7.36 AgHL	AgL_2 20.38 AgL_3 21.4	AgL 14.05 AgL_2 18.45
Al^{3+}		AlL 4.92		AlL 7.01 AlL_2 12.75 AlL_3 17.02 AlL_4 19.72 AlL_5 20.8 AlL_6 20.5			AlL 19.8 AlHL 22.5		
Ca^{2+}		CaL 2.91		CaL 0.94		CaHL 15.08			
Cd^{2+}	CdL 5.4 CdL_3 6.22 CdHL 12.4	CdL 2.46 CdL_2 3.5	CdL 1.98 CdL_2 2.6 CdL_3 2.4	CdL 1.1 CdL_2 1.5		CdL 3.9	CdL 16.28 CdHL 2.9	CdL 5.32 CdL_2 10.37 CdL_3 14.83 CdL_4 18.29	CdL 10.17 CdL_2 16.53 CdL_3 18.71 CdL_4 20.9
Co^{2+}		CoL 2.5	CoL 0.5				CoL 18.6 CoHL 21.6		
Cr^{3+}		CrL 1.34	CrL −0.25 CrL_2 −0.96	CrL 4.92		CrH_2L 22.29			
Cu^{2+}	CuL 6.73 CuL_2 9.83 CuHL 13.6	CuL 2.31	CuL 0.43 CuL_2 0.16 CuL_3 −2.29 CuL_4 −4.59	CuL 1.26	CuL 5.8 CuL_2 10.7 CuL_3 14.7 CuL_4 17.6	CuHL 16.6	CuL 18.78 CuHL 11.2		CuL_3 25.9
Fe^{2+}		FeL 2.25	FeL 0.90 FeL_2 0.04			FeH_2L 22.25	FeL 16.7 FeHL 20.1	FeL_6 52.44 $FeHL_6$ 50 FeH_2L_6 45.61	FeL_2 8.95 FeL_3 10.99
Fe^{3+}		FeL 3.92 FeL_2 5.42	FeL 1.48 FeL_2 2.13 FeL_3 1.13	FeL 6.2 FeL_2 10.8 FeL_3 14		FeHL 17.78	FeL 27.8 FeHL 29.4	FeL_6 52.63	
Hg^{2+}		HgL 1.39	HgL 6.75 HgL_2 13.12 HgL_3 14.02 HgL_4 14.43	HgL 1.98	HgL 8.76 HgL_2 17.43 HgL_3 18.4 HgL_4 19.17			HgL 18.07 HgL_2 34.55 HgL_3 38.3 HgL_4 41.31	HgL_2 37.72
Mg^{2+}									
Ni^{2+}	NiL 6.87 NiL_2 10.11 NiHL 12.47	NiL 2.29 NiL_2 1.02	NiL 0.4 NiL_2 0.96	NiL 1.3			NiL 20.33 NiHL 11.56	NiL_2 14.59 NiL_3 22.64 NiH_3L_3 43.95	
Pb^{2+}	PbL 7.24 PbL_2 10.64 PbHL 13.2	PbL 2.75 PbL_2 3.47	PbL 1.6 PbL_2 1.8 PbL_3 1.7 PbL_4 1.38	PbL 1.25 PbL_2 2.56 PbL_3 3.42 PbL_4 3.1			PbL 17.86 PbHL 9.68 PbH_2L 6.22	PbL_4 10.6	PbL 15.27 PbL_2 16.57
Zn^{2+}	ZnL 5.3 ZnL_2 9.6 ZnHL 12.4	ZnL 2.37 ZnL_2 3.28	ZnL 0.43 ZnL_2 0.45 ZnL_3 0.5 ZnL_4 0.2	ZnL 1.15	ZnL 2.2 ZnL_2 4.5 ZnL_3 7.0 ZnL_4 9.0	ZnHL 15.7	ZnL 16.44 ZnHL 9	ZnL_2 11.07 ZnL_3 16.05 ZnL_4 16.72	ZnL 14.94 ZnL_2 16.1

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Table 8.4 Comparison of relationships between an acid/base and a metal/complex system

