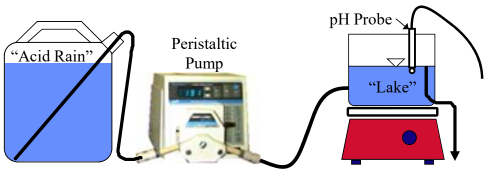
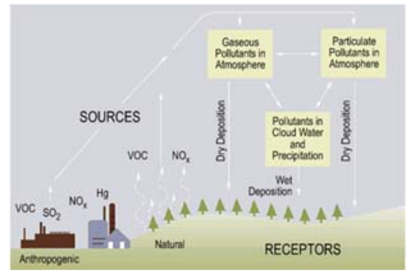
Acid Precipitation and Remediation of Acid Lakes



What is the Acid Source?

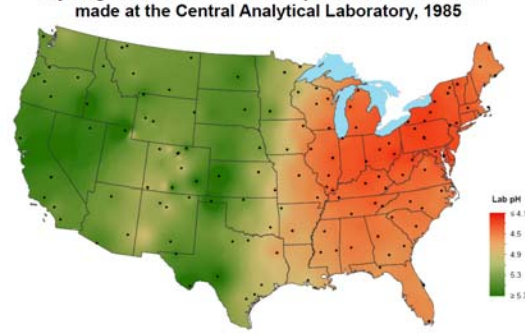


Data source: www.usepa.gov.

Chemistry of Acid Rain Formation

Combustion product precursors to acid rain	
SO_2	NO
Reactions	
$SO_2 + OH\cdot \rightarrow HOSO_2\cdot$	$HO_2\cdot + NO \rightarrow NO_2 + OH$
$HOSO_2\cdot + O_2 \rightarrow SO_3 + HO_2\cdot$	
$SO_3 + H_2O \rightarrow H_2SO_4$	$OH\cdot + NO_2 \rightarrow HNO_3$
Strong acids	
H_2SO_4 Sulfuric acid	HNO_3 Nitric acid

Hydrogen ion concentration as pH from measurments made at the Central Analytical Laboratory, 1985



National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

What Determines Lake Susceptibility to Acidification?

- Acidification = f(acid inputs, ANC)
  - Acid inputs = f(power plants, cars, wind currents, mine tailings)
  - Acid Neutralizing Capacity = f(?)
    - Carbonates obtained from dissolution of minerals such as
      - $CaCO_3$ (calcite or aragonite)
      - $MgCO_3$ (magnesite)
      - $CaMgCO_3$ (dolomite)
      - ...

Fate of Strong Acids in the Environment

- Strong acids completely dissociate in water

$HNO_3 \rightarrow H^+ + NO_3^-$ $\qquad$ $H_2SO_4 \rightarrow 2H^+ + SO_4^{-2}$

- ➢ If 0.1 mol of nitric acid is added to 1 liter of pure water, what is the concentration of H^+? __________
- ➢ What is the pH? [pH = -log[H^+]] _________
- ➢ What else can happen to the hydrogen ions if it isn't pure water? _________________

Fate of Strong Acids: Reactions

- Weak acids/bases can react with the added H^+ and reduce the final concentration of H^+
- Examples of weak acids and bases in the environment:
  - carbonates
    - carbonate, bicarbonate, carbonic acid
  - organic acids (A^-)
    - acetic acid (pK = 4.7) $HA \rightarrow H^+ + A^-$

$$K_A = \frac{[H^+][A^-]}{[HA]}$$

____

Carbonate System

species $\quad H^+ \quad CO_{2(aq)} >> H_2CO_3 \quad HCO_3^- \quad CO_3^{-2}$

definition $\quad [H_2CO_3^*] = [CO_{2(aq)}] + [H_2CO_3]$

$H_2CO_3^* \overset{K_1}{\leftrightarrow} H^+ + HCO_3^-$

$K_1 = 10^{-6.3} \quad pK_1 = \underline{6.3}$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}$$

____

____

$HCO_3^- \overset{K_2}{\leftrightarrow} H^+ + CO_3^{-2}$

$K_2 = 10^{-10.3} \quad pK_2 = \underline{10.3}$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

Alpha Notation

$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \quad C_T =$ ________________

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} \Rightarrow [H_2CO_3^*] = \frac{[H^+][HCO_3^-]}{K_1}$$

$$K_2 = \frac{[H^+][CO_2^{2-}]}{[HCO_3^-]} \Rightarrow [CO_3^{2-}] = \frac{K_2[HCO_3^-]}{[H^+]}$$

$$C_T = \frac{[H^+][HCO_3^-]}{K_1} + [HCO_3^-] + \frac{K_2[HCO_3^-]}{[H^+]}$$

$$C_T = [HCO_3^-] * \left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}\right)$$

