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CEE 680: Water Chemistry

Lecture #6

Acids & Bases: Analytical Solutions

(Stumm & Morgan, Chapt.3)

(Benjamin, Chapt. 3; pg.131-150)

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Definitions

- Early
  - Acids
    - turns blue litmus red
    - tastes sour
    - neutralizes bases
    - reacts with active metals to evolve H_2
  - Bases
    - turns red litmus blue
    - tastes bitter
    - feels soapy

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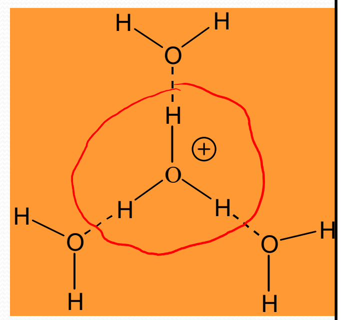
Definitions (cont.)

- Arrhenius (1887)
  - Acids
    - solutions which contain an excess of hydrogen ions
    - e.g., $HNO_3 = H^+ + NO_3^-$
      - H^+ doesn't exist free in solution
  - Bases
    - solutions which contain an excess of hydroxide ions



Definitions (cont.)

- Bronsted-Lowry (1923)
  - Acids: (proton donor)
    - any substance that can donate a proton to any other substance
  - Bases: (proton acceptor)
    - any substance that accepts a proton from any other substance

Acid$_1$	+	Base$_2$	=	Acid$_2$	+	Base$_1$
HNO_3	+	H_2O	=	H_3O^+	+	NO_3^-
$HOCl$	+	H_2O	=	H_3O^+	+	OCl^-
NH_4^+	+	H_2O	=	H_3O^+	+	NH_3
H_2O	+	H_2O	=	H_3O^+	+	OH^-

- Acid strength of a conjugate acid-base pair is measured relative to the other pair
- the stronger the acid, the weaker the conjugate base, and vice versa

Amphoteric

Definitions (cont.)

- Lewis
  - Acids
    - can accept and share a long pair of electrons
  - Bases
    - can donate and share a lone pair of electrons

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

A more general definition:
includes metal ions as acids

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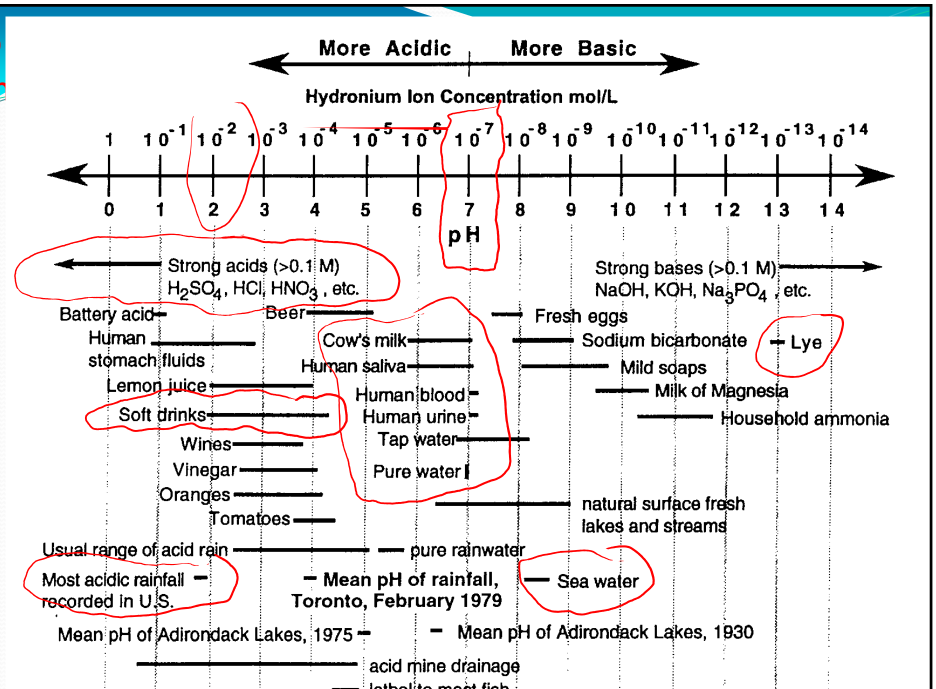


Alkalinity: a capacity factor

What are the limits of pH?

