

# Solids in contact with natural waters

A Chem1 Reference Text

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Natural waters interact with rocks and sediments containing ionic solids having limited solubilities, thereby acquiring solutes which may be transported to other locations where they can be removed by chemical precipitation or uptake by organisms. The hard parts of marine organisms consist largely of solids such as calcite and silica which are formed and destroyed in accordance with the same equilibria; these play an important role in determining the composition of ocean water. The solubility profiles of the compounds of Cd, Hg and Pb are of interest as they affect the deposition and movement of these toxic pollutants in the environment.

The simplified treatment of solubility equilibria that is commonly presented in introductory Chemistry courses is somewhat misleading. Actual equilibria between dissolved species and solids may occur slowly or not at all, and species or phases other than the ones that attention is focussed on are frequently involved. These include aquo-complexes in various states of deprotonation, other complexes including those involving organic material, polynuclear species, ion exchange with clay solids, and interaction with gaseous carbon dioxide. In addition, the solubilities of a number of important metallic elements are markedly different in different oxidation states, so oxidation and reduction (the latter often brought about by reaction with organic matter) can be an important mechanism in element cycling.

The kinetics of heterogeneous processes are dependent on surface phenomena, and frequently lead to supersaturated solutions and formation of phases other than the thermodynamically predicted one.

## 1 Nucleation and growth

Contrary to what you may have been taught, precipitates do *not* form when the ion concentration product reaches the solubility product of an ionic solid; to form a precipitate from a homogeneous solution, a certain degree of supersaturation is required. Smaller crystals are more soluble because they contain a larger number of edges and corners per unit of mass; ions in these locations are less tightly bound to the rest of the solid.

In any ionic solution, small clumps of oppositely-charged ions are continually forming by ordinary collisional processes. The smallest of these aggregates possess a higher free energy than the isolated solvated ions, and they rapidly dissociate. Occasionally, however, one of these proto-crystallites reaches a critical size whose stability allows it to remain intact long enough to serve as a surface onto which the deposition of additional ions can lead to still greater stability. At this point, the process passes from the *nucleation* to the *growth* stage.

Theoretical calculations predict that nucleation from a homogeneous solution is a rather unlikely process; tenfold supersaturation should produce only one nucleus per  $\text{cm}^3$  per year. Most nucleation is therefore believed to occur heterogeneously on the surface of some other particle, possibly a dust particle. The efficiency of this process is critically dependent on the nature and condition of the surface that gives rise to the nucleus.

Once a crystallite enters the growth phase, deposition of further material occurs largely by formation of successive layers on the surface, and by propagation of screw dislocations. Presence of adsorbed species on the surface can inhibit growth. In some cases this inhibition can be selective, leading to the formation of a metastable phase such as aragonite instead of the thermodynamically stable calcite phase of  $\text{CaCO}_3$ .

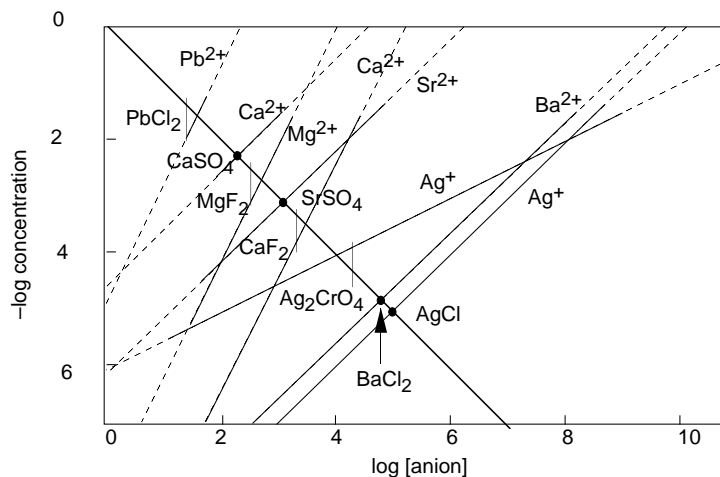


Figure 1: Solubility of “non-hydrolyzing” salts as a function of the common ion concentration. Dashed lines indicate regions of ion-pair or complex formation.

## 2 Solubility products

The solubility of a substance such as  $\text{CaSO}_4$  is governed by the equilibrium relation

$$K_s = \frac{\{\text{Ca}^{2+}\}\{\text{SO}_4^{2-}\}}{\{\text{CaSO}_4(s)\}} \quad (1)$$

and by the electroneutrality condition which in the absence of a common ion and in neutral solution is simply

$$[\text{Ca}^{2+}] + [\text{SO}_4^{2-}] = 0 \quad (2)$$

If the activity of the solid phase is unity (which is not always the case; many natural solids form solid solutions), the equilibrium relation reduces to the familiar solubility product expression:

$$K_s \approx [\text{Ca}^{2+}][\text{SO}_4^{2-}] \quad (3)$$

### 2.1 Common ion effect

In many practical cases involving natural waters, the solubility of a metal cation is controlled by the concentration of the same anion that is present in the solid. This always has the effect of reducing the solubility of the solid.

The common ion effect is best illustrated by means of logarithmic plots of the equilibrium metal ion concentration as a function of the anion concentration. The plots in Fig. 1 express the following conditions for three typical cases:

<i>solid</i>	<i>solubility</i>	<i>electroneutrality condition</i>
$\text{CaSO}_4$	$\log [\text{Ca}^{2+}] = -\text{p}K_s + \text{pSO}_4^{2-}$	$\log [\text{Ca}^{2+}] = \log [\text{SO}_4^{2-}]$
$\text{Ag}_2\text{SO}_4$	$\log [\text{Ag}^+] = -\frac{1}{2} \text{p}K_s + \frac{1}{2} \text{pSO}_4^{2-}$	$\log [\text{Ag}^+] = .3 + \log [\text{SO}_4^{2-}]$
$\text{MgF}_2$	$\log [\text{Mg}^{2+}] = -\text{p}K_s + 2 \text{pF}^-$	$\log [\text{Mg}^{2+}] = -.3 + \log [\text{F}^-]$

Note that the slopes of the log plots are determined by the stoichiometry of the solids. Also, the solubility of the solid in pure water can be found from the plot of the anion concentration having a slope of  $-1$ , if the electroneutrality condition is suitably applied.

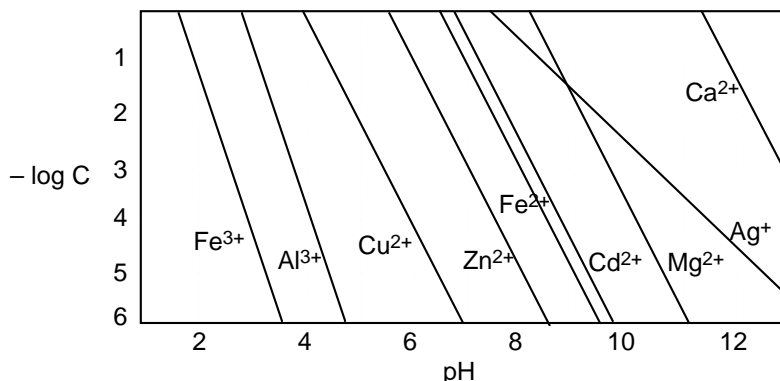
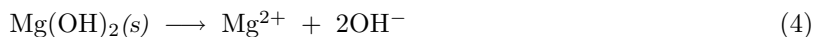


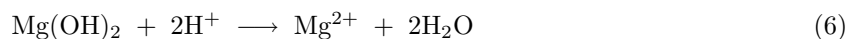
Figure 2: Solubilities of oxides and hydroxides as a function of pH

### 3 Solubility of oxides and hydroxides

Metallic oxides and hydroxides both form solutions containing  $\text{OH}^-$  ions. For example, the solubilities of the oxide and hydroxide of magnesium are represented by



Note that the solubility product  $K_s = [\text{Mg}^{2+}][\text{OH}^-]^2$  is the same for each these reactions. The pH dependence of the solubility is expressed by



for which the equilibrium constants have the form

$$K_s' = \frac{[\text{Mg}^{2+}]}{[\text{H}^+]^2} = K_s K_w^{-2} \quad (8)$$

Thus the slope of a  $\log\text{-}[\text{M}^{+n}]$  vs. pH plot depends on the cationic charge.