Alpha Notation

$$C_T = [HCO_3^-] * \left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}\right)$$

$$[HCO_3^-] = \frac{C_T}{\left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}\right)}$$

define $\rightarrow \quad \alpha_1 = \dfrac{1}{\left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}\right)}$

$$[HCO_3^-] = \alpha_1 * C_T$$

Alpha Notation

- All carbonate species concentrations are related to the hydrogen ion concentration

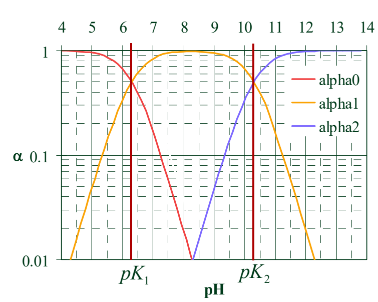
$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

$$\alpha_0 = \frac{1}{\left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right)} \quad \alpha_1 = \frac{1}{\left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}\right)} \quad \alpha_2 = \frac{1}{\left(\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1\right)}$$

$$[H_2CO_3^*] = \alpha_0 * C_T \quad [HCO_3^-] = \alpha_1 * C_T \quad [CO_3^{2-}] = \alpha_2 * C_T$$

$$C_T = C_T(\alpha_0 + \alpha_1 + \alpha_2) \quad \alpha_0 + \alpha_1 + \alpha_2 = \_$$

pH Diagram



$[H_2CO_3^*] = \alpha_0 * C_T$

$[HCO_3^-] = \alpha_1 * C_T$

$[CO_3^{2-}] = \alpha_2 * C_T$

Add acid to a carbonate solution at pH 9. What happens?

Acid Neutralizing Capacity (ANC)

- The ability to neutralize (react with) acid
- ANC has units of _______________ or eq/L
- Possible reactants in environment:

$$ANC = [HCO_3^-] + \_[CO_3^{-2}] + [OH^-] - [H^+]$$

Hydrogen Ion Concentration: The Master Variable

$$ANC = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-] - [H^+]$$

$$[HCO_3^-] = \alpha_1 * C_T \qquad [CO_3^{2-}] = \alpha_2 * C_T$$

$$H_2O \overset{K_w}{\leftrightarrow} H^+ + OH^- \qquad K_w = [H^+][OH^-] = 10^{-14}$$

$$\boxed{ANC = C_T(\alpha_1 + 2\alpha_2) + \frac{K_w}{[H^+]} - [H^+]}$$

$ANC = f$ _________________

ANC properties

- ANC = capacity to react with H^+ minus the concentration of H^+
- ANC can be positive or _________
- ANC is conservative with respect to mixing
- Example: 10 liters of a solution with an ANC of 0.1 meq/L is mixed with 5 liters of a solution with an ANC of -1 meq/L. What is the final ANC?

ANC Example

- Suppose we add 3 mM $Ca(OH)_2$ to distilled water. What is the ANC?

$$ANC = [\cancel{HCO_3^-}] + 2[\cancel{CO_3^{-2}}] + [OH^-] - [H^+]$$

$$ANC = [OH^-] - [H^+] \qquad \_\_\_\_\_\_\_\_$$

$$ANC = [OH^-] = 6 \times 10^{-3}\ eq/L$$

p(OH)= ____

- What is the resulting pH if the system is closed to the atmosphere?

$$K_w = [H^+][OH^-] = 10^{-14}$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{6x10^{-3}} = 1.67x10^{-12}$$

pH= _____

More Complications: Open to the Atmosphere

- Natural waters exchange carbon dioxide with the atmosphere

$$[CO_{2(aq)}] = P_{CO_2} * K_H$$

$$[CO_{2(aq)}] = \alpha_0 * C_T$$

The total concentration of carbonate species is affected by this exchange

$$\alpha_0 * C_T = P_{CO_2} * K_H$$

Is ANC affected? _____

$$C_T = \frac{P_{CO_2} * K_H}{\alpha_0}$$

$$ANC = C_T(\alpha_1 + 2\alpha_2) + \frac{K_w}{[H^+]} - [H^+]$$

$$\boxed{ANC = \frac{P_{CO_2} * K_H}{\alpha_0}(\alpha_1 + 2\alpha_2) + \frac{K_w}{[H^+]} - [H^+]}$$

ANC Example (continued)