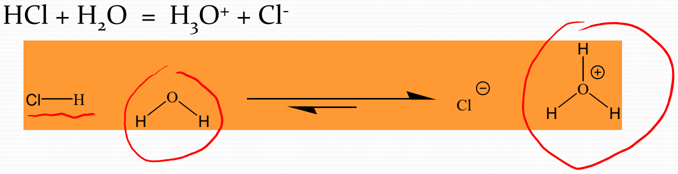
- How low can you go?
  - Volcanic lakes
    - Lake Katanuma in Japan; pH = 1.7
  - Hot springs
    - Near Ebeko Volcano in Russia; pH = -1.7
  - Acid mine drainage
    - Richmond mine near Redding CA, pH = -3.6

Nordstrom et al., 2000 [ES&T 34:254]

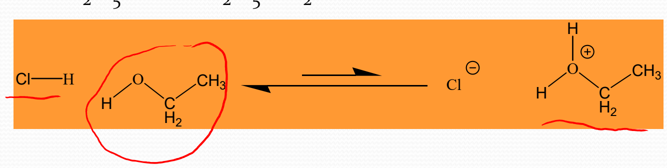
From: Brezonik & Arnold, 2011

Effect of proton acceptor

- Strong acid in water
  - $HCl + H_2O = H_3O^+ + Cl^-$

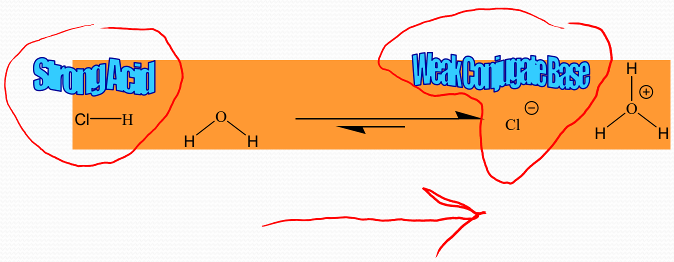


- Weak acid in organic solvent (ethanol)
  - $HCl + C_2H_5OH = C_2H_5OH_2^+ + Cl^-$



Acid/Conjugate Base

- Weak acids do not substantially donate a proton
  - e.g., H_2CO_3, HAc, H_2S, HOCl
- The stronger an acid is the weaker its conjugate base. The stronger a base is the weaker its conjugate acid



Acids & Bases

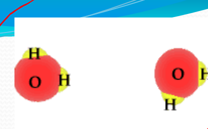
- pH of most mineral-bearing waters is 6 to 9. (fairly constant)
- pH and composition of natural waters is regulated by reactions of acids & bases
  - chemical reactions; mostly with minerals
    - carbonate rocks: react with CO_2 (an acid)
      - $CaCO_3 + CO_2 = Ca^{+2} + 2HCO_3^-$
    - other bases are also formed: NH_3, silicates, borate, phosphate
    - acids from volcanic activity: HCl, SO_2
  - Biological reactions: photosynthesis & resp.
  - Sillen: Ocean is result of global acid/base titration

$CO_2 + H_2O \rightleftharpoons H_2CO_3$

Acids & Bases (cont.)

- Equilibrium is rapidly established
  - proton transfer is very fast
- we call [H+] the Master Variable
  - because Protons react with so many chemical species, affect equilibria and rates
- Strength of acids & bases
  - strong acids have a substantial tendency to donate a proton. This depends on the nature of the acid as well as the base accepting the proton (often water).

