Lecture 12

Chemical Equilibrium in Atmospheric Processes

Acid Deposition

CACE and ATMO Special Seminar
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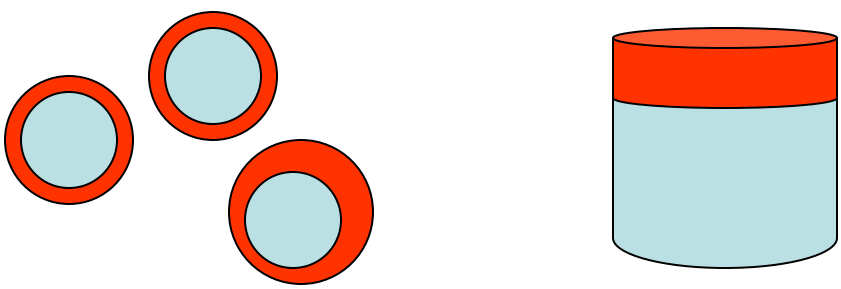
Title: Kinetics of Radical Reactions Studied by A Flow Reactor Coupled to Photoionization Mass Spectrometer

Room 1210 O&M Building 4 pm Wednesday October 5, 2005

Fatty acids in rainwater

Seidel, Atm. Environment, 34, 2000, 4917-4932

- Properties of acids between on length of hydrocarbon chain



Chain length determines:

1. Solubility in water

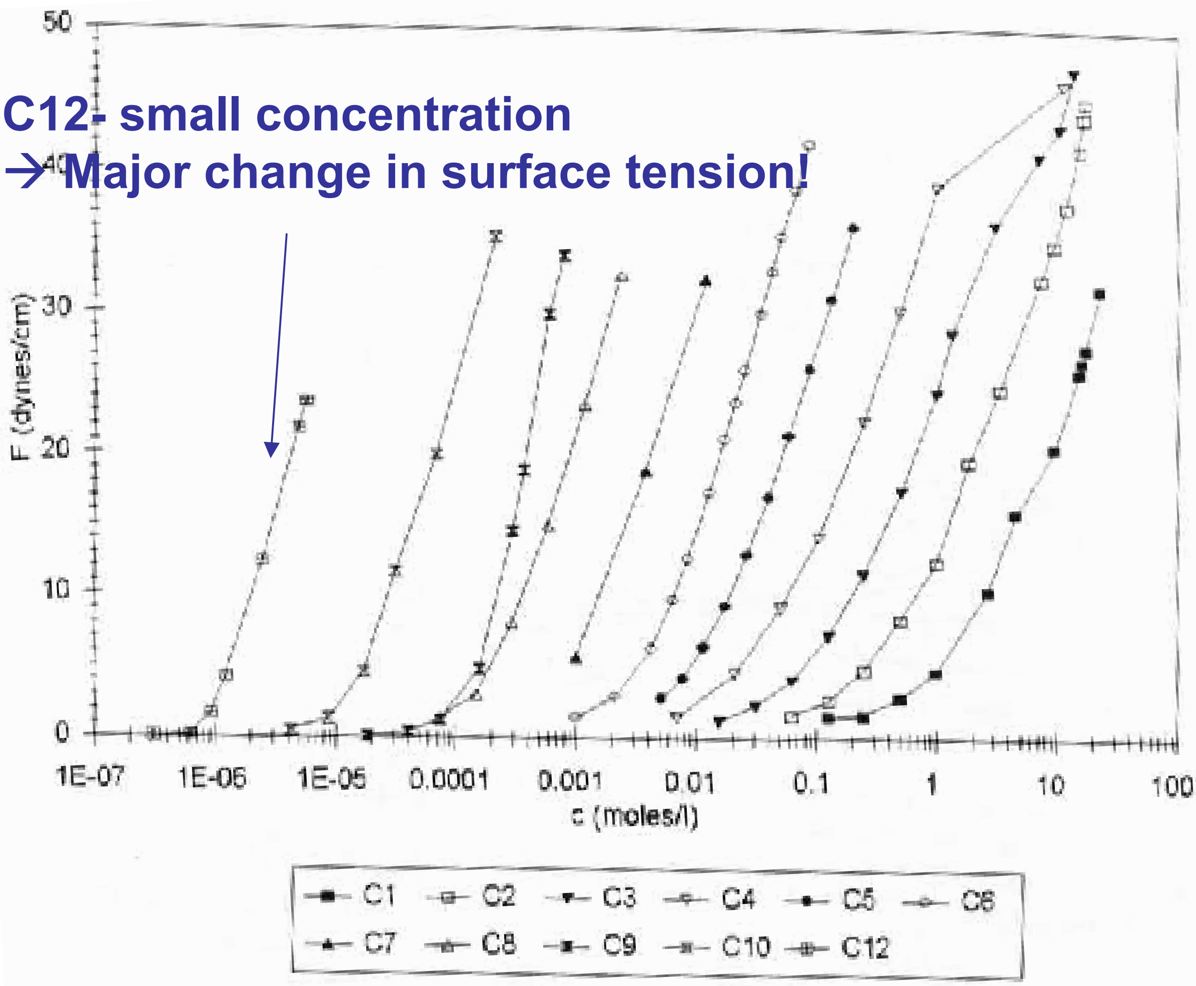
(~less than 12C = soluble)

