Announcements

- Section 16.4 was left out of the reading assignment. Please read.

- Quiz tomorrow on material since last quiz through concepts of pH and conjugate acid-base pairs today.

- You will not be asked about making buffers yet.

$\rightleftharpoons$
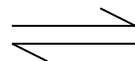
Review

- Quadratic in solving equilibria
- Relation between K and ΔG
  - $K = \exp(-\Delta G^o/(RT))$
  - $\Delta G^o = -RT\ln K$
- Le Châtelier's principle:
  - If a system at equilibrium is subjected to a stress, the position of the equilibrium will shift in the direction that will relieve that stress.
  - Examples: effect of changes of concentration, pressure and temperature.
  - Catalysts have no effect since they do not change ΔG^o.
- Heterogeneous equilibria: pure solids and solvents do not appear in mass action expression.

Review

- Acid-Base equilibria.
  - Strong acids: HNO_3, HCl and first proton on H_2SO_4 dissociate completely when mixed with water.
  - For weak acids $HA <\!\!-\!\!\!-\!\!> H^+ + A^-$ does not go 100%.
    - $K_a = [H^+][A^-]/[HA]$ is tabulated for many of these.
    - Can use K_a in normal equilibrium calculations.

- Important acid-base equilibrium situation is buffers.
  - Buffer = a solution that resists having its pH changed when acid or base is added.
  - Made by mixing a weak acid and a salt containing the same negative ion.

Review

- pH=$-\log_{10}[H^+]$, generally pX = $-\log_{10}X$, $10^{-pX} = X$

- Showed that when the [acid] and [salt] in a buffer are near 1.0 M we can use the Henderson-Hasselbach equation to estimate pH = pK_a + log[salt]/[acid]. The [..] are assumed to be the initial values.

  - When making a buffer pick pK_a ≈ desired pH.

  - Solve pH = pK_a + log[salt]/[acid] for ratio [salt]/[acid].

  - For ratio < 1 set minimum [salt]•(L sol'n) > # moles of acid to buffer.

  - For ratio > 1 set minimum [acid]•(L sol'n) > # moles of base to buffer.

Acid-Base & Solution Equilibria

- Brønsted-Lowry vs Lewis acids and Bases

- Conjugate pairs

- Equilibria and Bases

- Example equilibria - Acid Rain

- Structure-acidity relations

- pH and pOH

- pH of salt solutions--why New England lakes are acidic.

- How Buffers work

- Indicators

- Titration

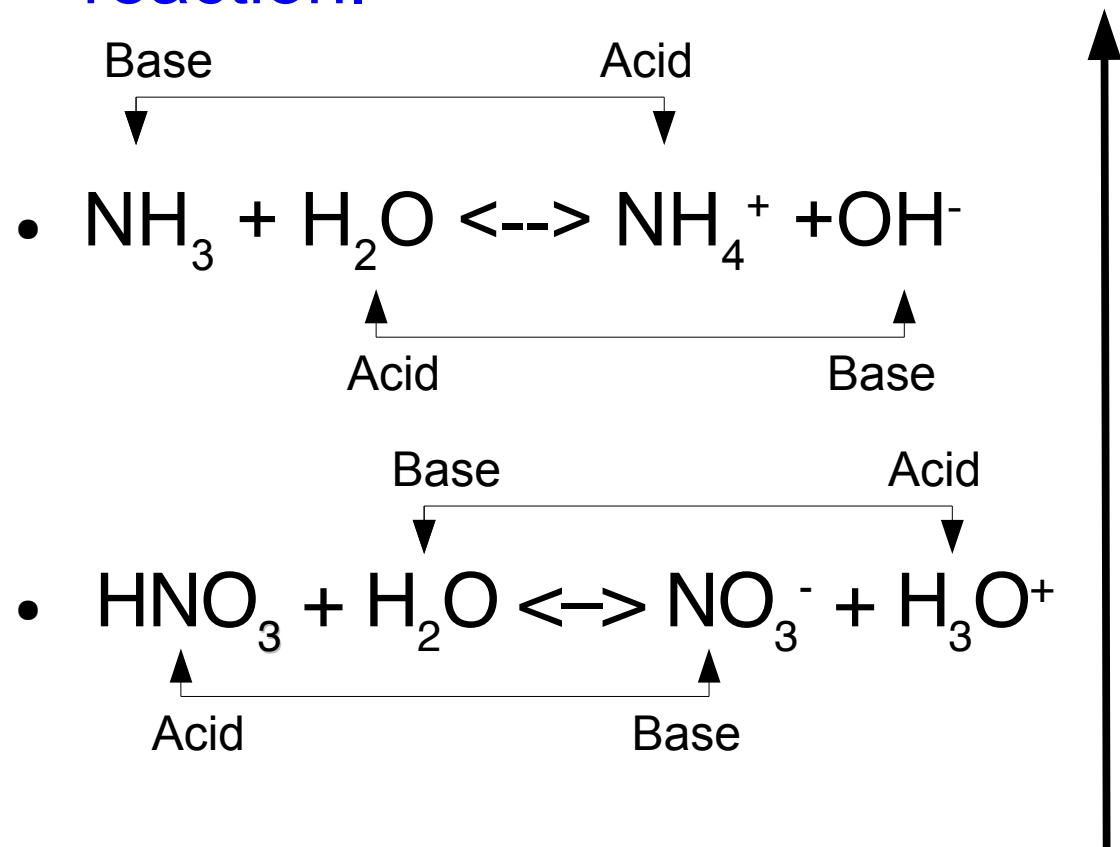- solubilities of solids (K_{sp})