The hydroxides of calcium and magnesium are both important in water treatment. Slaked lime,  $\text{CaCO}_3$ , is commonly added to hard water to remove  $\text{Mg}^{2+}$  by precipitation of  $\text{Mg(OH)}_2$ . From the solubility products for these two solids, we can write

$$-\log [\text{Ca}^{2+}] + 2\text{pOH} = 5.34 \quad (9)$$

and

$$-\log [\text{Mg}^{2+}] + 2\text{pOH} = 10.74 \quad (10)$$

which are plotted in Fig. 3. The electroneutrality condition is

$$2[\text{Ca}^{2+}] + [\text{H}^+] = [\text{OH}^-] \quad (11)$$

If  $[\text{H}^+] \ll 2[\text{Ca}^{2+}]$ , this simplifies to

$$2[\text{Ca}^{2+}] = [\text{OH}^-] \quad (12)$$

$$\text{pOH} = -\log [\text{Ca}^{2+}] - .3 \quad (13)$$

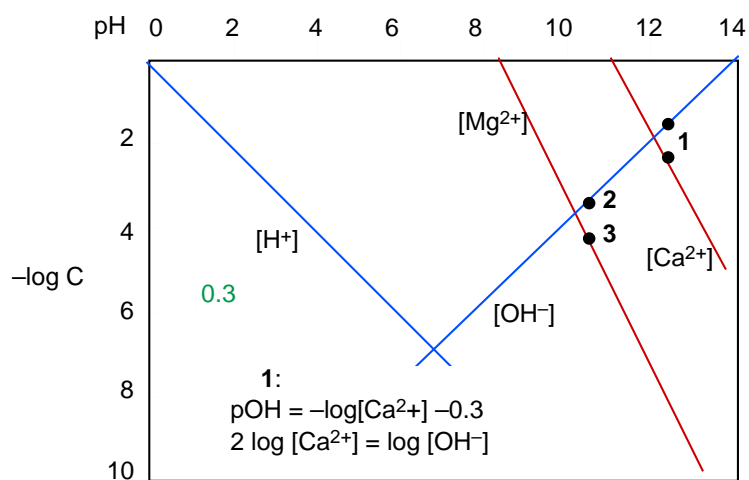


Figure 3: pC-pH plots for  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ . (From Snoeyink and Jenkins)

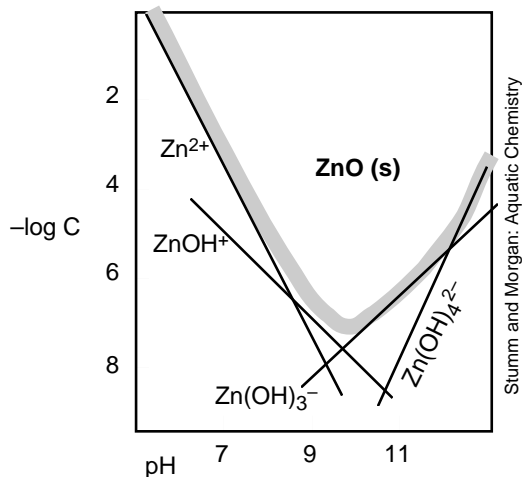


Figure 4: Stability of solid ZnO as a function of pH.

This condition is satisfied at point *A* in Fig. 3: a solution of  $\text{Ca}^{2+}$  in pure water will be  $.01\text{ M}$  in  $\text{Ca}^{2+}$  and have a pOH of 1.7. Similarly, the condition for  $\text{Mg}^{2+}$



is satisfied at  $[\text{Mg}^{2+}] = 10^{-3.8}$  and pOH= 3.5, corresponding to point *B*.

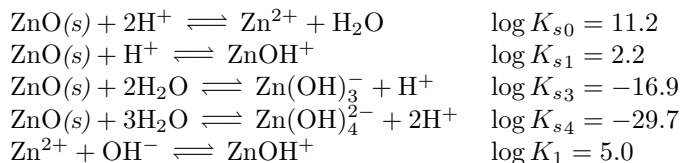
At what pH will a precipitate occur when solutions containing  $10^{-4}\text{ M}$   $\text{Mg}^{2+}$  and  $10^{-3}\text{ M}$   $\text{Ca}^{2+}$  are made more alkaline by adding NaOH?  $\text{Mg}(\text{OH})_2$  will be in equilibrium with a  $10^{-4}\text{ M}$   $\text{Mg}^{2+}$  solution at point **3**, indicating that this solid will form above pH 10.65. At this point, all the  $\text{Ca}^{2+}$  remains in solution, so only the magnesium will be removed.

### 3.1 Formation of hydroxo-complexes

4 Many di- and trivalent cations “hydrolyze” to form hydroxo-complexes whose concentrations also depend on the pH. The total cation concentration in a solution of such a salt is

$$M_T = [\text{M}^{z+}] + \sum_1^n [\text{M}(\text{OH})_n^{z-n}] \quad (15)$$

Typical values of  $n$  range from 1-4, so quantitative treatment of such equilibria can be extremely complicated. Thus for the dissolution of ZnO, we have the equilibria



On a log plot (Fig. 4) the slopes of the lines for  $[\text{Zn}^{2+}]$ ,  $[\text{Zn}(\text{OH})^+]$ ,  $[\text{Zn}(\text{OH})_3^-]$  and  $[\text{Zn}(\text{OH})_4^{2-}]$  are -2, -1, +1, and +2. The intercepts are determined by noting that  $[\text{Zn}(\text{OH})^+] = [\text{Zn}^{2+}]$  when  $\text{pH} = \text{p}K_1$ , etc. The region in which  $\text{ZnO}(s)$  is the stable species is bounded by the uppermost of the log- $C$  lines at any given pH value. The total “dissolved Zn” concentration is given by

$$C_{T,\text{Zn}} = K_{s0}[\text{H}^+]^2 + K_{s1}[\text{H}^+] + K_{s3}[\text{H}^+]^{-1} + K_{s4}[\text{H}^+]^{-2} \quad (16)$$

An oxide such as ZnO is said to be *amphoteric*, in that it is soluble in both acidic and strongly basic solutions.

## 4 Salts of weak acids and bases

The solubility of a salt containing an ion such as  $\text{CN}^-$ ,  $\text{S}^{2-}$ , or  $\text{NH}_4^+$  will depend on the pH just as it does in the cases of the oxides and hydroxides discussed above, and for the same reason: lowering the pH of a solution containing  $\text{CO}_3^{2-}$ , for example, will remove this ion from solution, thus favoring the dissolution of a solid carbonate.

As an example of the quantitative treatment of this kind of salt, consider a hypothetical substance MA, and assume that HA, the conjugate acid of the anion, is a weak acid with dissociation constant  $K_a$ . There are six unknowns: the solubility  $S$ ,  $[\text{M}^+]$ ,  $[\text{A}^-]$ ,  $[\text{HA}]$ ,  $[\text{H}^+]$ , and  $[\text{OH}^-]$ . The six independent equations required include the expressions for  $K_s$ ,  $K_a$ , and  $K_w$ . Two more are contained in the mass balance expression

$$S = [\text{M}^+] = C_{\text{T,M}} \quad (17)$$

$$S = \text{HA} + \text{A}^- = C_{\text{T,A}} \quad (18)$$

and the sixth is the electroneutrality condition

$$[\text{H}^+] + [\text{M}^+] = [\text{A}^-] + [\text{OH}^-] \quad (19)$$

Eq 17 can be simplified by substituting the equilibrium constant expression for  $K_a$ , and using the distribution fraction  $\alpha_1$ :

$$\alpha_1 = \frac{K_a}{[\text{H}^+] + K_a} \quad (20)$$

$$[\text{A}^-] = \alpha_1 S \quad (21)$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \quad (22)$$

$$K_s = [\text{M}^+][\text{A}^-] = (S)(\alpha_1 S) = \alpha_1 S^2 \quad (23)$$

$$S = \left( \frac{K_s}{\alpha_1} \right)^{\frac{1}{2}} \quad (24)$$

Substituting Eqs. (17) and (21) into (19),

$$[\text{H}^+] + S = \alpha_1 S + \frac{K_w}{[\text{H}^+]} \quad (25)$$

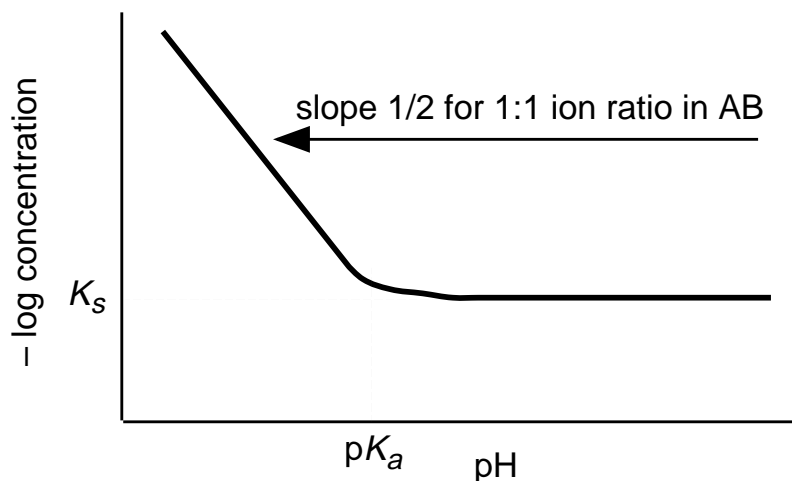
$$[\text{H}^+] + \left( \frac{K_s}{\alpha_1} \right)^{\frac{1}{2}} - \alpha_1 \left( \frac{K_s}{\alpha_1} \right)^{\frac{1}{2}} - \frac{K_w}{[\text{H}^+]} = 0 \quad (26)$$

The root of this equation (which is solved by trial-and-error) gives the pH of a solution of the salt in pure water; this controls  $\alpha_1$ , which can be used to find the solubility in Eq 21.

