5) Water chemistry

I Chemistry of important chemical species in natural waters.

II Chemical reactions in water

How important is water? NASA

A) Oxygen

Dissolved oxygen (DO)

Half reactions in water

Under acidic conditions

$O_2 + H^+ = H_2O$

$O_2 + 4H^+ + 4e^- = 2H_2O$

Under basic conditions

$O_2 + H_2O = 4OH^-$

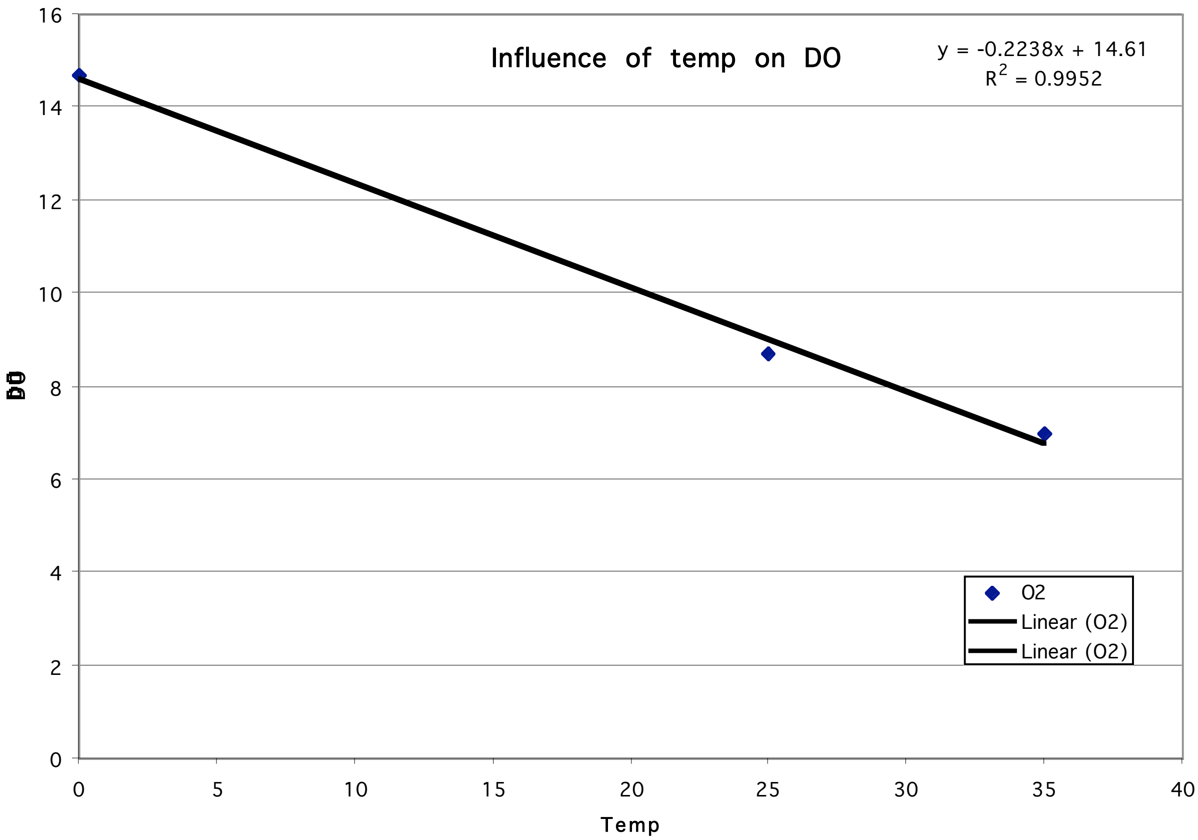
$O_2 + 2H_2O + 4e^- = 4OH^-$

Conc of DO in water

Henry's Law - at constant temp the solubility of a gas in a liquid is proportional to the partial pressure of the gas in contact with the liquid.