2. Gas-particle phase partitioning
3. State of film which forms on water surface

Film Pressure F = reduction in surface tension compared to pure water

Effects of surface tension reduction INCREASE as # of Cs increases

C12- small concentration
→ Major change in surface tension!



m pressure *F* as function of the bulk aqueous phase concentration *c* for the *n*-alkanoic acids with 1–12 carbon aton

Measurements of rainwater show up to ~380ug/g of long chain fatty acids!
→ Leads to reduced surface tension, reduced barrier to cloud condensation and cloud formation.

Important Chemical Equilibrium

- Acid deposition affects on freshwater

- Air-sea interactions

- Gas-Aerosol Phase

- Heterogeneous Chemistry

What is this?

Figure 10.7. Liming of a lake in Sweden by helicopter. Photo by Tero Niemi, available from ublic.

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$$pH = -\log[H_3O^+]$$

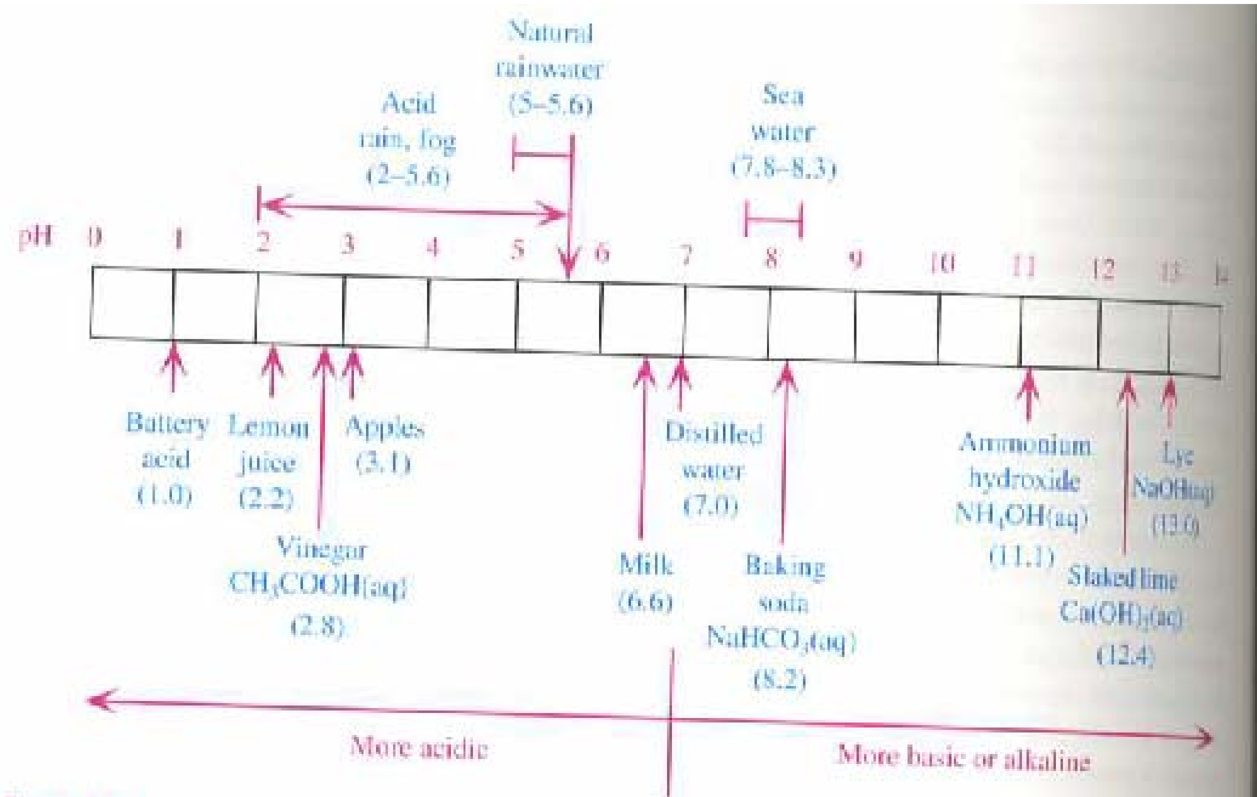

Figure 10.3. Diagram of the pH scale and the pH levels of selected solutions.

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pH of Rain in USA

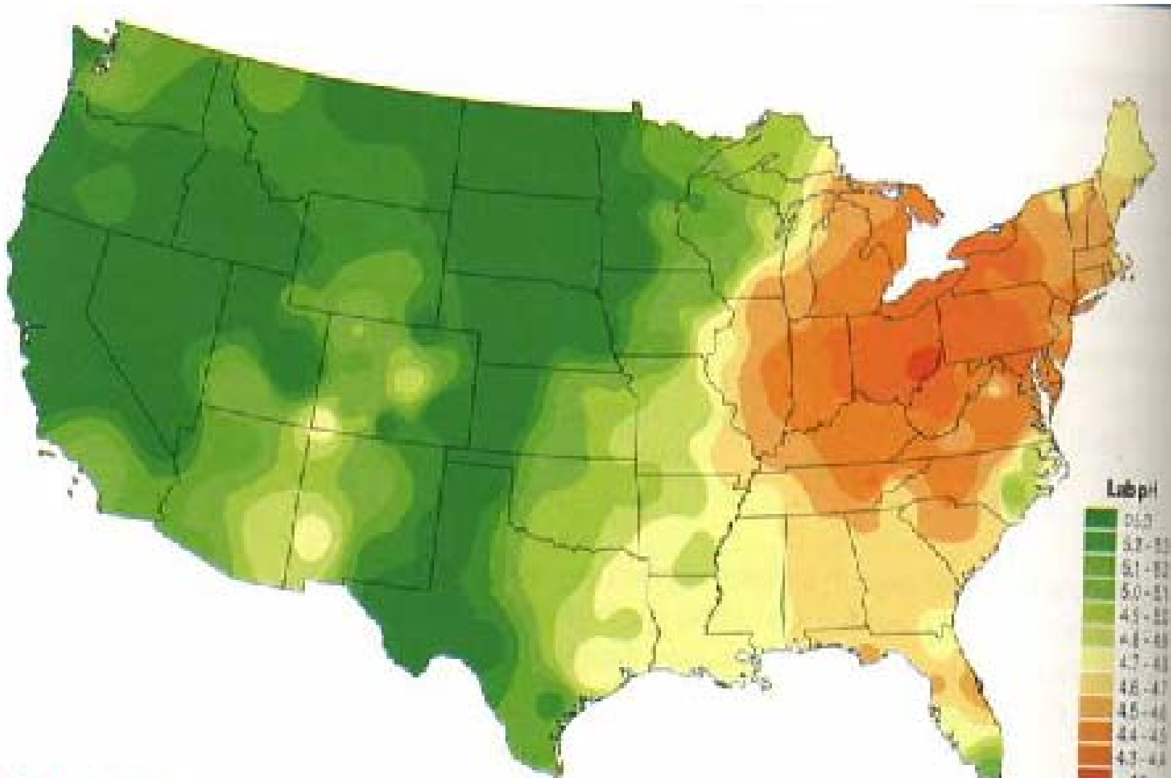

Figure 10.4. Map of rainwater pH in the United States in 1999 (National Atmospheric Deposition Program/National Trends Network, 2000).