It is instructive to examine the pH dependence of the solubility of a salt of a weak acid. Since  $S = [\text{HA}] + [\text{A}^-]$ , we can use  $K_a$  to write

$$S = \frac{[\text{H}^+][\text{A}^-]}{K_a} + [\text{A}^-] = \frac{[\text{A}^-]( [\text{H}^+] + K_a )}{K_a} \quad (27)$$





The solubility of a sparingly soluble salt MA of a weak acid depends on the relative abilities of  $H^+$  and  $M^+$  to bind the anion  $A^-$ . When the pH is higher than the pK of the acid, the latter is almost entirely in its base form and the solubility of the salt is practically independent of the pH. When the pH is lower, more HA forms, thus allowing  $M^+$  ions to dissolve. The slope of the solubility curve in this region is governed by the stoichiometry of the salt.

Figure 5: Solubility of a salt of a weak acid as a function of pH.

and thus

$$S = \frac{[A^-]}{\alpha_1} \quad (28)$$

$$[A^-] = S\alpha_1 \quad (29)$$

Also, from the expression for  $K_s$ ,

$$[A^-] = \frac{K_s}{[M^+]} = \frac{K_s}{S} \quad (30)$$

Substituting for  $[A^-]$  from Eq 29,

$$S\alpha_1 = \frac{K_s}{S} \quad (31)$$

Solving for  $S$ ,

$$S = \left(\frac{K_s}{\alpha_1}\right)^{\frac{1}{2}} = \left[\left(\frac{K_s}{K_a}\right) ([H^+] + K_a)\right]^{\frac{1}{2}} \quad (32)$$

In solutions of higher pH where  $[H^+] \ll K_a$ , this expression is approximated by

$$S = K_s^{\frac{1}{2}}, \quad \log S = \frac{1}{2} \log K_s \quad (33)$$

In acidic solutions with  $[H^+] \gg K_a$ ,

$$S = \left(\frac{K_s[H^+]}{K_a}\right)^{\frac{1}{2}} \quad (34)$$

and

$$\log S = \frac{1}{2}(pK_a - pK_s - pH) \quad (35)$$

## 5 Solubility of carbonates

Carbonates, mainly  $CaCO_3$ , but also  $MgCO_3$  and  $Fe_2(CO_3)_3$  (and mixtures of these with  $CaCO_3$ ) are major components of marine sediments and of deposits of sedimentary origin that cover large regions of land areas. These carbonates react with natural waters and with rainwater, and can also exchange  $CO_2$  with the atmosphere.

## 5.1 CaCO<sub>3</sub>, Closed system

In the simplest treatment, we consider H<sub>2</sub>CO<sub>3</sub>\* to be a nonvolatile acid, so  $P_{\text{CO}_2}$  is not a variable. The relations between the six solute species Ca<sup>2+</sup>, H<sub>2</sub>CO<sub>3</sub>\*, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, H<sup>+</sup> and OH<sup>-</sup> are defined by the four mass laws  $K_w$ ,  $K_1$ ,  $K_2$  and  $K_s$ , together with the two additional relations expressing the mass conservation of Ca and electroneutrality; these last two vary in form with the specific case being considered.

### Solubility of calcite in pure water

In this case, the latter two relations are

$$[\text{Ca}^{2+}] = C_T = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (36)$$

and

$$2[\text{Ca}^{2+}] + 2[\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (37)$$

Using the H<sub>2</sub>CO<sub>3</sub> ionization fractions  $\alpha_n$  to express the concentrations of the dissolved carbonate species, we can rewrite the above relation:

$$[\text{Ca}^{2+}] = \frac{K_s}{[\text{CO}_3^{2-}]} = \frac{K_s}{C_T \alpha_2} = C_T \quad (38)$$

$$[\text{Ca}^{2+}] = C_T = \left( \frac{K_s}{\alpha_2} \right)^{\frac{1}{2}} \quad (39)$$

This is substituted into the electroneutrality condition to obtain

$$\left( \frac{K_s}{\alpha_2} \right)^{\frac{1}{2}} (2 - \alpha_1 - 2\alpha_2) + [\text{H}^+] - \frac{K_w}{[\text{H}^+]} = 0 \quad (40)$$

Which can be solved by trial-and-error.

### Dissolution of calcite in acidic or basic solution

In this more general case, which describes the acidimetric titration of a CaCO<sub>3</sub> suspension, the electroneutrality condition becomes

$$- [\text{SID}] = C_A - C_B = \left( \frac{K_s}{\alpha_2} \right)^{\frac{1}{2}} (2 - \alpha_1 - 2\alpha_2) + [\text{H}^+] - \frac{K_w}{[\text{H}^+]} \quad (41)$$

The slopes of the lines of a log  $C$ -pH plot (see Fig. 6) are readily approximated in the three pH regions of interest:

$$\text{pH} > \text{p}K_2: \quad \frac{d(\log C_T)}{d(\text{pH})} = 0 \quad (42)$$

$$\text{p}K_1 < \text{pH} < \text{p}K_2: \quad \frac{d(\log C_T)}{d(\text{pH})} = -\frac{1}{2} \quad (43)$$

$$\text{pH} < \text{p}K_1: \quad \frac{d(\log C_T)}{d(\text{pH})} = -1 \quad (44)$$

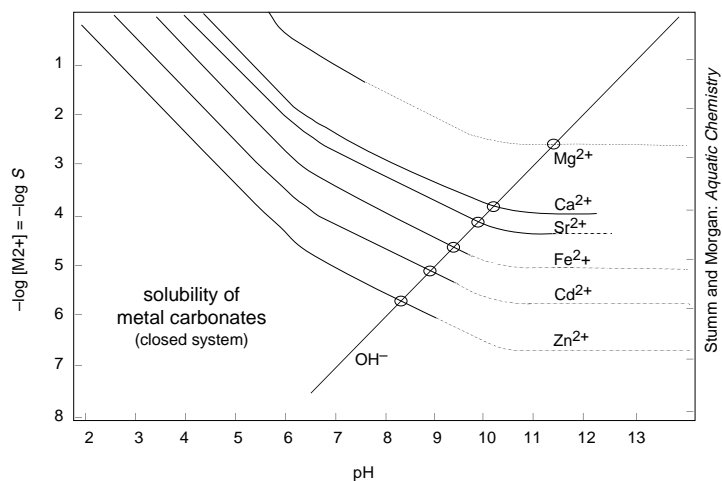


Figure 6: Log  $C$ -pH diagram for the solubility of metal carbonates in a closed system. The insert shows how the details of this plot are derived for  $\text{CaCO}_3$ . (After Stumm and Morgan).

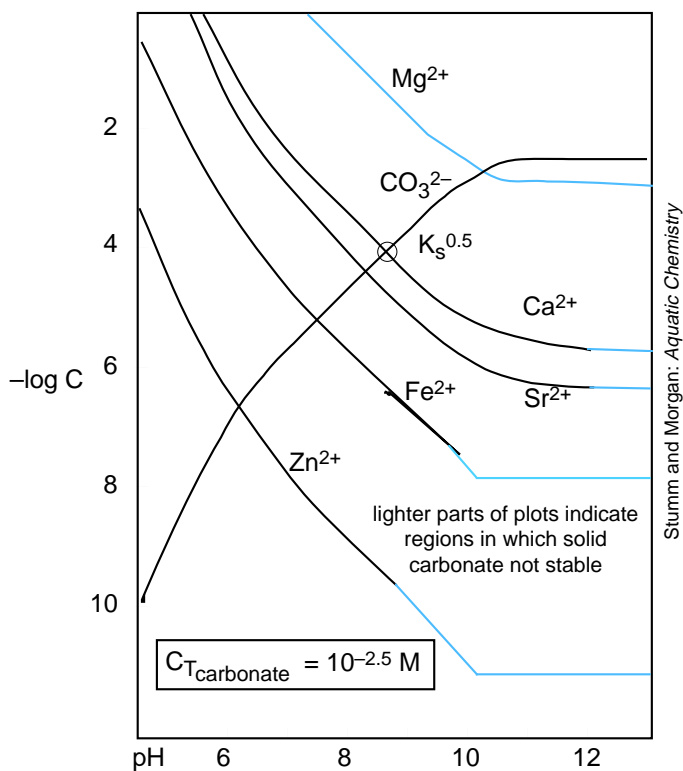


Figure 7: Solubility of metal carbonates for a closed system with constant total carbonate.

