Updated: 3 February 2020

Print version

CEE 680: Water Chemistry

Lecture #8

Acids & Bases: Analytical Solutions with simplifying assumptions II

(Stumm & Morgan, Chapt.3)

(Benjamin, Chapt. 3)

Question

- What is the pH of a 10^{-3} M solution of HCl?
  - A. 7
  - B. 3
  - C. 0
  - D. 9
  - E. Impossible to tell
  - F. None of the above

Hydrochloric Acid Example: 10^{-3}M

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

HCl, H_2O

- $[H^+] = [OH^-] + [Cl^-]$ (4)

HCl: Exact Solution

$$[H^+]^3 + K_a[H^+]^2 - \{K_w + K_aC\}[H^+] - K_WK_a = 0$$

- Exact solution: pH = 3.0000004
  - $[H^+] = 1.00 \times 10^{-3}$
  - $[OH^-] = 1.00 \times 10^{-11}$
  - $[Cl^-] = 1.00 \times 10^{-3}$
  - $[HCl] = 1.00 \times 10^{-11}$

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

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

$[HCl] = C-[Cl^-]$

HCl example (cont.)

- Can we simplify?

$$[H^+]^3 + K_a[H^+]^2 - K_w[H^+] - K_aC[H^+] - K_wK_a = 0$$

1.000E-9	0.001000	1.000E-17	0.001000	1.000E-11	0

- What about the PBE?
  - $[H^+] = [OH^-] + [Cl^-]$
  - ~0
- And the MBE too?
  - $C = [HCl] + [Cl^-]$
  - ~0

Simplified HCl Example

- 3. Use simplified PBE & MBE
  - (4) $[H^+] = [OH^-] + [Cl^-]$
  - $[H^+] \approx [Cl^-]$ Assumes $[H^+] >> [OH^-]$
  - (3) $C \approx [HCl] + [Cl^-]$, $C \approx [Cl^-]$, $[Cl^-] \approx C$ Assumes $[HCl] << [Cl^-]$
  - (3+4) $[H^+] = C$
  - $[H^+] = C$
- 4. Solve for other species

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

(1) $K_a = [H^+][Cl^-]/[HCl]$

(1+3) $K_a = [H^+]\,C / [HCl]$, $[HCl] = [H^+]\,C / K_a$

Assumptions

- Use both & Compare answers
  - Exact: pH = 3.0000004
  - Simplified: pH = 3.0000000
- Use simplified equation, and check assumptions!
  - $[OH^-] << [H^+]$
    - $1.00 \times 10^{-11} << 1.00 \times 10^{-3}$ yes!
  - $[Cl^-] >> [HCl]$
    - $1.00 \times 10^{-3} >> 1.00 \times 10^{-11}$ yes!

Simplified HCl Example for low C

- 3. Use simplified PBE & MBE
  - (4) $[H^+] = [OH^-] + [Cl^-]$
  - (2+3+4)
    - $[H^+] = K_W/[H^+] + [Cl^-]$
    - $[H^+] = K_W/[H^+] + C$
    - $[H^+]^2 - C[H^+] - K_w = 0$
    - $[H^+] = \{C \pm (C^2 + 4K_w)^{0.5}\}/2$
- 4. Solve for other species

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

(3) $C = [HCl] + [Cl^-]$
$C \approx [Cl^-]$
$[Cl^-] \approx C$

Assumes $[HCl] << [Cl^-]$

(1) $K_a = [H^+][Cl^-]/[HCl]$

(1+3)
$K_a = [H^+] C / [HCl]$
$[HCl] = [H^+] C / K_a$

Calculation for 2nd HCl example

- For a 10^{-7} solution of HCl
  - pH = 6.79
  - Check Assumptions
    - $[Cl^-] \approx C = 10^{-7}$
    - $[HCl] = [H^+]\, C / K_a$
      - $=10^{-6.79}10^{-7}/10^{+3}=10^{-16.79}$
    - $[Cl^-] >> [HCl]$, yes!

$$[H^+] = \frac{C \pm \sqrt{C^2 + 4K_w}}{2} = \frac{10^{-7} \pm \sqrt{10^{-14} + 4x10^{-14}}}{2} = \frac{1+\sqrt{5}}{2}10^{-7} = 1.62x10^{-7}$$

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

Hypochlorous Acid Example

- 1. List all species present
  - H^+, OH^-, HOCl, OCl^- Four total
- 2. List all independent equations
  - equilibria
    - $K_a = [H^+][OCl^-]/[HOCl] = 10^{-7.6}$ (1)
    - $K_w = [H^+][OH^-] = 10^{-14}$ (2)
  - mass balances
    - $C = [HOCl]+[OCl^-] = 10^{-6}$ (3)
  - proton balance: Σ(proton rich species) = Σ(proton poor species)

HOCl

H_2O

- $[H^+] = [OH^-] + [OCl^-]$ (4)

HOCl Example for low C

- 3. Combine equations and solve for H^+
- 4. $[H^+] = [OH^-] + [OCl^-]$
- 2+4: $[H^+] = K_W/[H^+] + [OCl^-]$
- $[H^+] = K_W/[H^+] + K_aC/[H^+]$
- $[H^+]^2 = K_W + K_aC$
- 1+2+3+4: $[H^+] = (K_aC + K_W)^{0.5}$
- 4. Solve for other species

2: $K_w = [H^+][OH^-]$, $[OH^-] = K_w/[H^+]$

3: $C = [HOCl]+[OCl^-]$, $[HOCl] \approx C$

Assumes $[HOCl] >> [OCl^-]$

1: $K_a = [H^+][OCl^-]/[HOCl]$, $K_a = [H^+][OCl^-]/C$

1+3: $[OCl^-] = K_aC/[H^+]$

Calculation for HOCl example

- For a 10^{-6} solution of HOCl
  - pH = 6.73
  - Check Assumptions
    - $[HOCl] \approx C = 10^{-6}$
    - $[OCl^-] = K_aC/[H^+]$
      - $= 10^{-7.6}10^{-6}/10^{-6.73} = 10^{-6.87}$
    - $[HOCl] >> [OCl^-]$, OK

$$[H^+] = \sqrt{K_aC + K_w}$$
$$= \sqrt{10^{-7.6}10^{-6} + 10^{-14}}$$
$$= \sqrt{3.51x10^{-14}}$$
$$= 1.87x10^{-7}$$

In-class Practice

- 10^{-4}M Hydrofluoric Acid
  - JQ & Ian
  - Godfrey
- 10^{-2}M Phenol
  - Cielo, Alvin, Chris
  - Hezron
- 10^{-3}M Carbonic Acid
  - Laura, Isaac, Bridgette
  - Naeldi
- 10^{-4}M Sulfuric Acid
  - Niall

NAME	EQUILIBRIA	pK_a	
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	pK_a
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

15

- To next lecture

DAR