Autodissociation of water



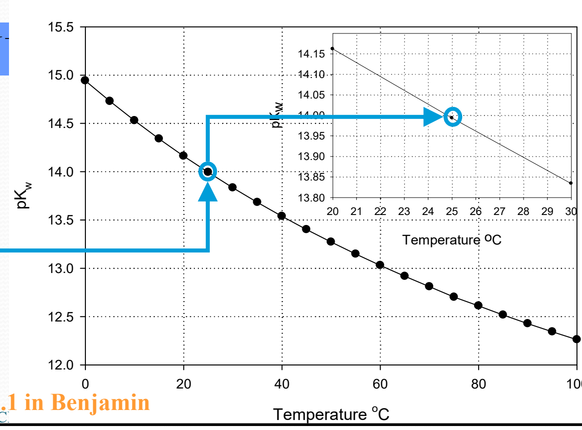
$$H_2O \leftrightarrow H^+ + OH^-$$

H_3O^+

- Actually donation of proton to neighboring water

$$2H_2O \leftrightarrow H_3O^+ + OH^-$$

$$K_w = \frac{\{H^+\}\{OH^-\}}{\{H_2O\}} \approx \{H^+\}\{OH^-\} \approx 10^{-14} @ 25^oC$$



See Table 3.1 in Benjamin

Mathematical Expression of Acid/Base Strength

- Equilibrium constant
  - acids: $HA = H^+ + A^-$
    - $HCl + H_2O = H_3O^+ + Cl^-$
    - $HCl = H^+ + Cl^-$
  - Bases: $B + H_2O = BH^+ + OH^-$
    - $NH_3 + H_2O = NH_4^+ + OH^-$

$$K_a = \frac{[H^+][Cl^-]}{[HCl]} \approx 10^3$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 10^{-4.76}$$

Relationship between K_a and K_b

- For the NH_3/NH_4^+ pair
  - $NH_4^+ = NH_3 + H^+$
  - $NH_3 + H_2O = NH_4^+ + OH^-$
- combining

$$K_a = \frac{[H^+][NH_3]}{[NH_4^+]} = 10^{-9.24}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 10^{-4.76}$$

$$K_aK_b = \left(\frac{[H^+][NH_3]}{[NH_4^+]}\right)\left(\frac{[NH_4^+][OH^-]}{[NH_3]}\right) = 10^{-9.24}10^{-4.76}$$

$$K_aK_b = [H^+][OH^-] = 10^{-14.00}$$ **$=K_w$**

See Table 3.1 (pg.94) for values of K_w at various pHs

NAME	EQUILIBRIA	pKa
Perchloric acid	$HClO_4 = H^+ + ClO_4^-$	-7 STRONG
Hydrochloric acid	$HCl = H^+ + Cl^-$	-3
Sulfuric acid	$H_2SO_4 = H^+ + HSO_4^-$	-3 (&2) ACIDS
Nitric acid	$HNO_3 = H^+ + NO_3^-$	-0
Hydronium ion	$H_3O^+ = H^+ + H_2O$	0
Trichloroacetic acid	$CCl_3COOH = H^+ + CCl_3COO^-$	0.70
Iodic acid	$HIO_3 = H^+ + IO_3^-$	0.8
Dichloroacetic acid	$CHCl_2COOH = H^+ + CHCl_2COO^-$	1.48
Bisulfate ion	$HSO_4^- = H^+ + SO_4^{-2}$	2
Phosphoric acid	$H_3PO_4 = H^+ + H_2PO_4^-$	2.15 (&7.2,12.3)
Ferric ion	$Fe(H_2O)_6^{+3} = H^+ + Fe(OH)(H_2O)_5^{+2}$	2.2 (&4.6)
Chloroacetic acid	$CH_2ClCOOH = H^+ + CH_2ClCOO^-$	2.85
o-Phthalic acid	$C_6H_4(COOH)_2 = H^+ + C_6H_4(COOH)COO^-$	2.89 (&5.51)
Citric acid	$C_3H_5O(COOH)_3 = H^+ + C_3H_5O(COOH)_2COO^-$	3.14 (&4.77,6.4)
Hydrofluoric acid	$HF = H^+ + F^-$	3.2
Formic Acid	$HCOOH = H^+ + HCOO^-$	3.75
Aspartic acid	$C_2H_6N(COOH)_2 = H^+ + C_2H_6N(COOH)COO^-$	3.86 (&9.82)
m-Hydroxybenzoic acid	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	4.06 (&9.92)
Succinic acid	$C_2H_4(COOH)_2 = H^+ + C_2H_4(COOH)COO^-$	4.16 (&5.61)
p-Hydroxybenzoic acid	$C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$	4.48 (&9.32)
Nitrous acid	$HNO_2 = H^+ + NO_2^-$	4.5
Ferric Monohydroxide	$FeOH(H_2O)_5^{+2} = H^+ + Fe(OH)_2(H_2O)_4^+$	4.6
Acetic acid	$CH_3COOH = H^+ + CH_3COO^-$	4.75
Aluminum ion	$Al(H_2O)_6^{+3} = H^+ + Al(OH)(H_2O)_5^{+2}$	4.8