### Maximum concentration of a cation in a carbonate solution

Natural waters always contain cations (mainly  $\text{Ca}^{2+}$ ) whose carbonates can precipitate out at higher pH values. In water treatment operations it is particularly important to know whether the water will be over- or undersaturated with respect to metal carbonates within the pH range of interest.

Using  $\text{CaCO}_3$  as an example, the solubility is given by

$$[\text{Ca}^{2+}] = \frac{K_s}{[\text{CO}_3^{2-}]} = \frac{K_s}{C_T \alpha_2} \quad (45)$$

and thus we have the slopes in Fig. 7 of

$$\frac{d \log[\text{Ca}^{2+}]}{d(\text{pH})} = -\frac{d \log[\text{CO}_3^{2-}]}{d(\text{pH})} = \begin{cases} 0 & \text{pH} > \text{p}K_2 \\ -1 & \text{p}K_1 < \text{pH} < \text{p}K_2 \\ -2 & \text{pH} < \text{p}K_1 \end{cases} \quad (46)$$

## 5.2 Solubility of carbonates in an open system

In the presence of gaseous  $\text{CO}_2$ , the condition  $C_T = [\text{Ca}^{2+}]$  no longer holds, since the atmosphere provides an additional source of carbonate. In addition to the four mass laws, we have the Henry's law constant  $K_H$  for the equilibrium with  $\text{H}_2\text{CO}_3^*$ , and the electroneutrality condition

$$2[\text{Ca}^{2+}] + [\text{H}^+] = C_T(\alpha_1 + 2\alpha_2) + [\text{OH}^-] \quad (47)$$

Making the substitutions:

$$[\text{Ca}^{2+}] = \frac{K_s}{C_T \alpha_2} \quad (48)$$

$$C_T = \frac{K_H P_{\text{CO}_2}}{\alpha_0} \quad (49)$$

$$[\text{CO}_3^{2-}] = \frac{K_H P_{\text{CO}_2} \alpha_2}{\alpha_0} \quad (50)$$

$$[\text{Ca}^{2+}] = \frac{(K_s / K_H P_{\text{CO}_2}) \alpha_0}{\alpha_2} \quad (51)$$

the electroneutrality condition becomes

$$\frac{K_s (K_H P_{\text{CO}_2}) \alpha_0}{\alpha_2} + [\text{H}^+] = \frac{K_H P_{\text{CO}_2}}{\alpha_0} (\alpha_1 + 2\alpha_2) + \frac{K_w}{[\text{H}^+]} \quad (52)$$

Examination of Fig. 8 shows that the partial pressure of  $\text{CO}_2$  controls both the pH of the solution, and thus the relative amounts of  $\text{H}_2\text{CO}_3^*$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ . The effect of opening a saturated solution of calcite to the atmosphere is to depress the pH and raise the alkalinity and  $[\text{Ca}^{2+}]$  to values that are representative of natural waters: typically  $\text{pH} \sim 8.4$ ,  $[\text{Alk}] \approx .001$  and  $[\text{Ca}^{2+}] = 10^{-3.3} \text{ M}$ .

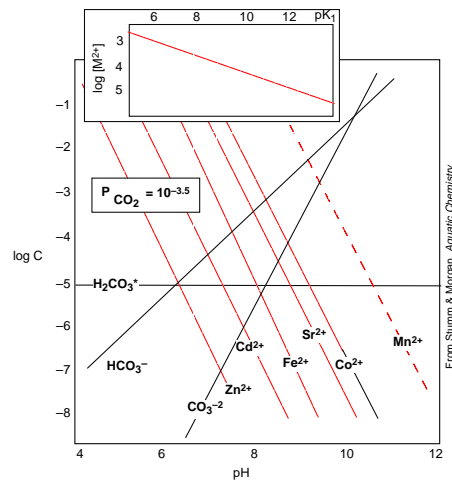


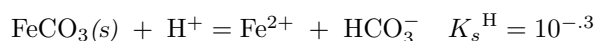
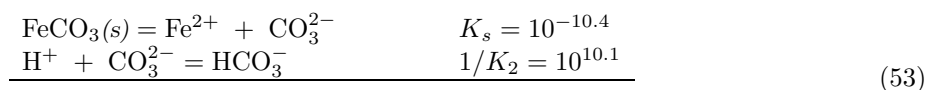
Figure 8: Solubility of metal carbonates as a function of pH in an open system with  $P_{\text{CO}_2} = 10^{-3.5}$  atm.

## 6 Competition between insoluble phases

Most metals that form insoluble carbonates also form insoluble hydroxides, sulfides, etc. In waters containing a mixture of these anions, it is important to know which solid will be favored under a given set of conditions.

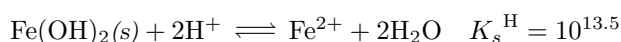
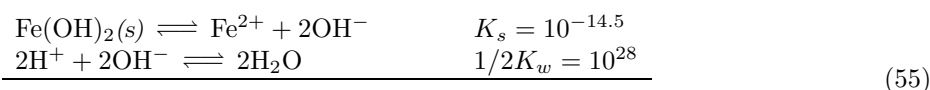
Simple comparison of solubility products is not enough; pH,  $C_T$  (total dissolved carbonate), [Alk] and  $P_{CO_2}$  must also be considered. Also, solubility products for substances of different stoichiometries cannot be compared directly.

Iron(II) serves as a good example of this kind of relationship; the carbonate and hydroxide are both insoluble, and both of these solids are encountered in sediments in contact with natural waters. For each of these solids, we can write a conditional “acid” solubility constant  $K_s^H$ :



$$\log [\text{Fe}^{2+}] = \log K_s^H - \text{pH} - \log[\text{HCO}_3^-] \quad (54)$$

The pH and  $[\text{HCO}_3^-]$  terms will of course depend on  $P_{CO_2}$  and [Alk].



$$\log [\text{Fe}^{2+}] = \log K_s^H - 2 \text{pH} \quad (56)$$

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**Problem:** Which of these two solids controls the solubility of Fe(II) in an anoxic water of [Alk]= $10^{-4}$  eq/l and pH = 6.8? (*Hint:* assume that all the alkalinity is due to  $\text{HCO}_3^-$ ).

---

A complete treatment of this system is complicated by the formation of hydroxy-complexes of Fe(II). By superimposing a predominance diagram for the Fe(OH)<sub>3</sub> system on the log C-pH plot for Fe(II) in Fig. 7, one can construct a predominance diagram for the mixed system, shown in Fig. 9.

## 7 CO<sub>2</sub>- pH phase diagrams

When the partial pressure of CO<sub>2</sub> can be a variable, one can construct a phase diagram whose lines define the conditions of  $P_{CO_2}$  and pH under which a given pair of phases can be in equilibrium.

Since we are plotting log  $P_{CO_2}$  as a function of pH, we recast the FeCO<sub>3</sub> dissolution in terms of CO<sub>2</sub>:



$$K_s' = \frac{P_{CO_2}[\text{Fe}^{2+}]}{[\text{H}^+]^2} \quad P_{CO_2} = \frac{K_s[\text{H}^+]^2}{[\text{Fe}^{2+}]} \quad (57)$$

$$\log P_{CO_2} = \text{pFe}^{2+} + \log K_s' - 2 \text{pH} \quad (\text{slope } 2) \quad (58)$$

The condition for the coexistence of Fe<sup>2+</sup> and Fe(OH)<sub>2</sub> is independent of the gas pressure; this equilibrium occurs at a pH that depends on the concentration of Fe<sup>2+</sup>.

