

Major Ions, Carbonate System, Alkalinity, pH
(Kalff Chapters 13 and 14)

A. Major ions

1. Common Ions

There are 7 common ions in freshwater: (e.g. Table 13-3, p207)

cations: Ca^{+2} , Mg^{+2} , Na^{+1} , K^{+1}

anions: Cl^{-1} , SO_4^{-2} , HCO_3^{-1}

In some surface waters, other ionic species are sometimes important (e.g. NH_4^{+1} , F^{-1} , organic acids, etc.), but in most cases the 7 ions listed above are the only ions present in significant concentration. In addition to the common ions, OH^{-1} and H^{+1} are important species because of the dissociation of water itself. In freshwater, the total concentration of ions and the relative abundance of each are highly variable, reflecting the influence of precipitation (rain), weathering and evaporation.

In contrast to freshwater, the world ocean is very uniform (Table 13-6, p214). The total concentration of ions varies only slightly, depending on local advection of freshwater from major rivers and regions of surplus rainfall or evaporation. For “standard” seawater, with “chlorinity” = 19.000 parts per thousand, the following concentrations are observed for the common ions. (Similar ratios are available for nearly the entire periodic table, although at lower concentrations.) These fixed ratios in the sea are the result of the “constancy of composition” of seawater.

<u>Ion</u>	<u>parts per thousand (g/kg)</u>
Cl^{-}	18.980 (the definition of "chlorinity" includes Br^{-} , I^{-} , etc.)
Na^{+}	10.556
SO_4^{-2}	2.649
Mg^{+2}	1.272
Ca^{+2}	0.400
K^{+}	0.380
HCO_3^{-}	0.140
Br^{-}	0.065

2. Sources of ions in freshwater

a. From the atmosphere.

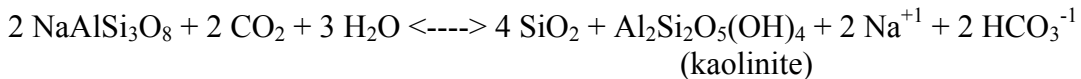
The principal atmospheric source of ions is from sea spray. Accordingly, the ratios of the common ions in rain and snow reflect the ratios in seawater: Na and Cl are often the most

abundant ions in rain. (The concentrations of ions in rain are of course much lower than the concentrations in seawater.)

b. From rock weathering.

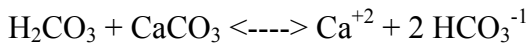
Watersheds contain soils and rock which consist of a wide variety of different minerals. Weathering of the soil and rock minerals produces runoff containing the common ions (and many other ions in lesser concentration). Some sample reactions which illustrate the general nature of weathering:

Na-feldspar weathering (incongruent)



Incongruent weathering reactions produce dissolved species and new solids that are more stable in the weathering environment than the original bedrock minerals. These new residual solids are the minerals that constitute saprolite and soil

Calcite weathering (congruent)



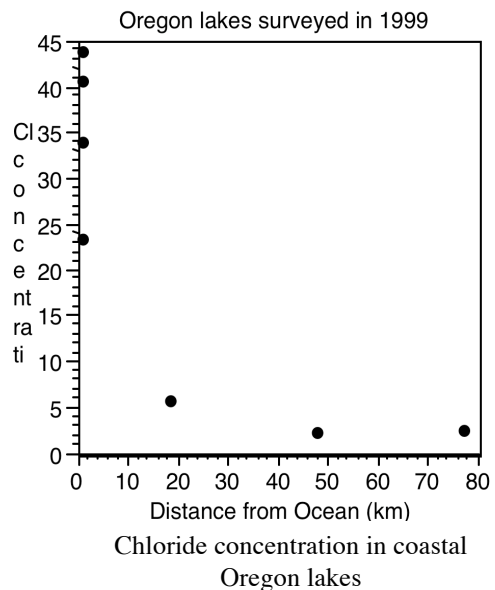
Congruent weathering results in all products being in the solution phase.

There are of course a host of other soil and rock minerals subject to similar weathering reactions. **In general, weathering reactions can be characterized as a weak acid (carbonic acid) slowly dissolving basic minerals.** Weathering reactions result in runoff containing dissolved ions, and commonly, undissolved particles of less soluble minerals such as clays.

3. Concentration patterns in surface water - Gibbs "boomerang" plot (for what its worth)

Atmospheric dominance

Lakes which receive rainwater and snowmelt (without much influence by rock weathering) contain water with low concentrations of ions. Because of the source of atmospheric ions, from sea spray, chloride and sodium are relatively more abundant than the other ions. (The relative abundance of salts is not precisely the same as sea water because there is some fractionation in evaporation and transport of sea salts.) In addition, rainwater is in equilibrium with atmospheric CO₂. In effect, rainwater is (approximately) a dilute solution of carbonic acid with an admixture of a small amount of sea salt.



Rock Dominance

Water more or less in equilibrium with the materials in the drainage basin is characterized by higher concentrations of ions and an increased significance of Ca, Mg, and bicarbonate ions. Many of the world's great rivers discharge water which can be characterized as rock-dominated.

Evaporation-Precipitation Dominance

Evaporation and fractional precipitation represent the third mechanism identified by Gibbs. The world ocean is the end of this process. Some rivers and lakes have a similar chemistry if they occur in regions which are arid. The overall concentration of ions increases with evaporation until selected minerals begin to precipitate because their solubility product is exceeded. Because CaCO_3 is commonly the first mineral to precipitate, the relative concentration of these ions begins to decline with evaporation. With further evaporation, other minerals, such as gypsum (CaSO_4) will also precipitate. As a consequence, the relative concentrations of Na^+ , K^+ , and Cl^- increase.