NAME	FORMULA	pKa
Propionic acid	$C_2H_5COOH = H^+ + C_2H_5COO^-$	4.87
Carbonic acid	$H_2CO_3 = H^+ + HCO_3^-$	6.35 (&10.33)
Hydrogen sulfide	$H_2S = H^+ + HS^-$	7.02 (&13.9)
Dihydrogen phosphate	$H_2PO_4^- = H^+ + HPO_4^{-2}$	7.2
Hypochlorous acid	$HOCl = H^+ + OCl^-$	7.5
Copper ion	$Cu(H_2O)_6^{+2} = H^+ + CuOH(H_2O)_5^+$	8.0
Zinc ion	$Zn(H_2O)_6^{+2} = H^+ + ZnOH(H_2O)_5^+$	8.96
Boric acid	$B(OH)_3 + H_2O = H^+ + B(OH)_4^-$	9.2 (&12.7,13.8)
Ammonium ion	$NH_4^+ = H^+ + NH_3$	9.24
Hydrocyanic acid	$HCN = H^+ + CN^-$	9.3
p-Hydroxybenzoic acid	$C_6H_4(OH)COO^- = H^+ + C_6H_4(O)COO^{-2}$	9.32
Orthosilicic acid	$H_4SiO_4 = H^+ + H_3SiO_4^-$	9.86 (&13.1)
Phenol	$C_6H_5OH = H^+ + C_6H_5O^-$	9.9
m-Hydroxybenzoic acid	$C_6H_4(OH)COO^- = H^+ + C_6H_4(O)COO^{-2}$	9.92
Cadmium ion	$Cd(H_2O)_6^{+2} = H^+ + CdOH(H_2O)_5^+$	10.2
Bicarbonate ion	$HCO_3^- = H^+ + CO_3^{-2}$	10.33
Magnesium ion	$Mg(H_2O)_6^{+2} = H^+ + MgOH(H_2O)_5^+$	11.4
Monohydrogen phosphate	$HPO_4^{-2} = H^+ + PO_4^{-3}$	12.3
Calcium ion	$Ca(H_2O)_6^{+2} = H^+ + CaOH(H_2O)_5^+$	12.5
Trihydrogen silicate	$H_3SiO_4^- = H^+ + H_2SiO_4^{-2}$	12.6
Bisulfide ion	$HS^- = H^+ + S^{-2}$	13.9
Water	$H_2O = H^+ + OH^-$	14.00
Ammonia	$NH_3 = H^+ + NH_2^-$	23
Hydroxide	$OH^- = H^+ + O^{-2}$	24
Methane	$CH_4 = H^+ + CH_3^-$	34

Analytical Solutions

- Basic Approach
  - combine mass balances with thermodynamic equilibria
  - consider exact solutions, as well as approximations
  - similar approaches used for other topics in CEE 680
- Four principal steps
  - 1. List all species present
  - 2. List all independent equations
    - equilibria, mass balances, proton balance (or electroneutrality equation)
  - 3. Combine equations and solve for proton
  - 4. Solve for other species

General Example

- 1. List all species present
  - H^+, OH^-, HA, A^- Four total
- 2. List all independent equations
  - equilibria
    - $K_a = [H^+][A^-]/[HA]$ (1)
    - $K_w = [H^+][OH^-]$ (2)
  - mass balances
    - $[HA]+[A^-] = C$ (formal or "analytical" concentration) (3)
  - proton balance (or electroneutrality equation)
    - PBE: Σ(proton rich species) = Σ(proton poor species)
    - ENE: Σ(cationic species) = Σ(anionic species)
    - $[H^+]=[OH^-]+[A^-]$ (4)

General Example (cont.)