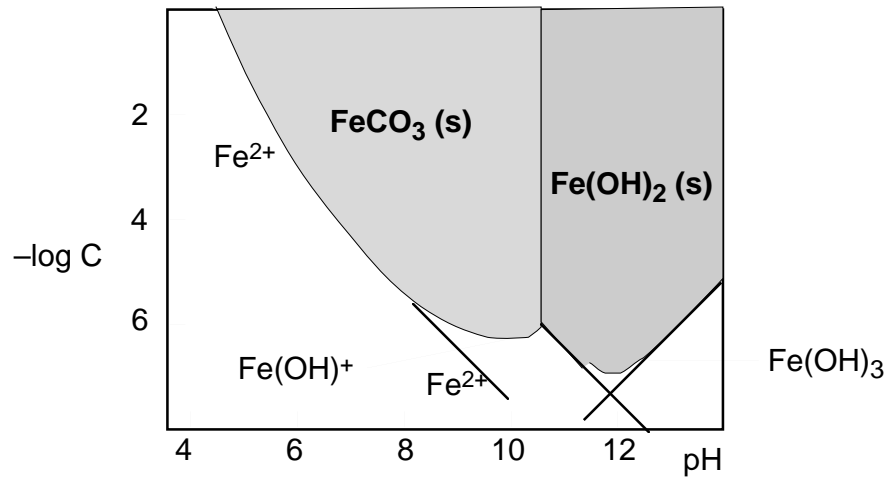


Figure 9: Solubility-pH diagram for the FeCO<sub>3</sub> - Fe(OH)<sub>2</sub> system with  $C_T = .001 M$ . (From Snoeyink and Jenkins)

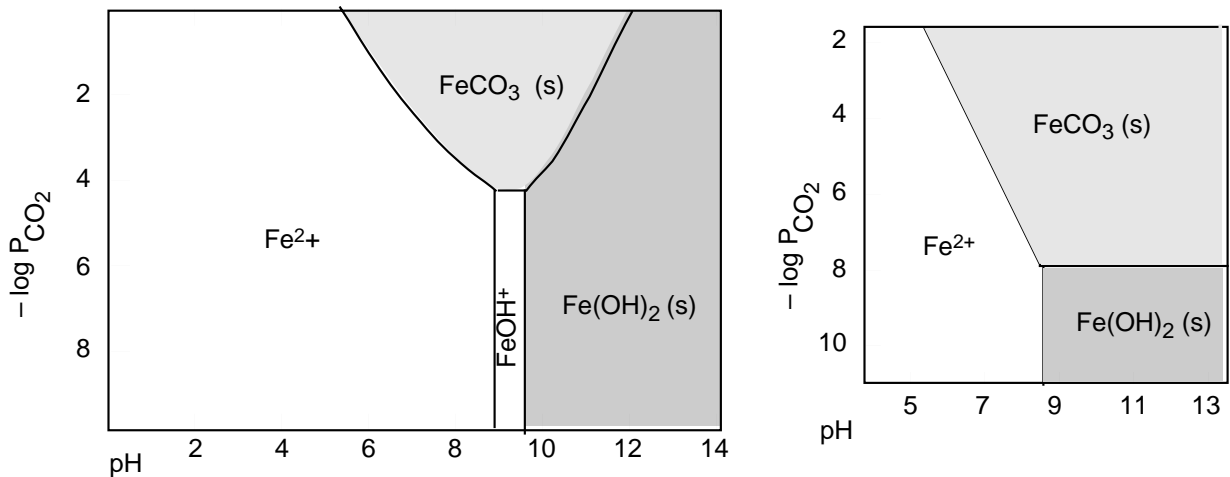
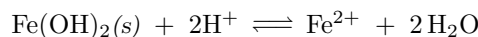
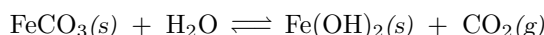


Figure 10: Phase diagrams for the FeCO<sub>3</sub> - Fe(OH)<sub>2</sub> - CO<sub>2</sub> system.



$$K_s^{\text{H}} = \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}; \quad \log [\text{Fe}^{2+}] = -\text{p}K_s^{\text{H}} - 2\text{pH} \quad (59)$$

For the coexistence of the solids  $\text{FeCO}_3$  and  $\text{Fe}(\text{OH})_2$ , we can write



the equilibrium constant for which is simply

$$K = P_{\text{CO}_2} \quad (60)$$

whose value is about  $10^{-6}$  atm in normal air. Thus  $\text{Fe}(\text{OH})_2$  is unstable with respect to  $\text{FeCO}_3$  when exposed to the air.

Metal ions in solution

An understanding of the behavior and role of metal ions in natural waters cannot be had without taking into account the tendency of such ions to form complexes of various kinds. The overall effect of complexing, of course, is to reduce the concentration of the free metal ion. This, in turn, can affect the solubility of the metal, and hence its geochemical distribution. This same effect is of considerable interest in connection with the movement of toxic heavy metals through the local environment; complexing agents, both natural ones and pollutants, can prevent the precipitation (and thus the immobilization) of heavy metals, allowing them to move through a stream or estuary.

## 8 Types of complexes

*Complexes* are generally defined as species that are composed of two or more entities which are each capable of independent existence. Within this very broad definition, it is usual to distinguish between *ion pairs* which are held together primarily by coulombic attraction of oppositely-charged ions (e.g.  $\text{CdI}^+$ ,  $\text{HgCl}_2^0$ ,  $\text{HgCl}_3^-$ ,  $\text{CaSO}_4^0$ ), and *coordination complexes* in which the main binding force is a coordinate covalent bond, as in  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Cu}(\text{NH}_3)_4^{2+}$ , etc. This will be the principal type of complex discussed in this section. Generally speaking, the component parts of ion pairs retain their hydration shells. This is not the case with coordination complexes, where there is direct electron sharing between the metal ion and its ligands.

Coordination complexes can be mononuclear or polynuclear. The latter, which are most frequently *aquo* complexes, are formed by condensation (with elimination of water) of two or more mononuclear complexes. These can build up to colloidal size, bridging the gap between homogeneous and heterogeneous matter.

A large variety of species can serve as ligands; the only requirement is possession of a pair of electrons that can be donated to the metal ion.  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{NH}_3$ ,  $\text{CN}^-$ , and  $\text{CH}_3\text{COO}^-$  are common examples. Some organic ligands possess more than one site at which complexation to the same metal ion can occur; such ligands are said to be *multidentate*, and the resulting complexes are known as *chelates*.

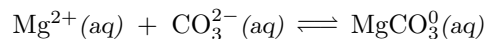
## 9 Formation and stability of complexes

The *formation-* or *stability constant* of a complex is the equilibrium constant for the reaction



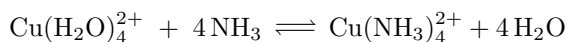
Thus for the ion-pair complex carbonatomagnesium(II),





$$K = \frac{\{\text{MgCO}_3^0\}}{\{\text{Mg}^{2+}\}\{\text{CO}_3^{2-}\}} = 10^{3.4}$$

Coordination complexes tend to have much larger formation constants that span a wide range of values. Introduction of a second ligand into a solution of a complex will lead to a certain amount of *ligand substitution* whose extent will depend on the relative stabilities of the two complexes. Since water is itself a coordinated ligand in solutions of most transition metals, the formation of a complex such as tetraamminecopper(II) can be regarded as a ligand substitution reaction in which the coordinated water molecules are displaced:



## 9.1 Stability trends

Extensive studies of the stability trends of various metal-ligand combinations have revealed a number of general trends:

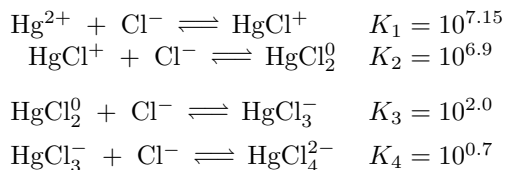
1. metal ions of small size and low polarizability (“Type A”, “hard-sphere” ions) such as those of the Group 1 and 2 elements form their most stable complexes with the fluoride ion and with ions in which oxygen serves as the electron donor. In other words, coulombic forces and electronegativity effects dominate. Since water is more strongly bound to these metals than are non-oxygen containing ligands, complexes with  $\text{NH}_3$ ,  $\text{CN}^-$  etc. are not formed. Similarly, insoluble sulfides are not formed, since  $\text{OH}^-$  can always displace  $\text{HS}^-$  or  $\text{S}^{2-}$ .
2. metals ions that are larger and which have a more deformable (polarizable) electron cloud are known as “Type B” or “soft-sphere” ligands. These are mostly transition metals possessing ten or more outer-shell electrons:  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , etc. These ions coordinate preferentially with ligands in which the donor atoms are N, S, I, or Cl (but not F). The greater distortion of the metal ion electron cloud frequently gives rise to *charge-transfer absorption* bands and highly colored complexes.
3. Transition metal ions containing fewer than ten outer-shell electrons generally fall into an intermediate category. These include a number of ions important in natural waters, such as  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$ .