Gibb's model of water chemistry

R.J. Gibbs proposed a general model to describe major ion water chemistry as a result of 3 main hydrologic processes: input from the atmosphere, rock weathering, and evaporation. (Science, vol 170, p1088-1090, 1970).

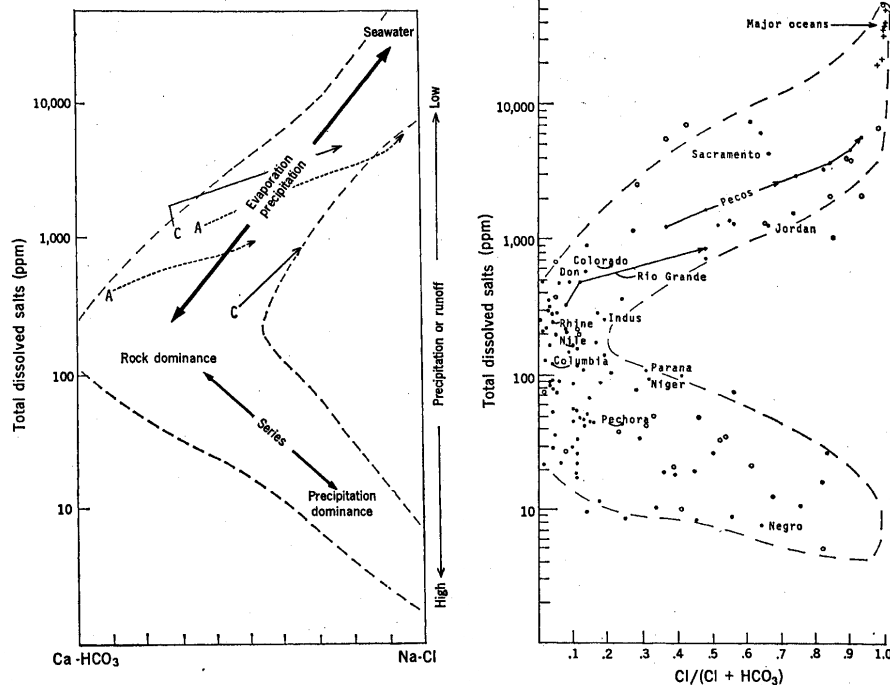


Fig. 3 (left). Diagrammatic representation of processes controlling the chemistry of world surface waters. Fig. 4 (right). Variation of $\text{Cl}/(\text{Cl} + \text{HCO}_3)$ as a function of the total dissolved salts of world surface waters. ●, Rivers; ○, lakes; +, oceans.

Gibbs model provides a simple and general framework for the characteristics of surface water chemistry. His view has been challenged by Kilham (L&O, vol35, pp 80-83, 1990) and by Eilers et al (L&O, vol 37, p1335-1337, 1992). They point out that many lakes fall outside the envelope proposed by Gibbs, both at the high end (African lakes) and at the low end (Alaska, Pacific Northwest). Gibbs responded by emphasizing that his model fits “Major” drainage systems, and that the exceptions concern only “Minor” water systems.

Kilham’s data from African lakes

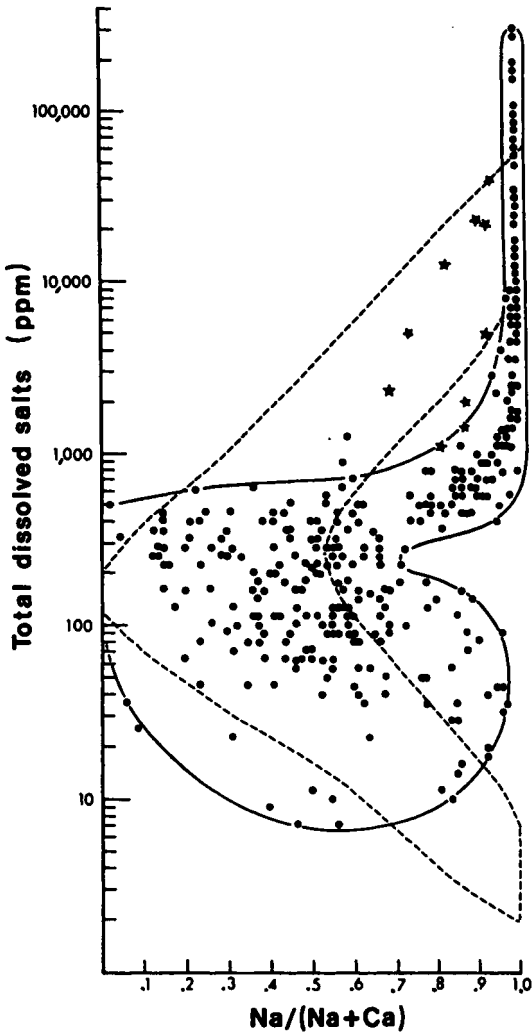


Fig. 1. Variation of the weight ratio $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ as a function of the total dissolved salts of world surface waters. The boomerang-shaped envelope (---) was observed by Gibbs (1971) for 135 surface waters from various regions of the world. The retort-shaped envelope (—) surrounds data for normal African waters (●). Stars represent springs with Cl^- or SO_4^{2-} as the dominant anion and moderate-salinity sodium chloride lakes (<10,000 ppm of TDS).