- Suppose we aerate the 3 mM $Ca(OH)_2$ solution. What happens to the pH?

$$ANC = \frac{P_{CO_2} * K_H}{\alpha_0}(\alpha_1 + 2\alpha_2) + \frac{K_w}{[H^+]} - [H^+]$$

- All the alphas are functions of pH and it is not possible to solve explicitly for $[H^+]$.

$$pH = -log[H^+]$$

$$[H^+] = 10^{-pH}$$

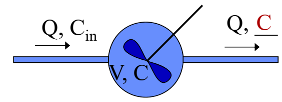
- Solution techniques
  - numerical methods (pH=9, C_T=0.0057M)
    - Solve for pH rather than for [H+] to make it possible for SOLVER to find a solution!

Beware of precision!

Open vs. Closed to the Atmosphere

- What is conserved in an open (volatile) system? ______________
- What is conserved in a closed (nonvolatile) system? ______________
- For conservative species we can use the Completely Mixed Flow Reactor equation to model a well mixed lake

Completely Mixed Flow Reactor



Mass in – Mass out = Increase of Mass in reactor

Mass balance

$$dt * \frac{Q}{V} = \frac{dC}{(C_{in} - C)} \qquad \frac{V}{Q} = \theta$$

Completely Mixed Flow Reactor

$$\int_0^t \frac{1}{\theta} dt = \int_{C_0}^{C} \frac{dC}{(C_{in} - C)}$$ Set up integration

$$\boxed{C = C_{in} * \left(1 - e^{-t/\theta}\right) + C_0 * e^{-t/\theta}}$$

What is C when t is large? _______

- Equation applies to any conservative species.
  - C_o = time zero concentration in reactor
  - C_{in} = influent concentration
  - C = concentration in the reactor as a function of time

Three Equations for C_T in CMFR

- CMFR for conservative species. (True if nonvolatile!)

$$C_T = C_{T_0} \cdot e^{-t/\theta}$$

- If in equilibrium with atmospheric CO_2…

$$C_T = \frac{P_{CO_2} * K_H}{\alpha_0}$$

- Can we measure C_T?

What is the measured concentration of carbonates?

- Measured C_T?

$$ANC = C_T(\alpha_1 + 2\alpha_2) + \frac{K_w}{[H^+]} - [H^+]$$

$$C_T = \frac{ANC - \frac{K_w}{[H^+]} + [H^+]}{(\alpha_1 + 2\alpha_2)}$$

- What is ANC?

$$ANC = ANC_{in} * \left(1 - e^{-t/\theta}\right) + ANC_0 * e^{-t/\theta}$$

Measuring ANC: Gran Titration

- The sample is titrated with a strong acid to "cancel" the sample ANC
- At the equivalence point the sample ANC is zero
- Further titration will result in an increase in the number of moles of H^+ equal to the number of moles of H^+ added.
- Use the fact that ANC is conservative…

Conservation of ANC

$V_T * ANC_T + V_s * ANC_s = (V_s + V_T)ANC_{T+S}$ _________ _________

$V_e = V_T \text{ such that } ANC_{T+S} = 0$ V_e= __________ volume = volume of titrant added so that ANC = 0

$V_e * ANC_T + V_s * ANC_s = 0$

$V_e = \frac{-V_s * ANC_s}{ANC_T}$ $\quad ANC_s = \frac{-V_e * ANC_T}{V_s}$

Need to find ANC_T and V_e

ANC of Titrant

$$ANC = C_T(\alpha_1 + 2\alpha_2) + \frac{K_w}{[H^+]} - [H^+]$$

$ANC_T = -N_T$ Why? ___________

$V_T * ANC_T + V_s * ANC_s = (V_s + V_T)ANC_{T+S}$

$ANC_s = \frac{-V_e * ANC_T}{V_s}$

$-V_T * N_T + V_e * N_T = (V_s + V_T)ANC_{T+S}$

$-N_T * (V_T - V_e) = (V_s + V_T)ANC_{T+S}$ Could solve for V_e, but what is ANC_{T+S}?

When can we measure ANC with a pH probe?

____

ANC of Titrated Sample

$-N_T * (V_T - V_e) = (V_s + V_T)ANC_{T+S}$

$ANC_{T+S} = -[H^+]$ When is this true? ____________

$-(V_T - V_e) * N_T = -(V_s + V_T) * [H^+]$

$V_e = V_T - \frac{(V_s + V_T) * [H^+]}{N_T}$

Finally! An equation for equivalent volume!