- Complex ions

Brønsted-Lowry Model

- acid = a proton donor   • base = a proton acceptor
- $HNO_3(aq) + H_2O(aq) \longleftrightarrow NO_3^-(aq) + H_3O^+(aq)$

    acid   base

- $Na^+(aq) + OH^-(aq) + H_2O(aq) \longleftrightarrow Na^+(aq) + H_2O(aq) + OH^-(aq)$

           base   acid

Lewis Model (does not require water)

- acid = electron pair acceptor   • base = electron pair donor
- $H_3P: + Cu^{2+} \longleftrightarrow H_3P—Cu^{2+}$

  base   acid   coordinate covalent bond

- $H_3N: + H–O–H \longleftrightarrow H_3N\text{-}\text{-}H^+ + OH^-$

  base   acid

Conjugate Acid-Base Pairs

- Acids and bases which interconvert during an acid base reaction.

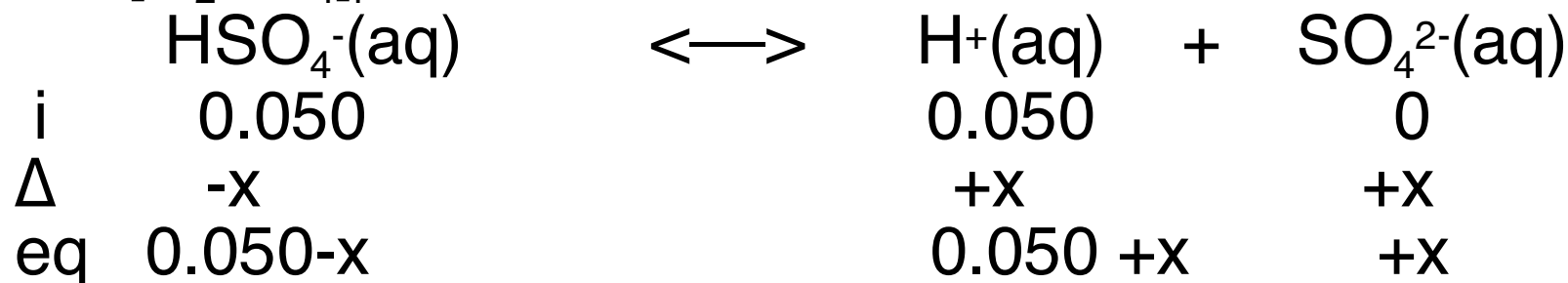$$\text{Base} \quad\quad\quad \text{Acid}$$

- $NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^-$

$$\text{Acid} \quad\quad\quad \text{Base}$$

$$\text{Base} \quad\quad\quad \text{Acid}$$

- $HNO_3 + H_2O \longleftrightarrow NO_3^- + H_3O^+$

$$\text{Acid} \quad\quad\quad \text{Base}$$

Chang Table 16.2

Bisulfate Equilibrium

$H_2SO_4(aq) <\!\!-\!\!-\!\!> H^+(aq) + HSO_4^-(aq)$ $K_{a1} >> 1$ like HNO_3
$HSO_4^-(aq) <\!\!-\!\!-\!\!> H^+(aq) + SO_4^{2-}(aq)$ $K_{a2} = 1.2 \times 10^{-2}$