The rates of reactions involving formation of coordination complexes and substitution of ligands extend over a wide range; some reactions are complete in milliseconds, while others take minutes, hours or days. The term *labile* is used to describe a complex whose formation or dissociation occurs rapidly. There is of course no relation between lability and stability. Reactions involving transformations of polynuclear complexes can be very slow, requiring weeks or years.

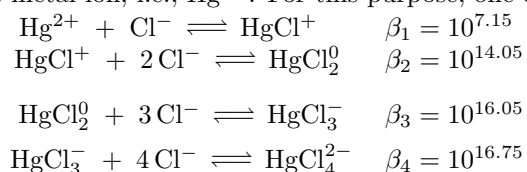
## 9.2 Formation constants

Quantitative treatment of equilibria involving coordination complexes is complicated by competition with ion-pair formation and, in seawater, by the presence of  $\text{Cl}^-$  and  $\text{Br}^-$ . It is therefore common to use *conditional equilibrium constants* rather than thermodynamic ones in which, for example  $[\text{Pb}^{+2}]$  represents the total concentration of all dissolved lead (II) species (such as  $\text{PbCl}^+$ ) other than the complex of interest.

A further complication arises from the multi-step sequences that lead to the formation of complexes containing more than one ligand. Thus for the various chloromercury(II) complexes, we can write the *stepwise* formation constants:



It is often more convenient to relate the concentrations of these various complexes to that of the parent metal ion, i.e.,  $\text{Hg}^{2+}$ . For this purpose, one defines *overall* formation constants



Needless to say, quantitative calculations on polycordinated complexes (and also on polynuclear complexes) can become exceedingly complicated. Thus for the common tetraamminecopper(II) complex, the species that have to be considered are  $\text{Cu}^{2+}$ ,  $\text{Cu}(\text{NH}_3)^{2+}$ ,  $\text{Cu}(\text{NH}_3)_2^{2+}$ ,  $\text{Cu}(\text{NH}_3)_3^{2+}$ ,  $\text{Cu}(\text{NH}_3)_4^{2+}$ ,  $\text{Cu}(\text{NH}_3)_5^{2+}$ ,  $\text{NH}_4^+$  and  $\text{NH}_3$ ; eight unknowns (assuming a fixed pH) requiring the solution of eight simultaneous equations.

Metal ions that form stable coordination complexes can be titrated with a suitable ligand, just as the ion  $\text{H}_3\text{O}^+$  can be titrated with the “ligand”  $\text{OH}^-$ . In the same way that the  $\text{H}_3\text{O}^+$  concentration is controlled by the ratio of the concentrations of protonated and unprotonated species, the metal ion concentration depends on the buffering action of a Lewis acid-base pair:

$$[\text{Me}] = \frac{[\text{eL}]}{[\text{L}]}K \quad (61)$$

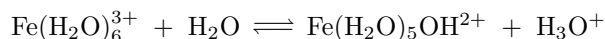
Use of metal ion solutions buffered in this way is just as important in studying the effects of trace concentrations of such ions on organisms, for example, as is the use of pH buffers, and for the same reasons.

## 10 Complexing and solubility

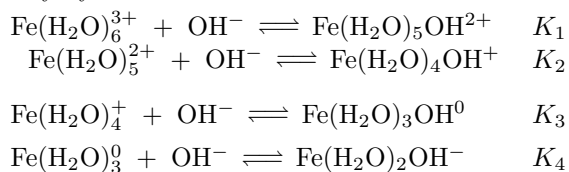
Everyone knows that if you add some aqueous ammonia to a solution containing  $\text{Cu}^{2+}$ , a light-blue precipitate of  $\text{Cu}(\text{OH})_2$  will form, but if excess concentrated  $\text{NH}_3$  is added, the precipitate will dissolve and you end up with a deep blue solution containing mostly  $\text{Cu}(\text{NH}_3)_4^{2+}$ . This is perhaps the best known instance of the competition between a solid and a complex for a metal ion, a phenomenon that is extremely important in controlling the concentration of metal ions in natural waters. Such waters commonly contain carbonate, sulfate, sulfide, and phosphate species, all of which tend to form insoluble compounds with a wide variety of metal ions.

### 10.1 Hydrolysis of metal ions

Most transition metal ions coordinate with water and with  $\text{OH}^-$ , forming a series of complexes that can be regarded as conjugate bases resulting from the loss of a proton from successive water molecules: from the loss of a proton from successive water molecules:

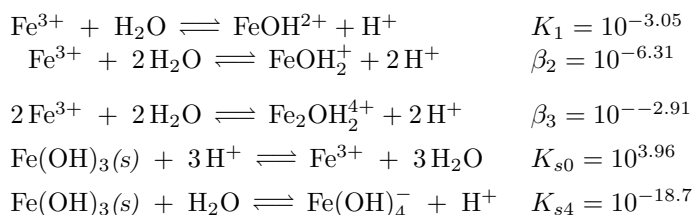


Alternatively, these various complexes can be regarded as the results of ligand substitution of coordinated water by hydroxide ion:



These two formulations are essentially equivalent, being related through the dissociation equilibrium of water.

In addition to the complex stability constants (which are commonly given as overall equilibrium constants), we must consider the formation of the solid  $\text{Fe}(\text{OH})_3$ , and its ampholyte  $\text{Fe}(\text{OH})_4^-$ . Thus in order to treat a solution of iron(III) in contact with amorphous ferric hydroxide, we need to consider the equilibria



The plot in Fig. 11 shows the equilibrium concentrations of  $\text{Fe}^{3+}$  and of its hydroxo complexes in contact with freshly precipitated  $\text{Fe}(\text{OH})_3$ . The shaded boundary on this plot defines the conditions under which the solid can exist. Its ordinate at any pH is simply the sum of the concentrations of all the soluble species at that particular pH. From this diagram, it is apparent that  $\text{Fe}(\text{OH})_2^+$  (i.e.,  $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^+$ ) is the predominant soluble iron(III) species within the pH range of natural waters;  $\text{Fe}^{3+}$  itself is a significant actor only at very low pH values.

## 11 Organic complexes in natural waters

There is always a certain amount of dissolved organic matter in natural waters. The quantity varies greatly; up to 10 mg/l in productive lakes and estuaries, about a tenth of this amount in seawater. Interstitial waters in sediments derived from organic-rich materials may contain up to 100 mg of carbon per litre.

Among the organic substances found in most waters that are known to form complexes or chelates with metal ions are amino acids, amino sugars, fatty acids, organic phosphates, porphyrins, and polysaccharides. Most of these have a natural biological origin, often from algae. Leaching of bark and leaf litter gives rise to polyhydroxy aromatic acids known as *tannins*. *Humic substances* are polymeric materials related to tannins which are soluble degradation products of plant materials. In addition to these naturally-occurring compounds, substances such as nitrilotriacetic acid (NTA; a commonly-used substitute for phosphates in household detergents) are frequently present in waters affected by pollution.

Most of these substances are known to form stable complexes with many multivalent cations. The actual extent of complex formation by organics in natural waters and its overall significance is not very well known, however, owing largely to the complicating effects of competing equilibria and ionic interactions.

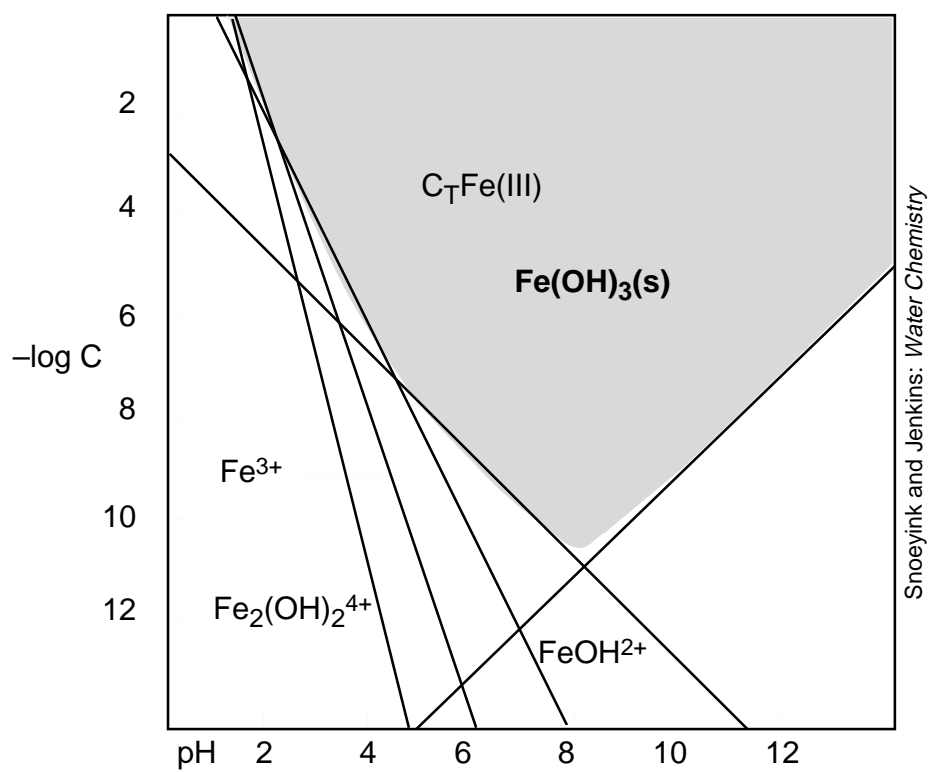


Figure 11: log  $C$  - pH diagram for iron(III) solutions at 25 °C. (From Snoeyink and Jenkins)

For example, waters of high alkalinity contain  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  at concentrations sufficient to successfully compete with the binding of heavy metal ions which form more stable complexes but are commonly present at much lower concentrations. Most of the detailed studies of these effects have been carried out on model systems in which a sample of fresh water, seawater, or sewage (these the three cases of major interest) is simulated.