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Acid Rain Formation

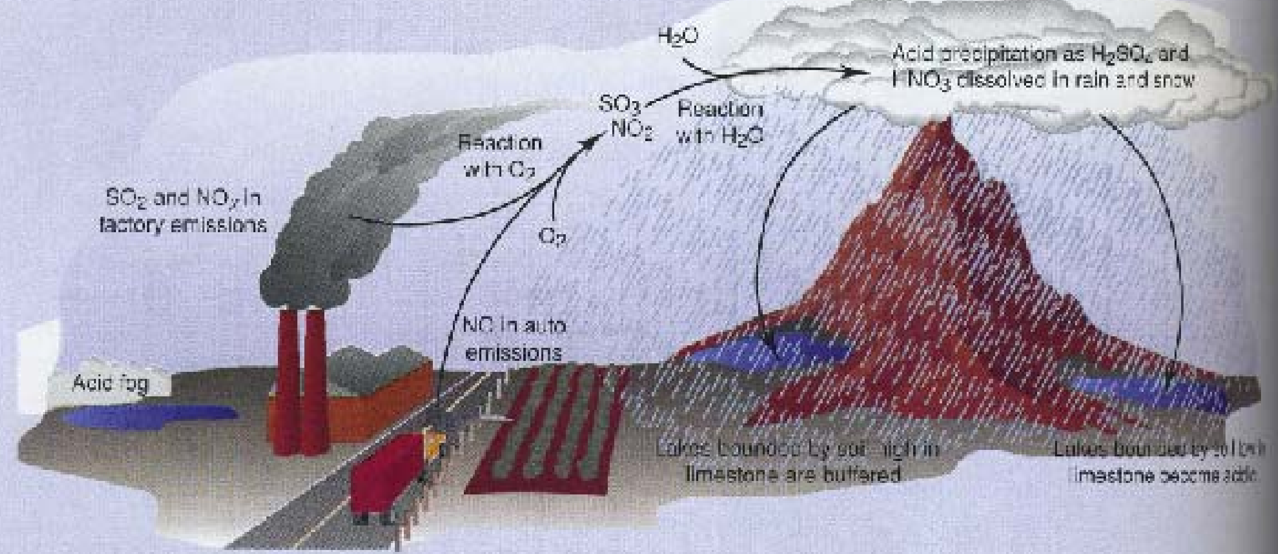

FIGURE 18.B
Formation of acidic precipitation. A complex interplay of human activities, atmospheric chemistry, and environmental distribution leads to acidic precipitation. Car exhaust and factory waste gases provide lower oxides of nitrogen and sulfur. These are oxidized by O_2 to higher oxides (NO_2, SO_3), which react with moisture to form acidic rain, snow, and fog. In contact with acidic precipitation, many lakes become acidified, whereas limestone-bounded lakes form a carbonate buffer that prevents acidification.

Silberberg, Chemistry: the Molecular Nature of Matter and Change

Acid Rain Components

1. Sulfurous acid, H_2SO_3

SO_2 (coal burning) + H_2O → H_2SO_3

2. Sulfuric acid, H_2SO_4

$SO_2(g) + O_3(g) \leftrightarrow SO_3(g) + O_2(g)$

$$2SO_2(g) + O_2(g) \xleftrightarrow{\text{dust}} 2SO_3(g) \rightarrow H_2SO_4$$

3. Nitric Acid, HNO_3

NO,NO_2(combustion) + H_2O →→ HNO_2, HNO_3

Impacts of acid rain-Acidified Forest

(b)

Figure 10.5. (a) Acidified forest, Oberwiesenthal, Germany, near the border with the Czechoslovakia, taken in 1991. The trees are of the *Picea* family. Photo by Stefan Rosengren, available from Naturbild. (b) Acidified forest in the Erzgebirge Mountains, north of the town of Most, Czechoslovakia, taken in 1987. Photo by Owen Bricker, USGS.