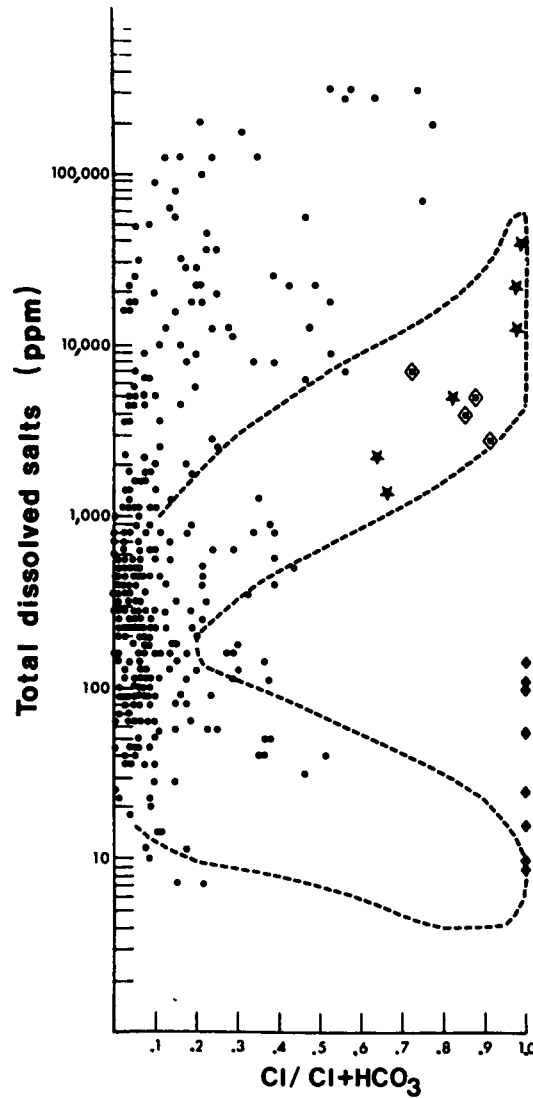


Fig. 2. Variation of $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ as a function of the total dissolved salts of world surface waters. Envelope surrounds data presented by Gibbs (1971). Normal African waters—●; springs with Cl^- as the dominant anion—★; moderate-salinity sodium chloride lakes—◆; swamps—◆.

Eilers et al. data from Cascades, Sierra Nevada, Minnesota and Wisconsin, and Norwegian lakes

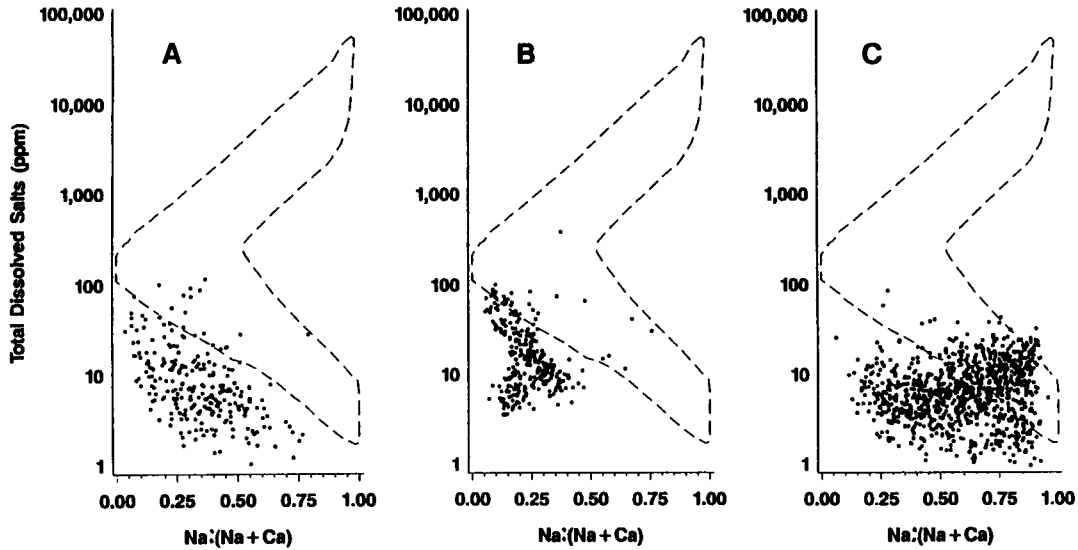


Fig. 1. Weight ratios of Na:(Na + Ca) plotted against total dissolved salts (calculated from the sum of individual ions). A—For lakes in the Oregon-Washington Cascades and Sierra Nevada ($n = 244$; Eilers et al. 1987); B—in subregions 2A and 2C from the Eastern Lake Survey, northeastern Minnesota and north-central Wisconsin ($n = 300$; Kanciruk et al. 1986); C—in Norway ($n = 1,005$; Henriksen et al. 1988).