Besides dissolved organics, it is known that insoluble complex-forming organic materials, including polysaccharides and other polymeric substances, are present on the surfaces of suspended particulate material, where they can selectively adsorb metal ions.

The solid-solution interface

## 12 The nature of interfaces

Where two phases are in contact, an *interfacial region* exists whose properties are different from those of either of the two bulk phases. The binding forces that act within a phase are necessarily unbalanced near the surface; molecules and ions in this region are less tightly bound, and thus possess a higher escaping tendency or free energy. When the surface area of a phase is increased (for example, by dispersing it into smaller particles or by decreasing its curvature), work must be done to overcome intermolecular attractions as molecules move from the bulk phase to the surface. The increase in free energy per unit of surface created is the *surface tension*

$$\gamma = \left( \frac{\partial G}{\partial A} \right)_{T,P,n} \quad (62)$$

whose usual units are  $\text{N cm}^{-1}$  or  $\text{J cm}^{-2}$ .

Surface energies generally reflect the binding energies of phases; thus the surface tension of water is  $73 \times 10^5 \text{ N cm}^{-1}$ , whereas that of *n*-decane is  $24 \times 10^5 \text{ N cm}^{-1}$ . An ionic solid or a semi-ionic solid such as  $\text{Fe}_2\text{O}_3$  or glass will have a higher surface energy than a soft organic solid such as paraffin wax or polyethylene. Finely-divided materials such as clay solids have surface areas of several hundreds of  $\text{m}^2$  per gram, leading to total surface energies of around  $100 \text{ J g}^{-1}$ .

Solids possessing high surface energies tend to adsorb films that lead to lower-energy surfaces. Thus water is strongly adsorbed (even from the vapor phase) by glasses, metals, and most ionic solids. Binding of the adsorbed film to the surface may involve direct chemical bonding *chemisorption* or the operation of non-specific longer-range electrostatic and van der Waals forces (*physical adsorption*).

Most of the chemical reactions that take place in natural waters occur at the surfaces of sediments and suspended solids. These include clay particles, the oxides, hydroxides, carbonates, and sulfides of metals, microorganisms, and the colloidal detritus from dead organisms. The role of the liquid-air interface in lakes and the ocean is less understood, but it is known to be coated with organic material which some believe to have important effects on certain geochemical processes.<sup>1</sup>

## 13 The electric double layer

Another feature of interfaces is that there is always an *electrical potential difference* between the two phases. The source of this electrification may be due to differences in the escaping tendency of charged particles from the two phases, isomorphic substitution within the surface, the presence of polar or ionizable surface groups, or selective adsorption of ions or polar molecules (such as water) in one particular orientation.

<sup>1</sup>See P.S. Liss, in *Chemical Oceanography*, J.P. Riley and G. Skirrow, eds., Chapter 10, Vol 2, 2nd ed., Academic, N.Y., 1975.

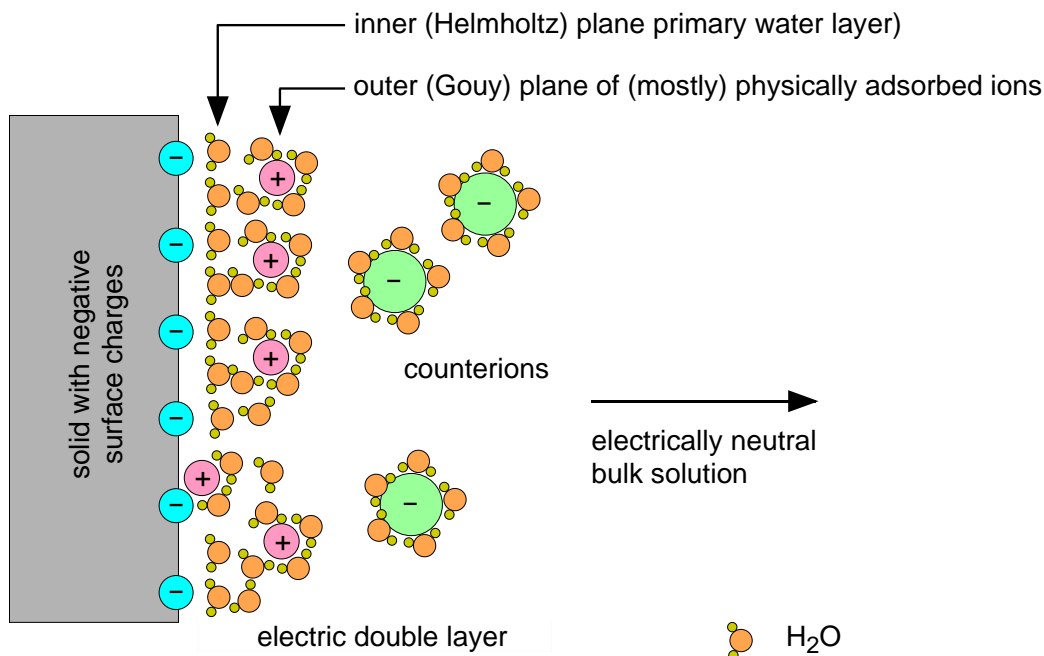


Figure 12: Model of the electric double layer at a solid-ionic solution interface.

Although electroneutrality can be violated locally, it must apply over larger regions. In the case of a solid in contact with a liquid, the interfacial region is characterized by an *electric double layer* in which the surface-charged particle is surrounded by a diffuse layer of *counterions* sufficient to maintain overall electrical neutrality.

### 13.1 Electrokinetic phenomena

Any relative motion of one phase with respect to another tends to cause some of the counterions to shear off of the solid, giving rise to a *streaming potential* when the liquid is moved with respect to the solid (as when a liquid flows through a capillary tube). If the solid moves through the liquid, the analogous effect is known as *sedimentation potential*. Conversely, an external electrostatic field imposed on a suspension of particles will cause the particles and the outer parts of their double layers to move in opposite directions, producing the phenomenon of *electrophoresis*. Finally, *electroosmosis* is observed when a potential gradient along a capillary pulls off some of the counterions near the capillary walls, causing them (and the liquid along with them) to move through the tube. These are all examples of *electrokinetic phenomena*.

### 13.2 Ion exchange

This is a general term for a variety of processes; for example, the replacement of one ion with another of similar size within the structure of a solid. In connection with the electric double layer, it is worth noting that the cloud of counterions surrounding a surface is always subject to exchange and replacement by other ions of the same charge sign. Detailed development of electric double layer theory shows that a negatively-charged inner layer will attract doubly-charged counterions in preference to those that are singly-charged.

<i>material</i>	$\text{pH}_{zpc}$	<i>material</i>	$\text{pH}_{zpc}$
$\alpha - \text{Al}_2\text{O}_3$	9.1	MgO	12.5
$\alpha - \text{Al}(\text{OH})_3$	5.0	$\text{SiO}_2$	2.0
CuO	9.5	feldspars	2-2.4
$\text{Fe}_3\text{O}_4$	6.5	kaolinite	4.6
$\text{Fe}(\text{OH})_3$	8.5	montmorillonite	2.5

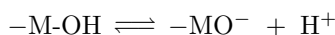
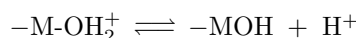
Table 1: Zero point of charge for some common sedimentary surfaces.

All surfaces therefore possess inherent ion-exchange capability, and this can lead to significant geochemical effects, particularly in zeolites<sup>2</sup> and clays in which the effective “surface” extends into interior cavities or between planes.