$[X(aq)] = K\ P_x$

aqueous conc of gas = Henry's Law constant * the partial pressure of the gas



The graph above was made from values on pg. 427 of your textbook. The author states that 5 ppm of DO is the lower limit for fish survival, using the graph determine 1) the temp. at which fish cannot survive and 2) the temp. at which DO is zero.

What influences DO levels?

BOD - oxidation of C by biotic means (microbes)

COD - dichromate ion - $NA_2Cr_2O_7$ - very harsh

TOC

DOC

Anaerobiosis creates gradients of O_2 depletion

Fig. 9-2 and stratification

pE scale

pH is related to conc of H^+

pE is related to effective activity of e^-

low pE indicates reducing conditions; high pE indicates oxidizing conditions

So what?

pE can be used to determine the speciation of an element

Fe^{3+} (insol) + e^- $\leftrightarrow$ Fe^{2+} (sol)

At neg pE (-4.1) $Fe^{3+}/Fe^{2+} = 5 \times 10^{-18}$

At pos pE (13.9) $Fe^{3+}/Fe^{2+} = 5$

Problem (9-8) - At what pE is the ratio of $Fe^{3+}/Fe^{2+} = 1$? 100?

B) Sulfur

Reduced state H_2S - oxidized state SO_4^{2-}

Problem 9-10a: Balance the reduction half rxn that converts SO_4^{2-} to H_2S under acidic conditions.

C) Carbonate equilibria

The acid base chemistry of lakes is dominated by the carbonate system.

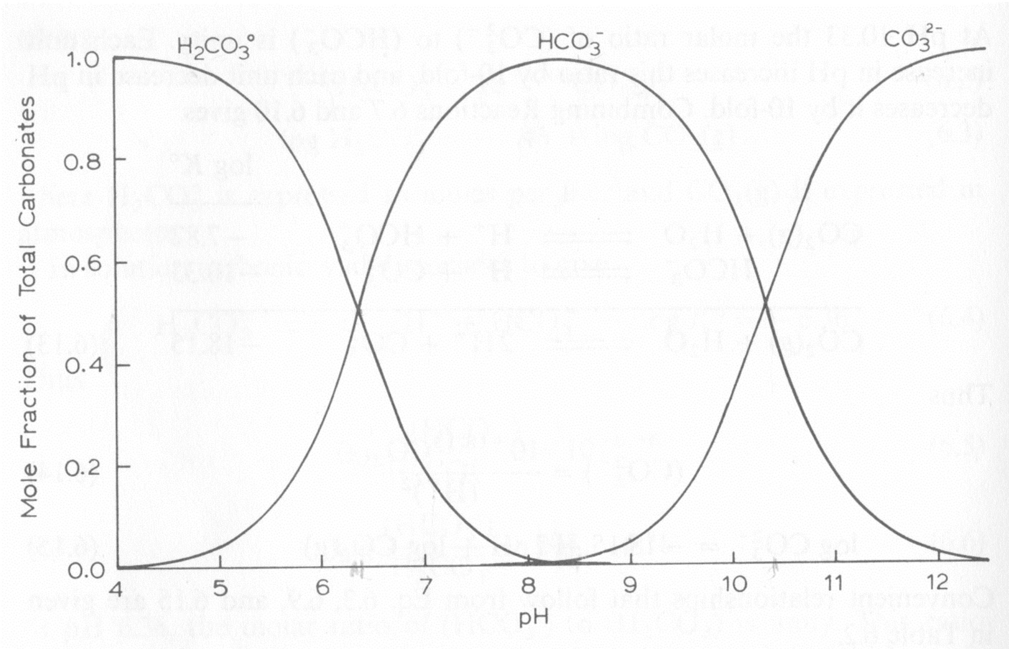


Fig. 6.1 The effect of pH on the distribution of carbonate species in solution.

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

If you wanted to determine the amount of C in a water sample how might you go about this by manipulating the pH?