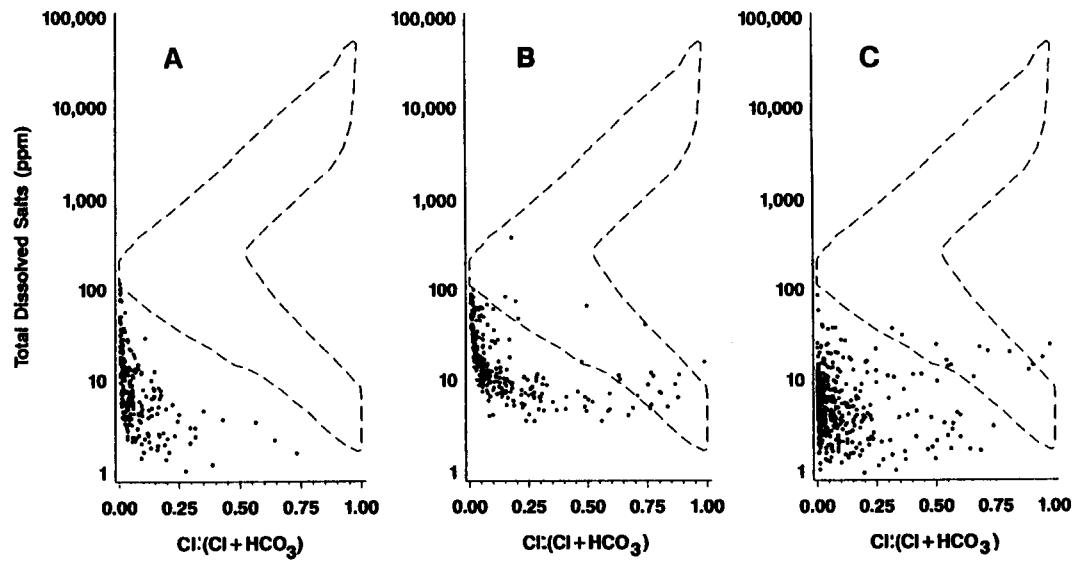


Fig. 2. As Fig. 1, but of Cl:(Cl + HCO₃).

Gibbs' modification of his model to account for discrepancies pointed out by Kilham and Eilers et al.

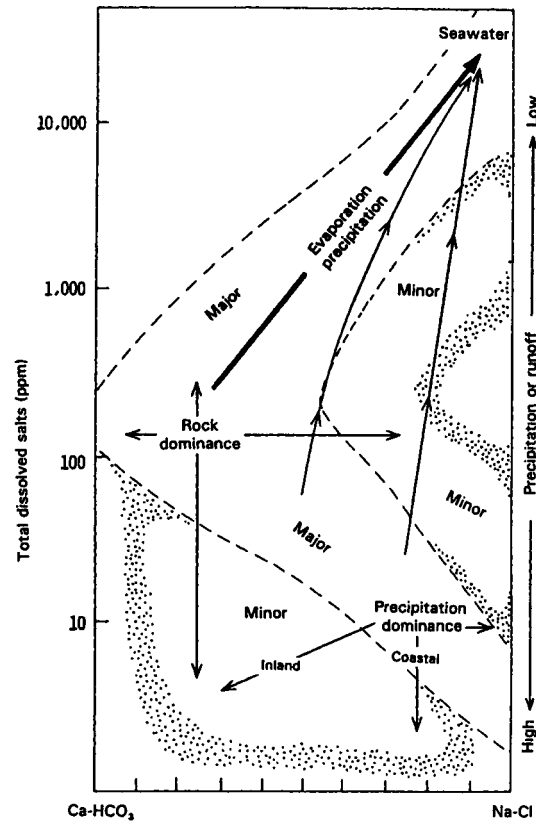


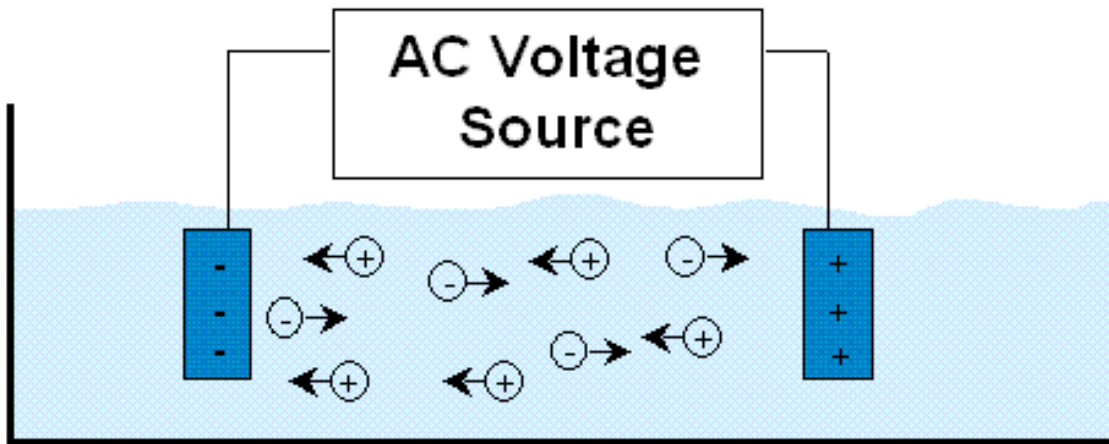
Fig. 2. Diagrammatic representation of processes controlling the chemistry of world surface waters modified after Gibbs (1970).

According to a classic paper in Ecology by Richard Levins (American Scientist, 1966, 54: 421-431) models cannot be simultaneously **general, precise, and realistic**. Model construction requires the sacrifice of one of these characters to accomplish the other two, e.g., fish stock models are precise and realistic but not general, they only work under very limited and specific conditions. Similarly, realistic and general models are not very precise — it may apply widely and provide realistic results, but only indicate in a vague way how the system responds. A model cannot be general and realistic, as Gibbs tried to accomplish in his original model, and precise. Gibbs attempts to include more precision in his model in his reply to Eilers, but the model then loses its predictive power.

4. Conductivity or conductance

Water conducts electricity (p205 Kalf). The greater the concentration of ions, the greater the conductivity of the water. Generally, the conductivity of a water sample is equal to the sum of the individual ion conductivities. Each ion has its own effect on conductivity (influenced by charge, mobility, and other characteristics). Temperature has a strong effect on conductivity, and for that reason, conductivity is measured at a particular temperature, usually 25 degrees C, or is corrected using various correction terms.

Conductivity is typically measured with a conductivity cell, which is basically an anode and cathode separated by some know distance. A current is passed through the circuit and the resistance to current is measured (resistance measured in ohms). The inverse of the resistance is the conductance (mhos = Siemens). Since conductance of a solution is a function of temperature, distance between and size of the anode and cathode, the measurements are standardized to 25C, 1 cm, and 1 cm² (platinum).