Assume: $[H_2SO_4]_i = 0.050$ M

	$HSO_4^-(aq)$	$<\!\!-\!\!-\!\!>$	$H^+(aq)$	+	$SO_4^{2-}(aq)$
i	0.050		0.050		0
Δ	-x		+x		+x
eq	0.050-x		0.050 +x		+x
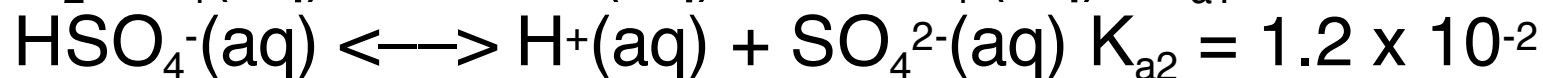
$=> 1.2 \times 10^{-2} = (0.050 + x)x/(0.050 -x)$

solve using quadratic: x = 0.0085 or -0.071(not possible).
So $[H^+] = 0.050 + 0.0085 = 0.059$ M
   $[HSO_4^-] = 0.050-x = 0.041$ M
   pH = -log[0.059] = 1.23

Carbonic Acid & Bicarbonate Equilibrium
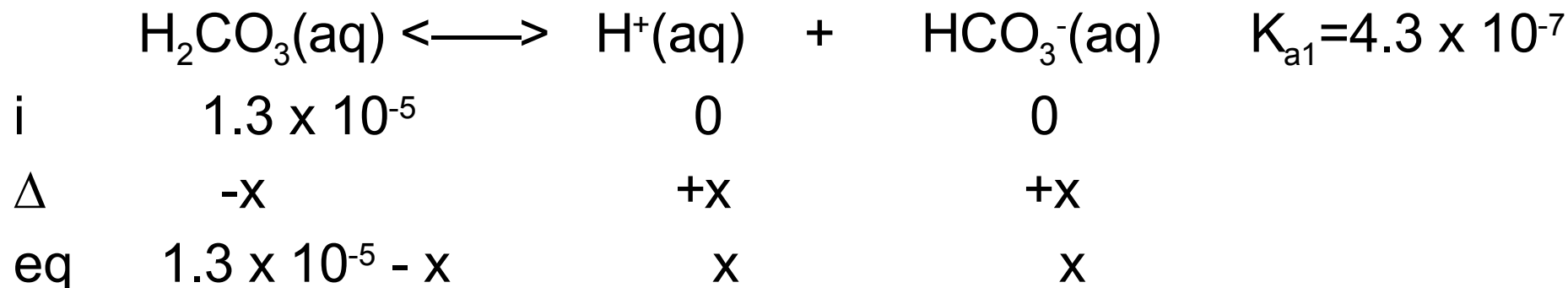
$$H_2CO_3(aq) \longleftrightarrow H^+(aq) + HCO_3^-(aq) \qquad K_{a1}=4.3 \times 10^{-7}$$

	$H_2CO_3(aq)$	$H^+(aq)$	$HCO_3^-(aq)$
i	1.3×10^{-5}	0	0
Δ	-x	+x	+x
eq	1.3×10^{-5} - x	x	x

$4.3 \times 10^{-7} = x^2/(1.3 \times 10^{-5} - x)$

$x^2 = 5.59e\text{-}12 - 4.3e\text{-}7x => x^2 + 4.3e\text{-}7x - 5.59e\text{-}12 = 0$

$[HCO_3^-] = [H_+] = x = (-4.3e\text{-}7/2)\pm(1/2)sqrt(4.3e\text{-}7^2 - 4(-5.59e\text{-}12))$

$= 2.2e\text{-}6$ or ~~2.6e-6~~.

Second equilibrium: $HCO_3^-(aq) \longleftrightarrow H^+(aq) + CO_3^{2-}(aq)$
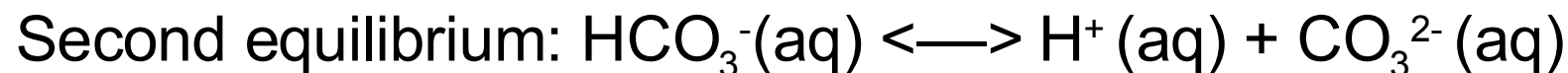
$K_{a2} = 4.7 \times 10^{-11}$