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Impacts of acid rain of statues

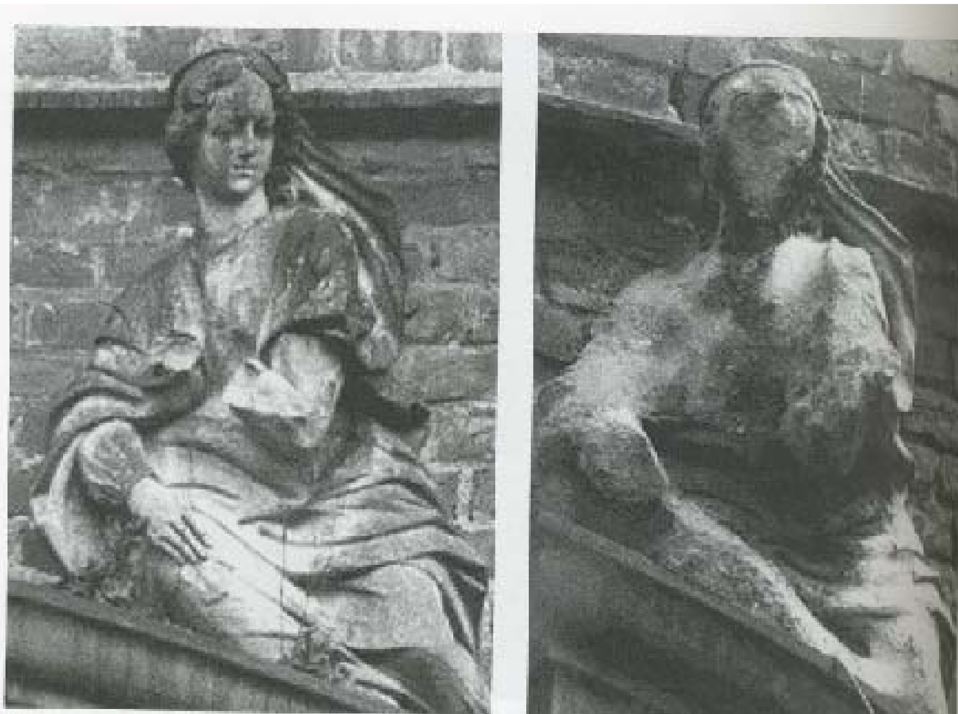

Figure 10.6. Sandstone figure over the portal of a castle, built in 1702, in Westphalia Germany, photographed in 1908 (left) and in 1968 (right). The erosion of the figure is due to a combination of acid deposition and air pollution produced from the industrialized Ruhr region of Germany. Courtesy Herr Schmidt-Thomsen.

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Impacts on Lakes and Rivers

- Depends on whether the lake or river is chemically buffered or not!

- Most aquatic insects, algae, and plankton can only live above pH 5.

- In a poorly buffered lake, these die → No fish food,

  also reproductive failure, fish mutation.

Equilibrium Constants

K = molar concentration of products/molar concentration of reactants

Ka - acid dissociation constant

pKa = -log Ka

Kb -base dissociation constant

Ksp - Solubility Constant.

Here the concentration of solids is assumed to be "1" or constant, as if a constant supply of the solid will be introduced into solution as possible.

For example,

$PbSO_4(s) \leftarrow\rightarrow Pb^{+2}(ag) + SO_4^{-2}(ag)$

$Ksp = \frac{[Pb^{+2}][SO4^{-2}]}{1}$ $Ksp = 1.98 \times 10^{-8}$

Chemical Buffers Any solution that lessens the changes in [H3O+]

Chemical buffers--weak acid HA, conjugate base A-

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

Equilibrium expression for reaction is:

$$\frac{[H_3O^+][A^-]}{[HA]} = K_a$$

Rearrange:

$$[H_3O^+] = \frac{K_a[HA]}{[A^-]}$$

Henderson-Hasselbach equation- To calculate the pH of a buffer:

$$pH = pK_a - \log \frac{[HA]}{[A^-]}$$

How to make Buffers

- First decide- What pH do we want?

★ Buffers are most effective when pH = ~pKa.

Choose a compound whose pKa is close to the pH desired, and then decide what the buffer concentration should be.

1. Weak acid and conjugate base.

   CH_3COOH, CH_3COONa (in water CH_3COO^-)

Common ion, CH_3COO^- represses dissociation of CH_3COOH, keeping solution less acidic.