Schematic of a conductance meter

Other measures of ion concentration include **salinity** (sum of concentration of major ions) and **total dissolved solids (TDS)** (a gravimetric measure of salts in an evaporated sample).

A table of specific conductivities for the common ions (no corrections):

<u>Ion</u>	<u>Specific conductivity (microSiemens/cm equivalent)</u>
Na ⁺¹	50.11
K ⁺¹	73.52
Ca ⁺²	59.5
Mg ⁺²	53.06
HCO ₃ ⁻¹	44.48
Cl ⁻¹	76.34
SO ₄ ⁻²	79.8

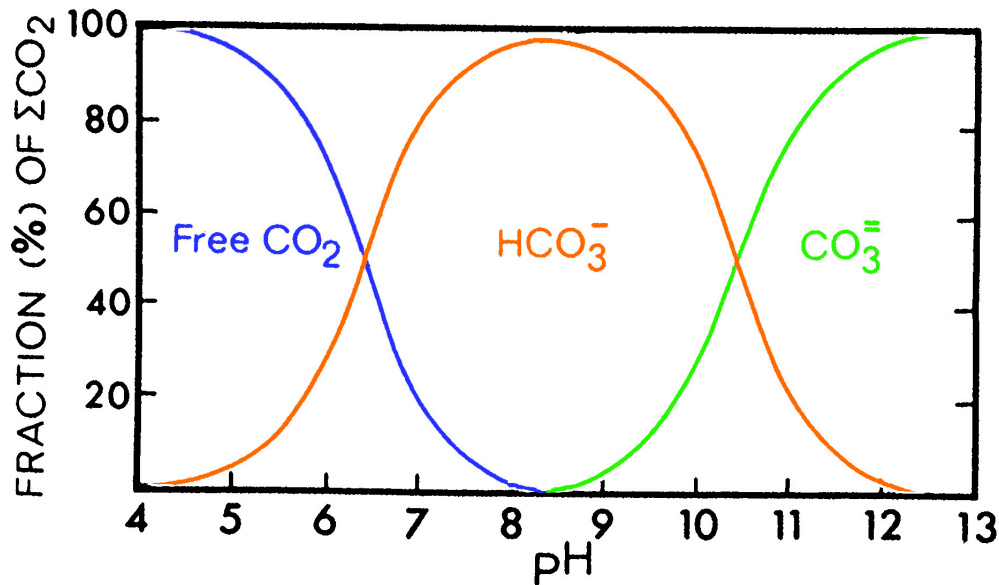
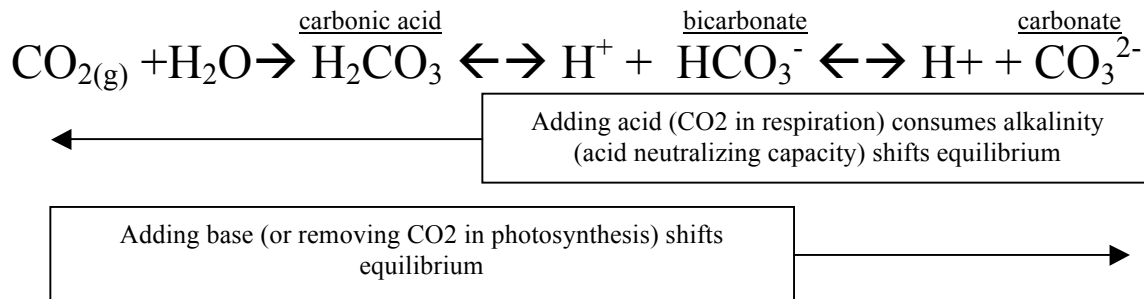
Obviously, if the concentrations of individual all ions are known, the overall conductivity

can be calculated, but conductivity alone cannot predict the concentration of ions (except for seawater). Conductivity can be used to confirm measures of ionic composition.

B. The carbonate system (Chapter 14, Kalf)

The carbonate system is important for a number of reasons. Natural waters are buffered with respect to pH mostly because of the content of inorganic carbon species. In turn, pH is an important controlling variable for many important geochemical reactions (e.g. solubility of carbonates). Many important biochemical reactions, such as photosynthesis and respiration, interact with the pH and the carbonate system.

The dominant form of inorganic carbon in water is a function of pH



Don't let what follows frighten you. It is presented just so you know that there are analytical methods of calculating concentration of the various components of the carbonate system at any given pH. I won't expect you to use these formulae. You will do that in a water chemistry course. [The treatment here follows Stumm and Morgan: "Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters."]

1. The chemical species of interest.

The *carbonate species*: CO_2 , H_2CO_3 , HCO_3^- , CO_3^{2-}

Water and its ionization products: H_2O , H^+ , OH^-

The *other common ions*: Na, K, Ca, Mg, Cl, SO_4^{2-}

2. Some definitions.

Carbonate alkalinity is defined as: $A = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$

(where [species] implies the concentration, in moles/liter, of the species in question.)