Acid/Base Pair (HA/A^-)			Metal/Complex Pair (Me/MeL)		
$\{HAc\} = \{Ac^-\}$	at	$pH = pK_a$	$\{CdCl^+\} = \{Cd^{2+}\}$	at	$pCl^- = \log K_1$
$\{HAc\} > \{Ac^-\}$	at	$pH < pK_a$	$\{CdCl^+\} > \{Cd^{2+}\}$	at	$pCl^- < \log K_1$
$\{HAc\} < \{Ac^-\}$	at	$pH > pK_a$	$\{CdCl^+\} < \{Cd^{2+}\}$	at	$pCl^- > \log K_1$

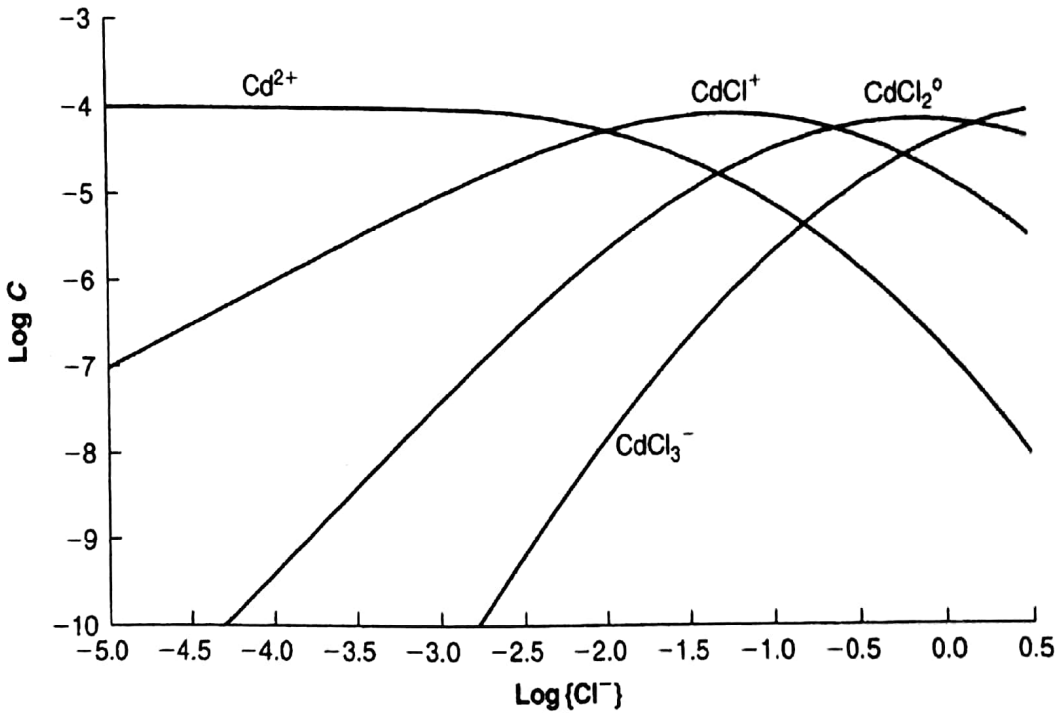

Figure 8.5 Log C–log $\{Cl^-\}$ diagram for a system containing 10^{-4} M *TOT*Cd, at a pH low enough that formation of Cd-OH complexes is negligible.

corresponding values against log $\{Cl^-\}$ yields the log C–log $\{Cl^-\}$ diagram shown in Figure 8.5.

The sum of the dissolved cadmium species in this system can be represented as a function of only $\{Cd^{2+}\}$, $\{Cl^-\}$, and the stability constants as follows:

$$TOTCd = \{Cd^{2+}\} + \sum_{i=1}^{3} \{CdCl_i\}$$

$$TOTCd = \{Cd^{2+}\}(1 + \beta_{Cl,1}\{Cl^-\}^1 + \beta_2\{Cl^-\}^2 + \beta_3\{Cl^-\}^3) \quad \textbf{(8.32)}$$

$$= \{Cd^{2+}\}\left(1 + \sum_{i=1}^{n} \beta_{Cl,i}\{Cl^-\}^i\right) \quad \textbf{(8.33)}$$

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The fraction of *TOT*Cd that is in a given form can then be easily computed. For instance, the fraction of *TOT*Cd that is present as free Cd^{2+} ion is

$$\alpha_{Cd^{2+}} = \frac{[Cd^{2+}]}{TOTCd} = \left(1 + \sum_{i=1}^{3} \beta_{Cl,i}\{Cl^-\}^i\right)^{-1} \quad \textbf{(8.34)}$$

The activity of Cl^- in seawater is approximately 0.5. Plugging this value and the appropriate values for $\beta_{Cl,i}$ into Equation (8.34), we find $\alpha_{Cd^{2+}} = 5.57 \times 10^{-3}$. In other words, only about 0.5% of the dissolved Cd in seawater is present as Cd^{2+} ions. (In truth, $\alpha_{Cd^{2+}}$ in seawater is even less than this value due to formation of complexes with other ligands in the solution, as described below.) The same approach can be used to compute α values of the other Cd species in the system.