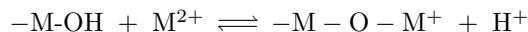
Ion exchange in clays can have significant effects on the physical properties of soils and sediments. For example,  $\text{Na}^+$  ions are more strongly hydrated than are doubly-charged ions such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and twice as many are required in the counterion region of the double layer. Intrusion of saline water into a clay will result in some replacement of the divalent cations; this will be accompanied by an osmotic flow of water into the regions between the sheets of the clay structure, causing it to swell. The same effect in soils and sediments fills their void spaces with water, adversely affecting their permeability.

## 14 Acid-base properties of surfaces

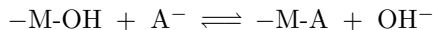
A very large fraction of the lithosphere consists of the oxides of Si, Al, Fe. Oxides of other metals, such as Mn and Cr, are also common in sediments. Contact with water causes the surfaces of these oxides to become covered with -OH groups, converting the surface into a polymeric oxoacid of amphoteric character:



Other metal ions can compete with protons for attachment to the surface:



Also, anions or other Lewis bases may successfully displace the  $\text{OH}^-$  ions and coordinate directly with the metal:



All of these reactions affect the electric charge of the surface. Since these equilibria are pH dependent, it follows that the net charge of the surface depends on the pH. Further, one can identify a pH at which the net surface charge will be zero; this is known as the pH of *zero point of charge* or the *isoelectric point* of the surface. At the isoelectric point, the electric double layer collapses and the surface will exhibit no electrokinetic phenomena.

<sup>2</sup>A *zeolite* is a crystalline aluminosilicate containing relatively large tetrahedral cavities which both cations and water molecules can enter and leave. Synthetic, “designer” zeolites are widely employed as highly selective ion exchange media.

## 15 Colloids

The more finely-divided a solid becomes, the greater the area of its surface. Eventually a point is reached where the bulk properties of the solid become dominated by its surface properties; this is the *colloidal* state of matter. Colloidal behavior usually becomes noticeable at particle diameters of around  $10^{-3}$  cm. Such particles have a gravitational settling rate in water of less than  $10^{-2}$  cm s $^{-1}$ , so they tend to remain in suspension. This range includes bacteria and viruses, and extends down to macromolecules.

Owing to their large surface energies, colloids can never be thermodynamically stable; the term *stability* has therefore been appropriated to denote slowness to agglomerate or crystallize.

Colloids are held in suspension by the mutual electrostatic repulsion exerted by their surface charges or by the inner layer of adsorbed ions and oriented polar molecule. This repulsion opposes the van der Waals forces that would normally tend to draw the particles together, and allows the particle to approach only close enough for their double layers to “bump” one another.

Any agent that disrupts the double layer or makes it more compact will allow the particles to approach each other sufficiently closely for van cause the suspension to *coagulate*. Electrolytes such as NaCl exert have this effect; this is responsible for the formation of deltas in places where clay-containing rivers empty into the ocean. Coordination of multivalent ions with surfaces containing negatively-charged functional groups is another important coagulation mechanism; in these cases, certain ions are much more effective than others, owing to differences in complex stability. (

Since suspended matter is transported and ultimately distributed differently from dissolved substances, colloid chemistry plays a vital role in many aspects of geochemistry and environmental chemistry. Small amounts of substances, such as certain amorphous precipitates and the polysaccharides excreted by microorganisms, can promote the formation and stability of colloidal dispersions, thus altering the distribution of the affected substances in the environment. Many colloidal particles are themselves selective adsorbers of ions and polar organic substances; it has been suggested that this may provide a mechanism for the removal of certain ions from the ocean.

Much of the organic matter in the effluent of a sewage treatment plant is in the form of colloidal solids. Adsorption of trace metals, radionuclides, and other substances on the large amounts of colloidal organic matter present in sewage treatment effluents can cause these pollutants to be released into solution as the material is transported from one local environment to another.

Considerable attention has been given to the colloidal nature of dispersed oil particles originating from oil spills. The dispersed oil particles tend to have the same (negative) charge sign as most natural colloids, so some care is required to select adsorbing-coagulating agents that will be effective in this application. Much of the organic matter in the effluent of a sewage treatment plant is in the form of colloidal solids.

## 16 Clay minerals

Clays are the end products of the weathering of rocks; they can be thought of as the skeletons of the rock material following leaching of the more soluble Na $^{+}$ , Ca $^{2+}$ , Mg $^{2+}$ , and CO $_3^{2-}$  components of the aluminosilicate rock substance. The formation of kaolin, for example, is summarized by



The unique structural feature of all clays is their organization into stacks of sheet-like structures. The simplest of these sheets consists of condensed hexagonal rings of SiO $_4$  tetrahedra (*T*-sheets); each sheet can be regarded as a layer of silicon atoms sandwiched between two layers of oxygen atoms. *O*-sheets are made up of a similar sandwich in which the sandwiched atoms are aluminum or magnesium; in this case, the metal ion is in an octahedral hole.



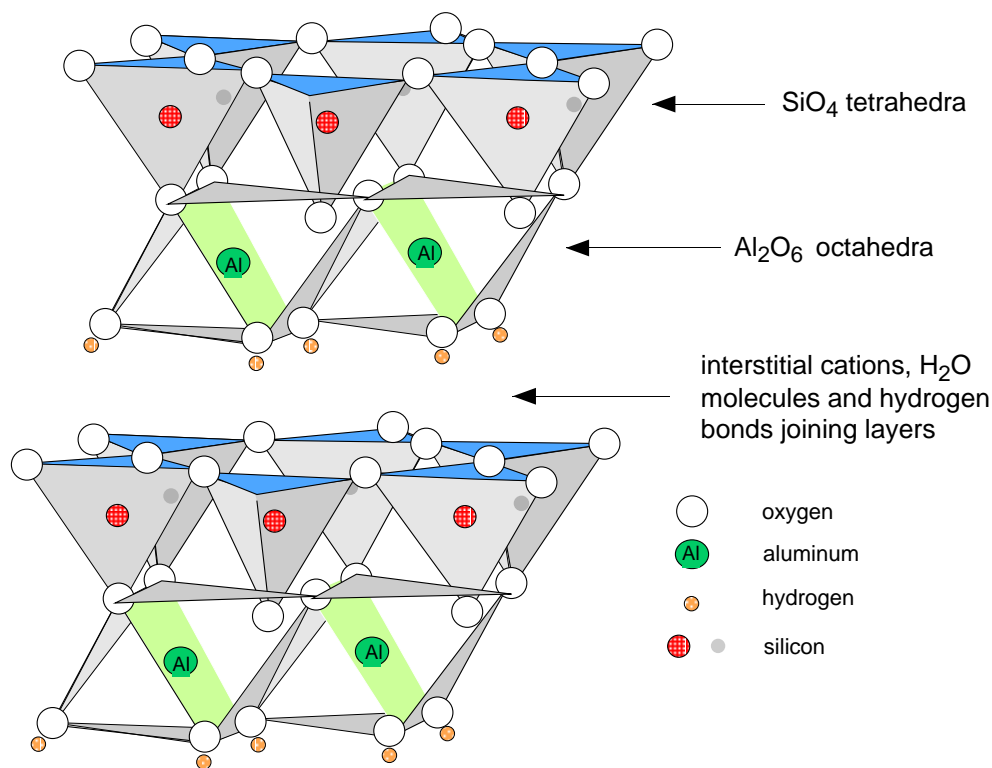


Figure 13: Structures of some common clay types

The clay structure is built up by stacking these sheets in units of twos or threes (T-O or T-O-T), with one layer of oxygen atoms serving as the top of one sheet and the bottom of the other. Kaolin (ordinary china-clay<sup>3</sup>) is the principal two-layer clay. Variations in the three-layer clays (the principal ones are montmorillonites, illites, and chlorites) are afforded by partial or complete replacement of the Al or Mg in the O-layers by Si and various metal atoms.

The T-O or T-O-T units are themselves stacked one on another, with layers of water (together with surface cations if required to neutralize uncompensated charges on the oxide ions) occupying the regions between the individual units. It is these regions that are responsible for the cation- and water-exchange properties of clays, as well as their thixotropic behavior in which agitation breaks the weak electrical bonds between the units and converts the material into a jelly-like mass. This latter property is exploited in bentonite (Na montmorillonite) drilling muds, and is deplored by owners of dwellings built on the clay Malibu Hills northwest of Los Angeles.

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<sup>3</sup>The name is a corruption of the Chinese *kau-ling*, “high ridge”, referring to the name of a hill where this clay occurs in China. The principal use of kaolin is now as a filler and coating for papers; about 25% of North American production finds its way into “china” crockery, plumbing fixtures and ceramic tiles.