By convention, $[\text{H}_2\text{CO}_3^*] = [\text{H}_2\text{CO}_3] + [\text{CO}_2]$

Total inorganic carbon, $C_T = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$

3. The carbonate system may be completely described by 6 equations:

$$(1) \quad \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} = K_1 = 10^{-6.3} \quad \begin{array}{l} \text{(First dissociation of carbonic acid)} \\ [\text{Kalff uses } 4.41 \times 10^{-7} = 10^{-6.36}] \end{array}$$

$$(2) \quad \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_2 = 10^{-10.25} \quad \begin{array}{l} \text{(Second dissociation of carbonic acid)} \\ [\text{Kalff uses } 4.7 \times 10^{-11} = 10^{-10.33}] \end{array}$$

$$(3) \quad [\text{H}_2\text{CO}_3^*] = p\text{CO}_2 \times K_{\text{CO}_2} \quad \begin{array}{l} \text{(Henry's law for CO}_2\text{)} [\text{But see Kalff, p218}] \\ (p\text{CO}_2 = 10^{-3.5} \text{ atm, } K_{\text{H}} = 10^{-1.5}) \end{array}$$

$$(4) \quad [\text{H}^+][\text{OH}^-] = K_{\text{w}} = 10^{-14} \quad \text{(Dissociation of water)}$$

$$(5) \quad [\text{Ca}^{+2}][\text{CO}_3^{2-}] = K_{\text{SO}} = 10^{-8.35} \quad \text{(Solubility of calcite)}$$

$$(6) \quad [\text{H}^+] + [\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{+2}] + 2[\text{Mg}^{+2}] = [\text{Cl}^-] + 2[\text{SO}_4^{2-}] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$

(Requirement for electroneutrality – this will be important for acid neutralizing capacity calculation below, so you should understand this part)

Working with these 6 equations without the help of graphs is difficult. Stumm and Morgan developed the use of log-log plots to describe the carbonate system. Figure 4.1 from Stumm and Morgan (see below) depicts this method of portraying the carbonate system. The figure is developed for $C_T = 10^{-3}$. Other versions can be developed for lower or higher concentrations of C_T .

Kalff p218 notes: "It is now evident that most lakes worldwide are supersaturated with CO_2 , with a partial pressure that is on average three times that of the atmosphere (Cole et al. 1994)."

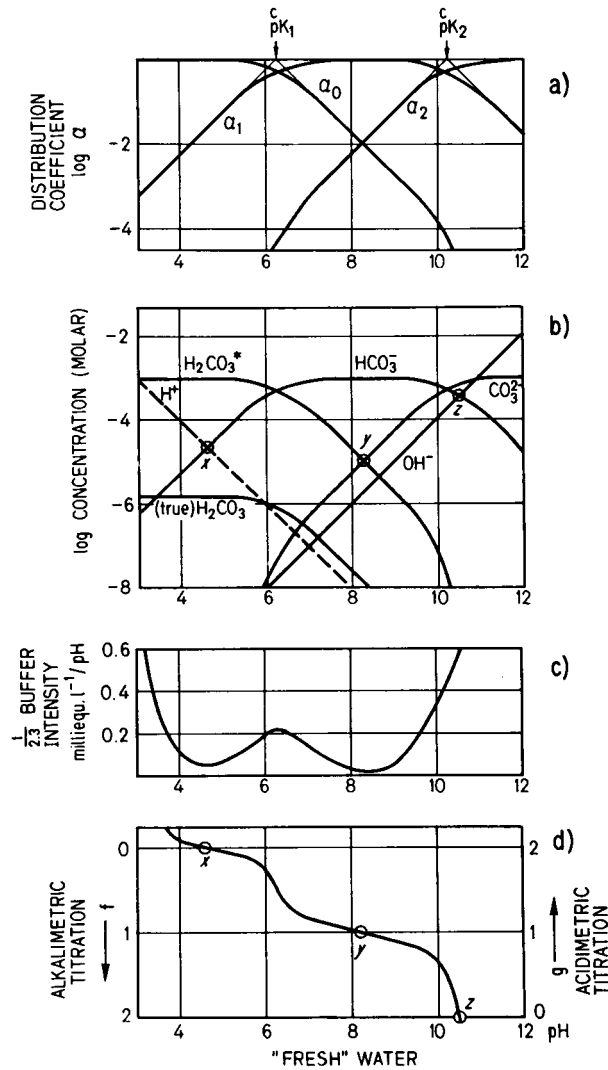


Figure 4.1 Distribution of solute species and buffering in aqueous carbonate systems. (a–d) Fresh water, 25°C; (e and f) seawater, 10°C. This figure has been constructed under the assumption that $C_T = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = \text{constant}$ (10^{-3} M in fresh water and $2.3 \times 10^{-3} \text{ M}$ in seawater). The following equilibrium constants corrected for salt effects have been used. Fresh water: $I = 10^{-3}$, $\text{p}K_1' = 6.3$, $\text{p}K_2' = 10.25$ (25°C, $p = 1 \text{ atm}$); seawater $\text{p}^c K_1 = 6.1$, $\text{p}^c K_2 = 9.3$ (10°C, $p = 1 \text{ atm}$), $\text{p}K_{\text{H}_3\text{BO}_3} (10^\circ\text{C}) = 8.8$. The hydration constant K [(1) in Table 4.2] was taken to be 630. (a) Ionization fractions as a function of pH. (b) Logarithmic equilibrium diagram for fresh water. Because $[\text{CO}_2(\text{aq})] \gg [\text{H}_2\text{CO}_3]$, $[\text{CO}_2 \text{ aq}] \approx [\text{H}_2\text{CO}_3^*]$. Note that H_2CO_3 is a much stronger acid than $\text{CO}_2(\text{aq})$ or H_2CO_3^* . Pure H_2CO_3 has a $\text{p}K$ value (where $[\text{H}_2\text{CO}_3] = [\text{HCO}_3^-]$) of $\text{p}K_{\text{H}_2\text{CO}_3} \approx 3.5$. The equivalence points corresponding to pure solutions (C_T molar) of H_2CO_3^* , NaHCO_3 , and Na_2CO_3 are marked x, y and z, respectively. (c) Buffer intensity is plotted as a function of pH. (d) Alkalimetric or acidimetric titration curve. Note that no pH jump occurs at the equivalence point z, because at this point the buffer intensity caused by high $[\text{OH}^-]$ is too large.