Gran Function

- A better measure of the equivalent volume can be obtained by rearranging the equation so that linear regression on multiple titrant volume - pH data pairs can be used.

$$V_e = V_T - \frac{(V_s + V_T) * [H^+]}{N_T} \longrightarrow \frac{(V_s + V_T) * [H^+]}{V_s} = \frac{N_T V_T}{V_s} - \frac{N_T V_e}{V_s}$$

- Define F_1 as:

$$F_1 = \frac{(V_s + V_T) * [H^+]}{V_s}$$

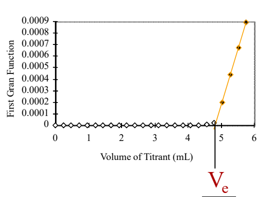
Gran Plot

$F_1 = \frac{N_T V_T}{V_s} - \frac{N_T V_e}{V_s}$

$y = mx + b_y$

$m = \frac{N_T}{V_S}$ $\quad b_y = -\frac{N_T V_e}{V_S}$

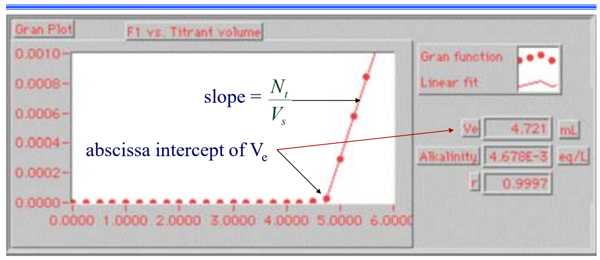
$b_x = \frac{-b_y}{m} = \frac{N_t V_e V_s}{V_s N_t} = V_e$



Minimum value of F_1 before it is worth attempting analysis?

Algorithm for choosing points to include?

Gran Plot using pH



F_1 plotted as a function of V_t. The abscissa has units of mL of titrant and the ordinate is a Gran function with units of $[H^+]$.

Calculating ANC

- The ANC is obtained from the equivalent volume.

$$ANC = \frac{V_e N_t}{V_s}$$

- The ANC of the acid rain can be estimated from its pH. At low pH (< pK_1) most of the carbonates will be carbonic acid and thus for pH below about 4.3 the ANC equation simplifies to

$$ANC = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-] - [H^+]$$

Titration Technique

- Titrate with digital pipette
  - Accuracy is important
- Measure pH before first addition of titrant
- Measure pH after each addition of titrant
- After ANC is consumed Gran function will be linear
- What should the incremental titrant volume be?
- Techniques to speed up titration

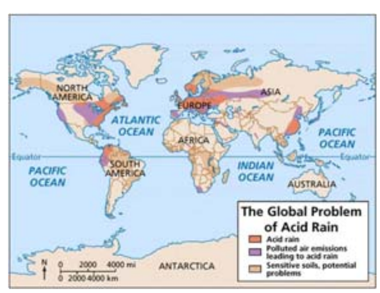
Titrant Incremental Volume

- Minimum? ______________________
- Maximum?
  - Constraints?
    - Number of data points ____________
    - Before reaching pH___
  - How do we determine titrant volume?
  - H^+ is conservative!

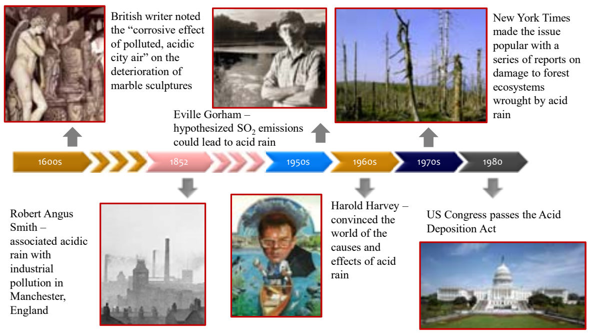
Freshwater pH: water quality issues/challenges

- Source of Acid Rain
- History of Acid Rain Research
- Fate of strong acids in the environment
  - Reactions
  - Carbonate System
    - Dissociation constants
    - Alpha notation
    - p-notation (pK_1, etc)
    - Volatile (open) vs non-volatile (closed)
- Acid Neutralizing Capacity (ANC)
  - Defined
  - Measured – Gran Plot
  - Titration

The Global Problem of Acid Rain



History of Acid Rain Research



Lake and/or Watershed Remediation

- Add a soluble mineral such as lime ($CaCO_3$) or sodium bicarbonate ($NaHCO_3$)
- Application options
  - ________________
  - ________________
  - ________________

At what pH is ANC 0?

$$ANC = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-] - [H^+]$$