Next, consider a system in which complexation by chloride is significant, but the assumption that the hydroxo complexes are negligible does not necessarily apply. Specifically, say we wished to analyze the Cd speciation in a solution containing 10^{-4} *M TOT*Cd in which $\{Cl^-\}$ is fixed at 0.5 *M*, but the pH is variable. Such a system can be represented by a log *C*–pH diagram for Cd in the system. However, we anticipate that the diagram will be different from Figure 8.2 because of the presence of Cl^-.

We first evaluate the relative concentrations of Cd^{2+} and the various Cd—Cl complexes. Because the reactions among these species do not involve exchange of H^+ or OH^-, the relative concentrations of these species must be independent of pH. This conceptual result can be demonstrated formally by manipulation of the relevant stability constant expressions:

$$Cd^{2+} + iCl^- \leftrightarrow CdCl_i^{2-i} \quad \textbf{(8.35)}$$

$$\beta_{Cl,i} = \frac{\{CdCl_i^{2-i}\}}{\{Cd^{2+}\}\{Cl^-\}^i} \quad \textbf{(8.36)}$$

$$\{CdCl_i^{2-i}\} = \beta_{Cl,i}\{Cd^{2+}\}\{Cl^-\}^i$$

$$\log\{CdCl_i^{2-i}\} = \log\beta_{Cl,i} + \log\{Cd^{2+}\} + i\log\{Cl^-\} \quad \textbf{(8.37)}$$

According to Equation (8.37), if $\{Cl^-\}$ is fixed, as it is in the system of interest, the expression for the activity of each $CdCl_i^{2-i}$ complex can be written in the following form:

$$\log\{CdCl_i^{2-i}\} = \log\{Cd^{2+}\} + \text{constant} \quad \textbf{(8.38)}$$

The absence of a term containing $\{H^+\}$ in Equation (8.38) indicates that the curve representing any $CdCl_i^{2-i}$ species on a log *C*–pH diagram will be identical to the curve for Cd^{2+}, except that it will be offset vertically from the Cd^{2+} curve by a constant amount. Hence, all the $CdCl_i^{2-i}$ lines are parallel to the Cd^{2+} line.

Figure 8.5 indicates that, at $\{Cl^-\} = 0.5$ (i.e., $\log\{Cl^-\} = -0.3$), the concentrations of all three chloro— complexes are greater than that of Cd^{2+}. As a result, the free, uncomplexed Cd^{2+} ion is never the dominant Cd species in this

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system. The same reasoning leads us to conclude that $CdCl^+$ and $CdCl_3^-$ will never be dominant, because the activity of $CdCl_2^o$ is always greater than that of these two species.

Now consider the relative concentrations of Cd^{2+} and the Cd—OH complexes. Because the relationships among these species are independent of $\{Cl^-\}$, the relative concentrations of those species at a given pH are the same as when no Cl^- is present. That is, $\{Cd^{2+}\} = \{CdOH^+\}$ at $pH = p^*K_{OH,1} = 10.08$, $\{CdOH^+\} = \{CdOH_2^o\}$ at $pH = p^*K_{OH,2} = 10.27$, etc.

Thus, we know the relationships among the activities of Cd^{2+} and the Cd—OH complexes, and those among the activities of Cd^{2+} and the Cd—Cl complexes; the only thing we have not yet determined is how the system speciation arranges itself such that all these equilibrium relationships are satisfied simultaneously. We can explore that issue by calculating the speciation at a particular pH value and then extrapolating the result to the entire range of pH values of interest.