Carbonic Acid & Bicarbonate Equilibrium Second Equilibrium

$$HCO_3^-(aq) <\longrightarrow> H^+(aq) \quad + \quad CO_3^{2-}(aq) \qquad K_{a2} = 4.7 \times 10^{-11}$$

i	2.2e-6	2.2e-6	0
Δ	-x	+x	+x
eq	2.2e-6 - x	2.2e-6+ x	x
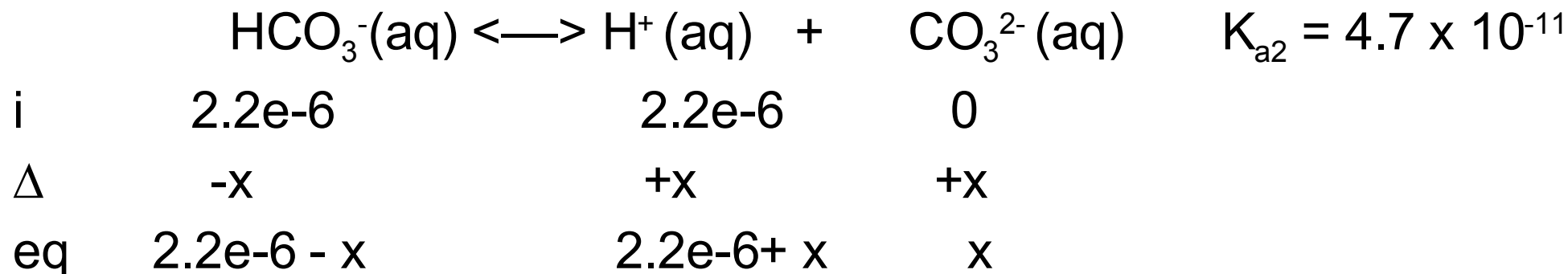
$$x(2.2e\text{-}6+x)/(2.2e\text{-}6\text{-}x) = 4.7x \ 10^{-11}$$

Try approx: $x(2.2e\text{-}6)/(2.2e\text{-}6) = x \approx 4.7 \times 10^{-11} <<< 2.2 \times 10^{-6}$
   => it won't change the concentrations appreciably

   => we're done. (If x were not so small we would have to iterate)

- You are not expected to iterate, but must show that second step change is small enough that you do not need to.
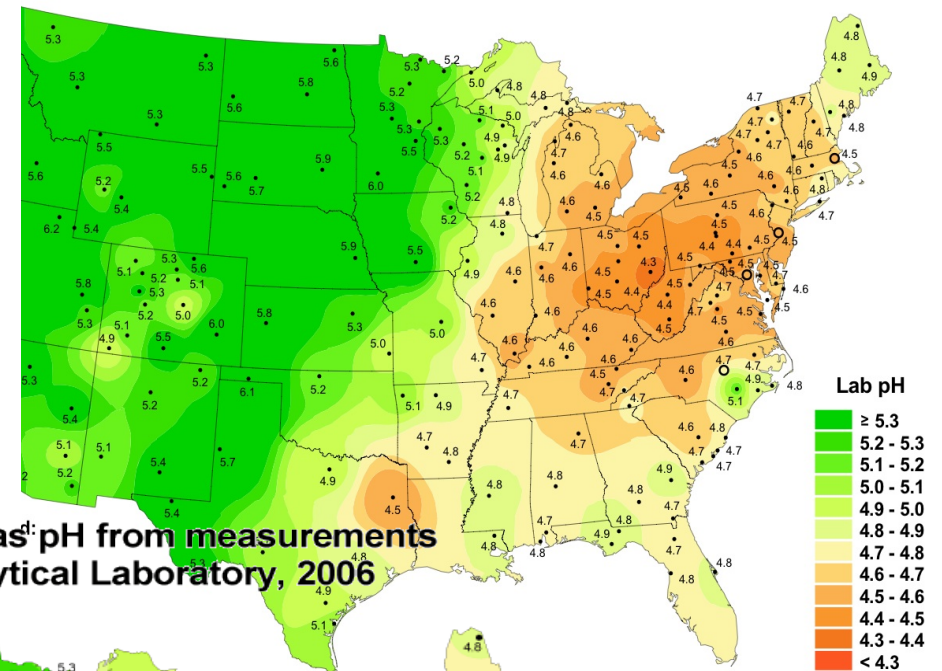
Acid Rain 1994-2006