- 3. Combine equations and solve for proton
  - use PBE or ENE and eliminate non-H^+ species by substituting in the other equations
- 4. Solve for other species

Acetic Acid Example

- What is the pH and solution composition when you add 1 mM acetic acid to 1 liter of water
  - The Reaction: $HAc \leftrightarrow H^+ + Ac^-$
  - The overall Gibbs Free Energy: $$\Delta G^o = \sum \nu_i \Delta G_f^o = \Delta G^o_{f-Ac^-} + \Delta G^o_{f-H^+} - \Delta G^o_{f-HAc} = -88.29 - 0 - (-94.8) = +6.51 Kcal$$
  - Recall: $$\Delta G^o = -RT \ln K = -2.303 RT \log K$$
  - at 25°C:
  - so for this problem: $$\Delta G^o = -2.303(0.001987)(298.13)\log K = -1.364 \log K$$

$$\log K = -\Delta G^o / 1.364 = -6.51/1.364 = -4.77$$

Acetic Acid Example (cont.)

- 1. List all species present
  - H^+, OH^-, HAc, Ac^- (Four total)
- 2. List all independent equations
  - equilibria
    - $K_a = [H^+][Ac^-]/[HAc] = 10^{-4.77}$ (1)
    - $K_w = [H^+][OH^-] = 10^{-14}$ (2)
  - mass balances
    - $C = [HAc]+[Ac^-] = 10^{-3}$ (3)
  - proton balance: Σ(proton rich species) = Σ(proton poor species)
    - HAc → $[Ac^-]$; H_2O → $[H^+]$, $[OH^-]$
    - $[H^+] = [OH^-] + [Ac^-]$ (4)

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HAc Example (cont.)

- 3. Combine equations and solve for H^+
  - (4) $[H^+] = [OH^-] + [Ac^-]$
  - (2+4) $[H^+] = K_W/[H^+] + [Ac^-]$
  - (1+2+3+4) $[H^+] = K_W/[H^+] + K_aC/\{K_a+[H^+]\}$
    - $[H^+]^2 = K_W + K_aC[H^+]/\{K_a+[H^+]\}$
    - $K_a[H^+]^2 + [H^+]^3 = K_WK_a + K_w[H^+] + K_aC[H^+]$
  - $\mathbf{H^+]^3 + K_a[H^+]^2 - \{K_w + K_aC\}[H^+] - K_WK_a = 0}$
- 4. Solve for other species

(2) $K_w = [H^+][OH^-]$
$[OH^-] = K_w/[H^+]$

(3) $C = [HAc]+[Ac^-]$
$[HAc] = C-[Ac^-]$

(1) $K_a = [H^+][Ac^-]/[HAc]$

(1+3)
$K_a = [H^+][Ac^-]/\{C-[Ac^-]\}$
$K_aC-K_a[Ac^-]= [H^+][Ac^-]$
$K_aC=[Ac^-]\{K_a+[H^+]\}$
$[Ac^-]=K_aC/\{K_a+[H^+]\}$

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Exact Solution

- Exact solution: pH = 3.913
  - $[H^+] = 1.22 \times 10^{-4}$
  - $[OH^-] = 8.19 \times 10^{-11}$
  - $[Ac^-] = 1.22 \times 10^{-4}$
  - $[HAc] = 8.78 \times 10^{-4}$

$[OH^-] = K_w/[H^+]$

$[Ac^-]=K_aC/\{K_a+[H^+]\}$

$[HAc] = C-[Ac^-]$

- To next lecture