Consider the conditions at pH 9.0. At this pH, the activity of each Cd—OH complex can be expressed in terms of the activity of Cd^{2+} as

$$\{Cd(OH)_i^{2-i}\} = \beta_{OH,i}\{Cd^{2+}\}\{OH^-\}^i = \beta_{OH,i}\{Cd^{2+}\}(10^{-5.0})^i$$

Similarly, since $\{Cl^-\}$ is fixed at 0.5, the activity of each Cd—Cl complex can be expressed in terms of $\{Cd^{2+}\}$ as

$$\{CdCl_i^{2-i}\} = \beta_{Cl,i}\{Cd^{2+}\}\{Cl^-\}^i = \beta_{Cl,i}\{Cd^{2+}\}(0.5)^i$$

Carrying out the various calculations associated with the above equations, we can summarize the relative activities of all the Cd species in solution as follows:

$$\{CdOH^+\} = 8.32 \times 10^{-2}\{Cd^{2+}\}$$
$$\{Cd(OH)_2^o\} = 4.47 \times 10^{-3}\{Cd^{2+}\}$$
$$\{Cd(OH)_3^-\} = 5.01 \times 10^{-7}\{Cd^{2+}\}$$
$$\{Cd(OH)_4^{2-}\} = 4.47 \times 10^{-12}\{Cd^{2+}\}$$
$$\{CdCl^+\} = 47.7\{Cd^{2+}\}$$
$$\{CdCl_2^o\} = 99.5\{Cd^{2+}\}$$
$$\{CdCl_3^-\} = 31.4\{Cd^{2+}\}$$

A mass balance on total Cd in the system can therefore be written as follows:

$$\begin{aligned} TOTCd &= \{Cd^{2+}\} + \{CdOH^+\} + \{Cd(OH)_2^o\} + \{Cd(OH)_3^-\} \\ &\quad + \{Cd(OH)_4^{2-}\} + \{CdCl^+\} + \{CdCl_2^o\} + \{CdCl_3^-\} \\ &= 179.8\{Cd^{2+}\} \\ 10^{-4} &= 179.8\{Cd^{2+}\} \\ \{Cd^{2+}\} &= 5.56 \times 10^{-7} \end{aligned}$$

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Having determined $\{Cd^{2+}\}$, we can plug into the relationships derived above to compute the activity of each of the other Cd-containing species:

$$\{CdOH^+\} = 4.63 \times 10^{-8} \qquad \{CdCl^+\} = 2.66 \times 10^{-5}$$

$$\{Cd(OH)_2^o\} = 2.48 \times 10^{-9} \qquad \{CdCl_2^o\} = 5.54 \times 10^{-5}$$

$$\{Cd(OH)_3^-\} = 2.79 \times 10^{-13} \qquad \{CdCl_3^-\} = 1.75 \times 10^{-5}$$

$$\{Cd(OH)_4^{2-}\} = 2.48 \times 10^{-18}$$

If we carried out analogous calculations at other pH values, we could determine the speciation of the system and plot the log C–pH diagram, which is shown in Figure 8.6.

As expected based on the discussion above, the lines for all $CdCl_i^{2-i}$ species are parallel to the Cd^{2+} line. Also, as must be the case, the various acid/base conjugate pairs of the Cd—OH system have equal activities at the corresponding $p^*K_{OH,i}$ values, e.g., $\{Cd^{2+}\} = \{CdOH^+\}$ at pH = $p^*K_1 = 10.08$. However, at these intersection points, each of the two species does not necessarily account for 50% of *TOT*Cd. For instance, at pH 10.08, $\{Cd^{2+}\} = \{CdOH^+\}$, but each of these species represents only about 0.31% of *TOT*Cd. The reason for this result, of course, is that the vast majority of the Cd in the system is present as Cd—Cl complexes. The fact that pH = p^*K_{OH} does not ensure that each of the acid/base species related by the $^*K_{OH}$ expression will account for 50% of the total concentration in the system, only that the acid and conjugate base will be present at equal activities. Thus, the result that $\{Cd^{2+}\} = \{CdOH^+\} = 0.0031\,TOT$Cd is entirely consistent with the constraint imposed by the equilibrium constant.