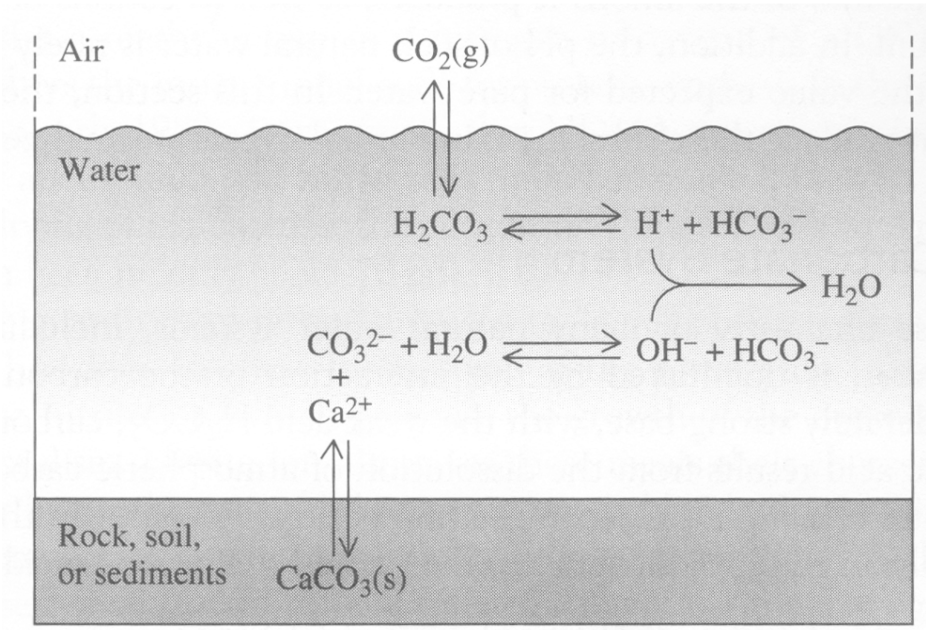


Fig. 9-5 in Baird

What does increasing CO_2 do to this balance?

What about limestone ($CaCO_3$)?

Alkalinity - the number of moles (or equivalents) required to neutralize H^+ additions.

So it is a measure of the ability of a water sample to resist acidification.

total alkalinity = $2\,[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+]$

How do alkalinity and basicity differ? How can 2 bodies of water with the same pH differ in their resistance to acidification?

What else contributes to alkalinity?

D) Nitrogen

What results in elevated N concentrations?

What form of N is typically applied as fertilizer? Why?

N transformations due to bacteria

Ammonification - Organic N → NH_4^+; NH_3

Nitrification - NH_4^+ → NO_2^- → NO_3^-

Denitrification - NO_3^- → N_2O and N_2

What are the oxidation states of N above?

Which would occur under oxidizing or reducing conditions?

If NO_2^- is not commonly found in the environment yet is the causitive agent of methemoglobinemia. So then why is NO_3^- a health concern (contrary to what your book says it still is in some small farming communities)?

Problem: In terms of total N what is more stringent, a nitrate standard of 50 ppm or a limit of 10 ppm N?

E) Aluminum

One of the most abundant elements in soils, approx. 7.1% of the earth's crust by weight.

Levels are typically low in water with pH 6 - 9. Why?

The K_{sp} of $Al(OH)_3 = 10^{-33}$

What is K_{sp}? The solubility product.

definition - when an insoluble or slightly soluble compound is placed in solution an equilibrium between the solid and ions in solution is established.

For example: $AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$

$K_{sp} = 1.7 \times 10^{-10} = [Ag^+][Cl^-]$

So how many g of Ag are in a liter of water <u>saturated</u> with AgCl?

$Al(OH)_3 \leftrightarrow Al^{3+} + 3OH^-$

$[Al^{3+}]\,[OH^-]\,[OH^-]\,[OH^-] = [Al^{3+}]\,[OH^-]^3 = 10^{-33}$

Problem 9-22: So, what's the concentration of Al at pH 5.5?

at pH 4.5?

Therefore, for every unit decrease in pH the Al concentration increases 1000x!

In some acidified lakes, fish kills have been found to be due to Al toxicity rather than directly due to the pH.

At pH < 4.5 Al^{3+} becomes the principal cation.