2. Strong acid /weak base

   example: HCl, sodium acetate (CH_3COONa)

3. Strong base/weak acid

   NaOH, Acetic acid (CH_3COOH)

What reactions take place if the buffer is "working"?

(1) $A^- + H_3O^+ \rightarrow HA + H_2O$

This will proceed to completion for as long as the initial number of moles of A^- is several times larger than the moles of $H3O^+$ added.

If strong base is added,

(2) $HA + OH^- \rightarrow A^- + H_2O$

Equations 1 and 2 change the ratio [HA-]/[A-] in

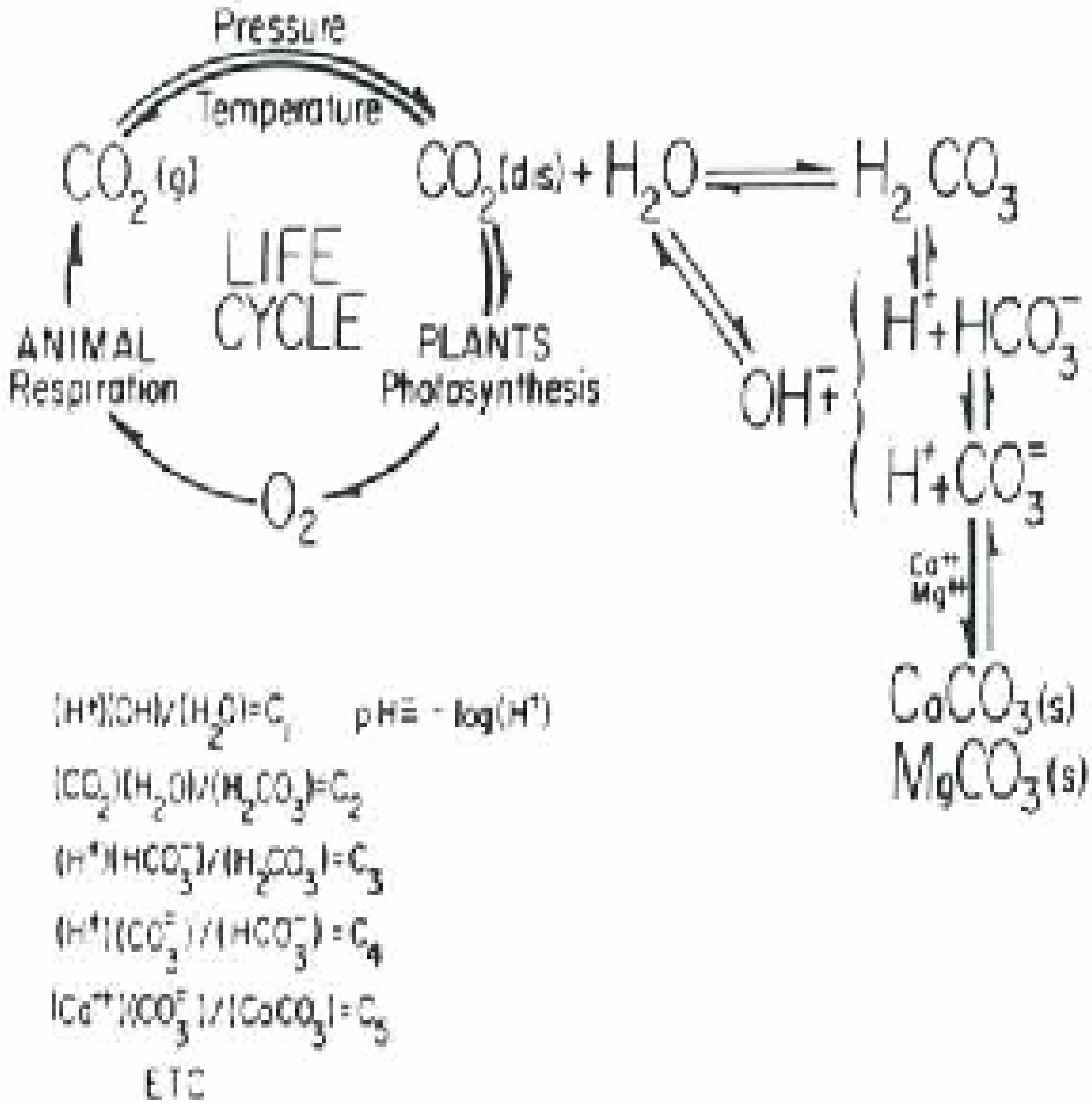
$$pH = pK_a - \log \frac{[HA]}{[A^-]}$$

Buffer Capacity

$$\beta_{approx} = \frac{\Delta C_a}{\Delta pH}$$

- where β is buffer capacity, a measure of buffer's ability to resist change in pH when another acid or base is added (millimole H^+/liter solution)
- Ca, Cb are the number of moles of strong acid and based needed to change the pH of 1 liter of buffer by 1 pH unit