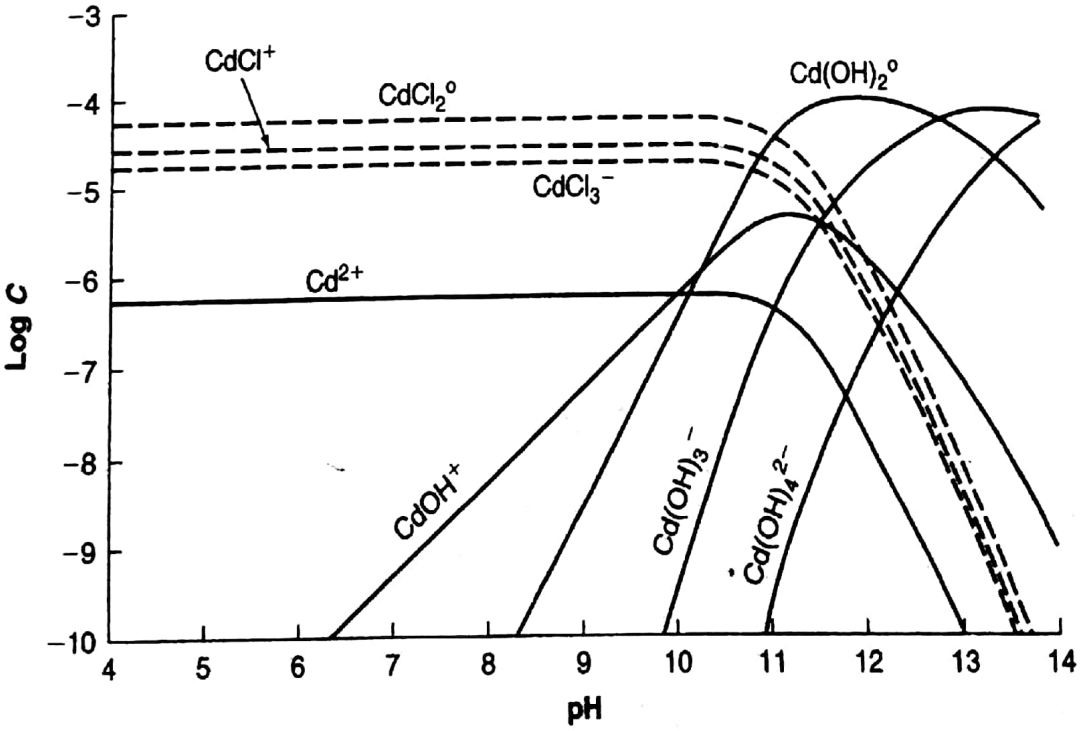

Figure 8.6 Log C–pH diagram for a system containing 10^{-4} *M TOT*Cd and $\{Cl^-\} = 0.5$.

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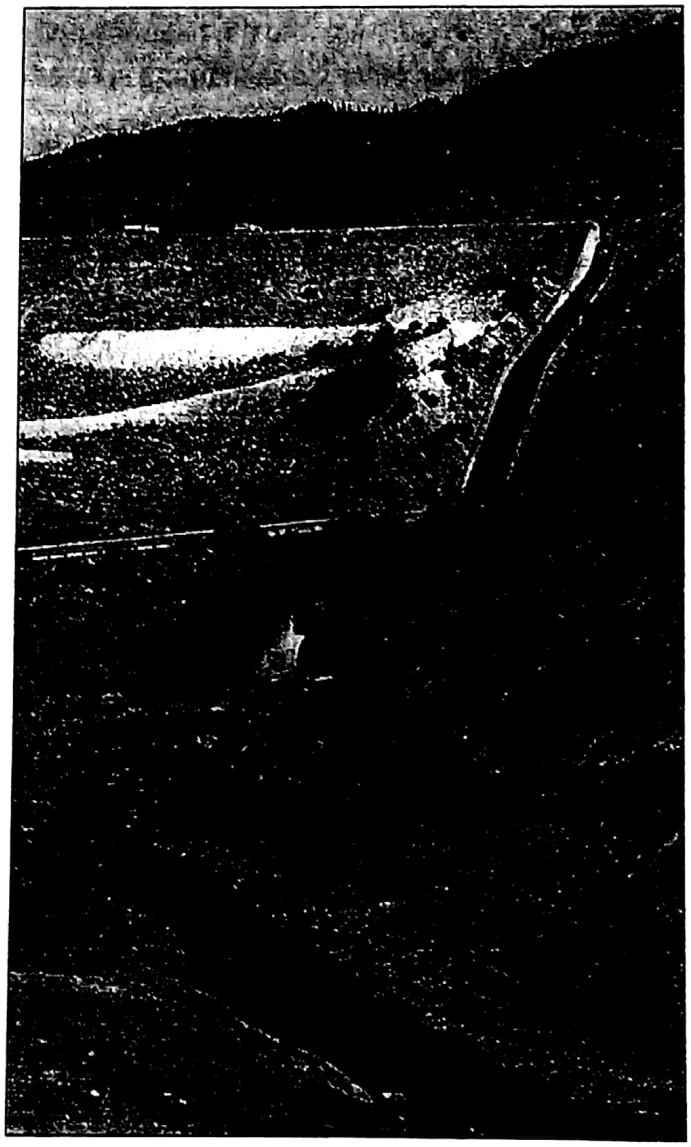