From Stumm and Morgan

4. The ionization fractions (top panel of figure labeled 4.1 above) are defined algebraically as:

$$[\text{H}_2\text{CO}_3^*] = C_T \times \alpha_0; \quad [\text{HCO}_3^-] = C_T \times \alpha_1; \quad [\text{CO}_3^{-2}] = C_T \times \alpha_2$$

$$\text{The sum of the } \alpha\text{'s: } \alpha_0 + \alpha_1 + \alpha_2 = 1$$

The numerical value of the α 's are a function of pH and the dissociation constants. They are defined as:

$$\alpha_0 = \{1 + K_1/[\text{H}^+] + K_1K_2/[\text{H}^+]^2\}^{-1}$$

$$\alpha_1 = \{[\text{H}^+]/K_1 + 1 + K_2/[\text{H}^+]\}^{-1}$$

$$\alpha_2 = \{[\text{H}^+]^2/K_1K_2 + [\text{H}^+]/K_2 + 1\}^{-1}$$

5. Definitions of equivalence points

a. Endpoint for an alkalinity titration: point x

This endpoint is defined by the proton condition:

$$[\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{-2}] + [\text{OH}^-] \quad (\text{Or, a pure solution of CO}_2)$$

b. Endpoint for “phenolphthalein” alkalinity titration: point y:

$$[\text{H}_2\text{CO}_3^*] + [\text{H}^+] = [\text{CO}_3^{-2}] + [\text{OH}^-] \quad (\text{Or, a pure solution of NaHCO}_3)$$

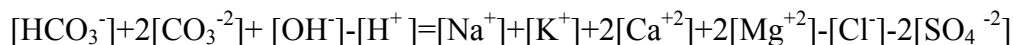
c. Point z:

$$2[\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{H}^+] = [\text{OH}^-] \quad (\text{Or, a pure solution of Na}_2\text{CO}_3)$$

C. An alternative definition of alkalinity

The current tendency is to use “acid neutralizing capacity”, or ANC, instead of “alkalinity” to describe the acid buffering capacity of a natural water. This usage is justified because of the method used to measure ANC: an acid titration to a particular pH endpoint.

An alternate definition of alkalinity (or ANC) can be developed from the requirement for electroneutrality. Beginning with the electroneutrality equation (#6 above), the terms may be rearranged to give:



Thus, Alkalinity (or ANC) can be defined as:

$$\text{Alk} = [\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{+2}] + 2[\text{Mg}^{+2}] - [\text{Cl}^-] - 2[\text{SO}_4^{-2}]$$

This version of alkalinity explains why it typically behaves as a “conservative” quantity. Samples may be collected, stored, and analyzed as much as 6 months later. The conceptual definition based on carbon species would seem to imply that alkalinity should be rather volatile. The alternative definition based on common ions also draws attention to conditions under which alkalinity would *not* be conservative. Some examples:

Redox processes which involve important buffering species will alter alkalinity. Examples are: oxidation of ammonia (NH₃) to nitrate (NO₃⁻) (nitrification), oxidation of sulfide or reduction of sulfate, oxidation or reduction of iron.

Precipitation or dissolution of minerals involving participating species will alter alkalinity. For example, the precipitation or dissolution of calcium carbonate can alter alkalinity.

Other participating species, such as organic acids, may influence ANC, and may not behave conservatively.

Note also that C_T and pH do not behave conservatively. They must be measured as quickly as possible to obtain an accurate estimate of the makeup of a water sample at the time of collection.

D. Relationships among CT, pH, and alkalinity

Kenneth Deffeyes pointed out (L&O, 10:p412) that (if the only important buffering species are carbonates) there is a fixed relationship between alkalinity (ANC), C_T, and pH. Accordingly, if any two of these are known, the other may be estimated. Commonly, pH and alkalinity are more easily measured. Note however that for critical work, which requires precise measures of C_T, other methods, such as GC should be employed.