Most Common Natural Buffer- Carbonate buffer system



Horne, Chemistry of Our Environment

Most Common Natural Buffer- Carbonate buffer system

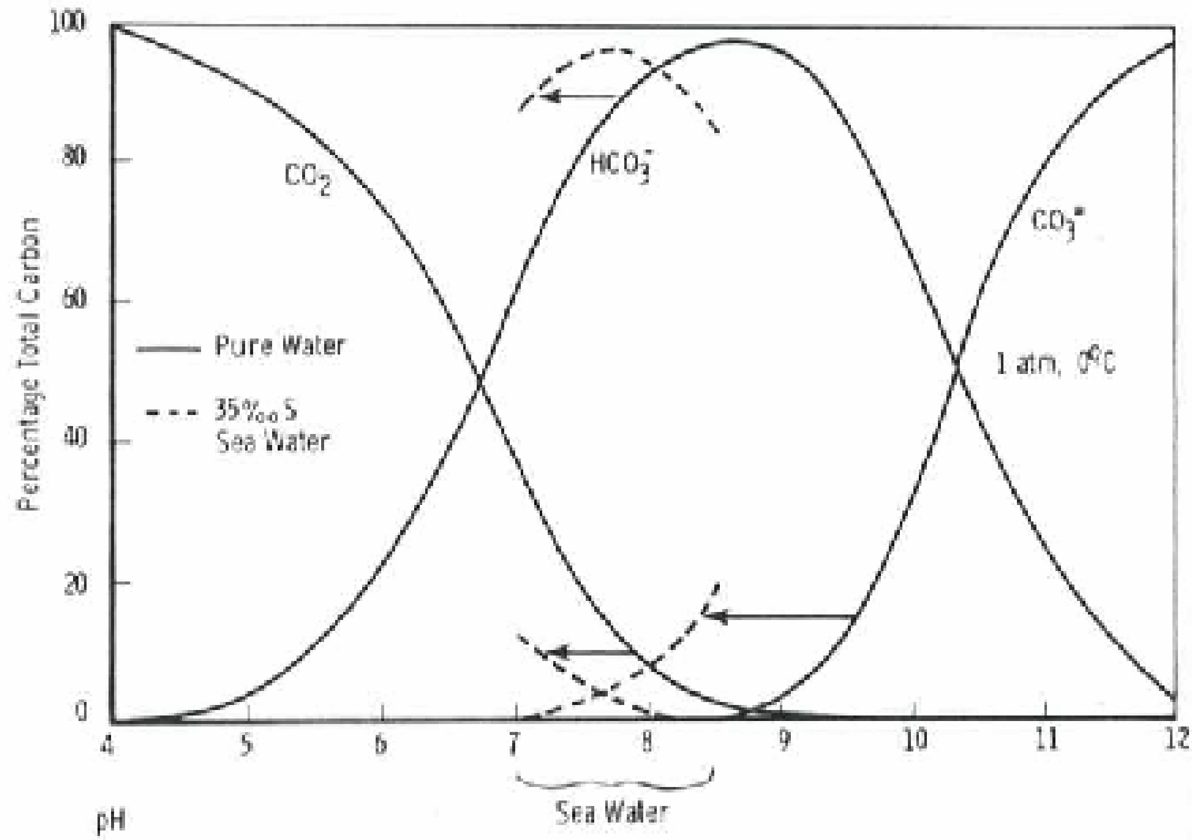


Figure 7.17. Speciation of the CO_2–HCO_3^-–CO_3^{2-} system in pure water and seawater as a func tion of pH at 1 atm (from Horne, 1969).

Horne, Chemistry of Our Environment