The acidic waters that drain from mines can contain large concentrations of metals. When these waters mix with others or are neutralized by some other process, large amounts of metals can precipitate in the stream.

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To summarize the key points of the above discussion, the presence of complexing ligands in a solution containing a weak acid metal group forces us to consider more equilibrium expressions and more terms in the metal mass balance than in their absence. Correspondingly, the log C–pH diagram contains curves for more species. However, the relationships among those species are the same as in simpler systems. The mass balance for the example system and for a generic system with m different ligands (including OH^-) can be written as follows:

Cl^- and OH^- as ligands:

$$TOTCd = \{Cd^{2+}\} + \sum_{i=1}^{4}\{Cd(OH)_i\} + \sum_{i=1}^{3}\{CdCl_i\}$$

$$= \{Cd^{2+}\}\left(1 + \sum_{i=1}^{4}\beta_{OH,i}\{OH^-\}^i + \sum_{i=1}^{3}\beta_{Cl,i}\{Cl^-\}^i\right) \qquad \textbf{(8.39)}$$

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m ligands:

$$TOTCd = \{Cd^{2+}\}\left(1 + \sum_{j=1}^{m}\sum_{i=1}^{n}\beta_{L_j,i}\{L_j\}^i\right) \quad (8.40)$$

Because Equation (8.40) is simply a concise way of writing the mass balance on Cd in a system with multiple ligands, it applies to any system containing Cd and ligands, regardless of what the ligands are or what other reactions affect the ligands' concentrations.

Comparing Figures 8.2 and 8.6, we see that the addition of 0.5 M Cl^- to the solution eliminates the dominance region of $CdOH^+$ and shifts that of $Cd(OH)_2^o$ to a narrower pH region. We might explain this observation as resulting from the fact that the addition of Cl^- and the corresponding formation of relatively strong Cd—Cl complexes (relative to Cd—OH complexes, that is) diminishes the importance of all Cd—OH complexes in the system, and that in some cases this effect prevents a Cd—OH complex from becoming dominant under conditions where it otherwise would be.

8.3 USE OF CHEMICAL EQUILIBRIUM SOFTWARE TO MODEL SYSTEMS CONTAINING METALS, LIGANDS, AND COMPLEXES

The analysis of metal speciation using chemical equilibrium software is a trivial extension from the analysis of acid/base speciation. Obviously, the software does not "know" whether two *components* that are combining are a base and an H^+ ion or a metal ion and a ligand. Furthermore, the types of equations that need to be solved to determine the speciation are the same in the two groups of systems, comprising a group of equilibrium constant equations and some mass balances. Therefore, all the procedures for providing the software with information about the total concentrations of *components,* the stoichiometry and equilibrium constants for forming *species,* and the chemical inputs used to prepare the solution are identical in the two types of systems. (The situation does get slightly more complicated in cases where a metal can precipitate out of solution, and we will consider how the software deals with those situations later in the chapter.)

Example 8.1

Prepare the input tableau for use of chemical equilibrium software to determine the speciation in the Cd-Cl-OH example system described above (pH 9.0, fixed Cl^- activity of 0.5, $TOTCd = 10^{-4}$ M).

Solution

The tableau is prepared exactly as it would be for a system that contained only acid/base species. We can choose Cd^{2+}, Cl^-, and H^+ as *components* (in addition to H_2O, which is included in the *component* list implicitly). All three of the *components* will be present in the equilibrium solution as corresponding Type 1 *species.* In addition, all the Cd—OH and Cd—Cl complexes will be present as Type 2 *species.*

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