Hydrogen ion concentration as pH from measurements made at the field laboratories, 1994
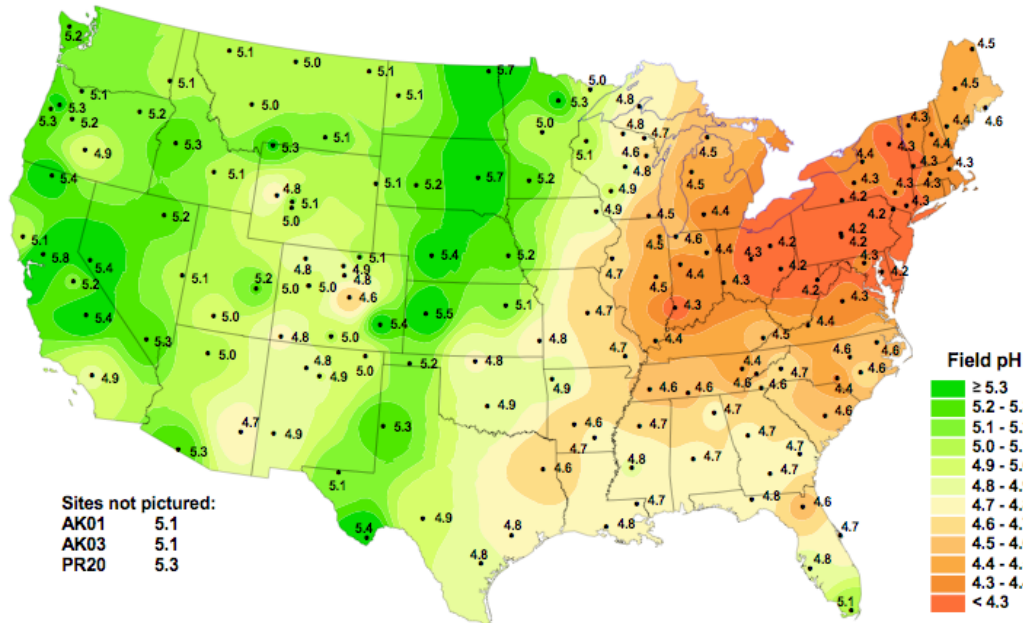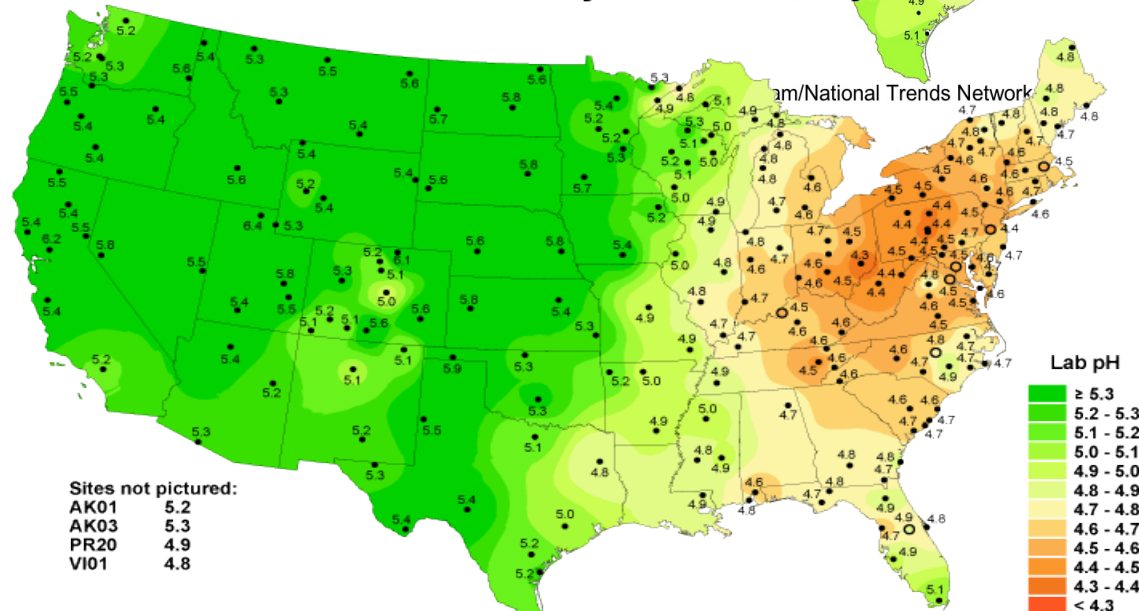
Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2005

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2006