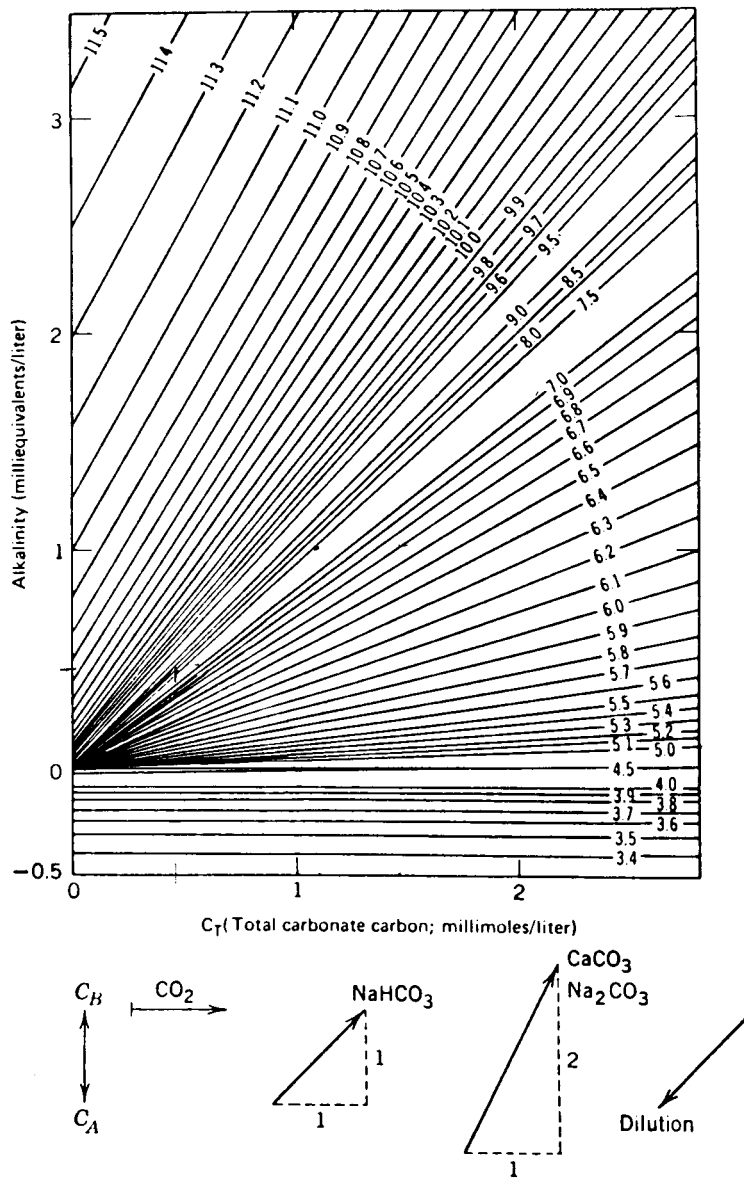


Figure 4.5 pH contours in alkalinity-versus C_T diagram. The point defining the solution composition moves as a vector in the diagram as a result of the addition (or removal) of CO_2 , NaHCO_3 , and CaCO_3 (Na_2CO_3) or C_B and C_A . (After K. S. Deffeyes [2].)

E. Acid Rain

Acid rain is a relatively recent (1970's to the present) phenomenon that has caused the acidification of natural waters in many regions. Sensitivity of a particular region depends on soil chemistry in the watershed as well as the input of atmospheric acids from industrial activities. The most serious effects of acid rain are decreased pH and alkalinity and increased base cation and aluminum concentrations that have produced drastic alterations in lake biota. Large scale sulfur emission control programs have been implemented with some success.

Keller et al [1999, "Acid rain- perspectives in lake recovery", *Journal of Aquatic Ecosystem Stress and Recovery* 6:207-216] report that the expected benefits of sulfur control programs have been slow to be realized. In spite of substantial biological recovery among many groups of organisms, not all species are capable of unassisted recovery. "Thus, stocking may be an important element in management strategies...."

Stoddard et al [1999, "Regional trends in aquatic recovery from acidification in North America and Europe", *Nature* 401:575-578] report dramatic improvements during the 1990s compared with slower recovery during the 1980s. "In concordance with general temporal trends in acidic deposition, lake and stream sulphate concentrations decreased in all regions with the exception of Great Britain; all but one of these regions exhibited stronger downward trends during the 1990s than in the 1980s." However, stream nitrate concentrations remain elevated. In only 1 of 5 regions of North America has alkalinity recovered. The failure to recover is attributed to a simultaneous decline in base cations along with a decrease in sulfate deposits.

Thies [1995, "May a fast-flushing dystrophic headwater lake mitigate acid rain?" *Water, Air, & Soil Pollution* 85:541-546] describes in-lake microbial processes [sulfate reduction, nitrate reduction, denitrification] that mitigate lake acidification.

Mueller et al [1998 "Influence of catchment quality and altitude on the water and sediment composition of 68 small lakes in Central Europe", *Aquatic Sciences*, 60:316-337 analysed the relationship between land use and lake water quality. Significant relationships were noted between surrounding land use patterns and lake water chemistry [agricultural, urban, etc]. Notably, even in remote areas, ... "precipitation is responsible for increased background concentrations [of nitrogen]."

Thornton and Dise [1998, "The influence of catchment characteristics, agricultural activities and atmospheric deposition on the chemistry of small streams in the English Lake District", *Science of the Total Environment* 216:63-75] studied water chemistry in 55 streams in the central English Lake District. Land use and geology play major roles in determining streamwater chemistry. Many streams, particularly where the parent geology produces little buffering capacity, have been impacted by acid rain.

Andersen and Vollestad [1996, "Recovery of piscivorous brown trout and its prey, Arctic char, in the acidified Lake Selura after liming" *Nordic Journal of Freshwater Res* 7:3-14] report on the effect of liming on two populations of brown trout. Liming has led to the recovery of the fish

populations, in part due to increased recruitment.

McNicol and Mallory [1994, "Trends in small lake water chemistry near Sudbury, Canada, 1983-1991", *Water, Air, and Soil Pollution* 73:105-120] report only short term improvements in water chemistry following reduced smelter emissions. They found no consistent, long-term trend of chemical recovery. [Note however that the later report by Keller, above, noted substantial recovery of lakes near Sudbury, where sulfur emission reductions were particularly large.]

Some homework problems

1. Listed below are 2 different situations with respect to pH and alkalinity in a lake. Use the accompanying diagrams to answer the questions. (Use the diagram from Deffeyes diagram and the Stumm and Morgan figures)

(a) Alkalinity = 1.2 meq; pH=8.

1) What is the concentration of total inorganic carbon in the water? (include units of concentration)

2) Which is the most abundant species of inorganic carbon?

3) If 1 mM of HCl is added to the sample, what is the resulting: pH ; Ct ; most abundant species of inorganic carbon; Alkalinity?

(b) Alkalinity =0.7 meq; pH= 6.5

1) What is the total inorganic carbon in the water?

2) Which is the most abundant species of inorganic carbon?

3) If 0.5 mM of Na_2CO_3 is added to the sample, what is the resulting pH; Ct; most abundant species of inorganic carbon; Alkalinity?

(c) For both (1) and (2), how much 0.02 N Hydrochloric acid would be required to titrate a 50 ml sample to a pH=4.2? (Starting from the beginning conditions as given.)

(1) = ? ml (2) = ? ml

hint 0.02 N HCl = 0.02 eq of acid. How many meq is that?