

CEE 680: Water Chemistry

Lecture #8

Acids & Bases: Analytical Solutions with
simplifying assumptions II
(Stumm & Morgan, Chapt.3)

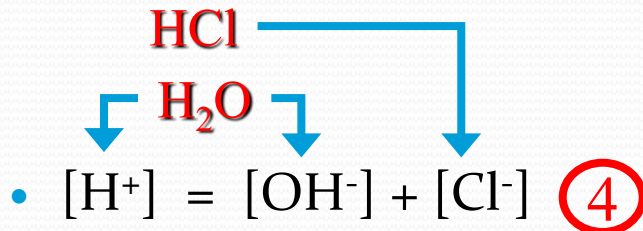
(Benjamin, Chapt. 3)

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
 - $K_a = [\text{H}^+][\text{Cl}^-]/[\text{HCl}] = 10^{+3}$ **①**
 - $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$ **②**
 - mass balances
 - $C = [\text{HCl}] + [\text{Cl}^-] = 10^{-3}$ **③**
 - proton balance: $\Sigma(\text{proton rich species}) = \Sigma(\text{proton poor species})$



HCl: Exact Solution

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

- Exact solution: $\text{pH} = 3.00000004$

- $[\text{H}^+] = 1.00 \times 10^{-3}$

- $[\text{OH}^-] = 1.00 \times 10^{-11}$

- $[\text{Cl}^-] = 1.00 \times 10^{-3}$

- $[\text{HCl}] = 1.00 \times 10^{-11}$

$$[\text{OH}^-] = K_w/[\text{H}^+]$$






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

$$[\text{HCl}] = C - [\text{Cl}^-]$$

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 $[H^+] \gg [OH^-]$

③ $C \approx [HCl] + [Cl^-]$

$C \approx [Cl^-]$

$[Cl^-] \approx C$

Assumes $[HCl] \ll [Cl^-]$

3+4

• $[H^+] = C$

• $[H^+] = C$

- 4. Solve for other species

① $K_a = [H^+][Cl^-]/[HCl]$

①+③ $\begin{cases} K_a = [H^+] C / [HCl] \\ [HCl] = [H^+] C / K_a \end{cases}$

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

Assumptions

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

Simplified HCl Example for low C

- 3. Use simplified PBE & MBE

$$\textcircled{2} \begin{cases} K_w = [\text{H}^+][\text{OH}^-] \\ [\text{OH}^-] = K_w/[\text{H}^+] \end{cases}$$

$$\textcircled{4} \bullet [\text{H}^+] = [\text{OH}^-] + [\text{Cl}^-]$$

$$\textcircled{3} \begin{cases} C = [\text{HCl}] + [\text{Cl}^-] \\ C \approx [\text{Cl}^-] \\ [\text{Cl}^-] \approx C \end{cases}$$

Assumes $[\text{HCl}] \ll [\text{Cl}^-]$

2+3+4

$$\begin{cases} \bullet [\text{H}^+] = K_w/[\text{H}^+] + [\text{Cl}^-] \\ \bullet [\text{H}^+] = K_w/[\text{H}^+] + C \\ \bullet [\text{H}^+]^2 - C[\text{H}^+] - K_w = 0 \\ \bullet [\text{H}^+] = \{C \pm (C^2 + 4K_w)^{0.5}\}/2 \end{cases}$$

- 4. Solve for other species

$$\textcircled{1} K_a = [\text{H}^+][\text{Cl}^-]/[\text{HCl}]$$

$$\textcircled{1+3} \begin{cases} K_a = [\text{H}^+] C / [\text{HCl}] \\ [\text{HCl}] = [\text{H}^+] C / K_a \end{cases}$$

Calculation for 2nd HCl example

- For a 10^{-7} solution of HCl

- $\text{pH} = 6.79$

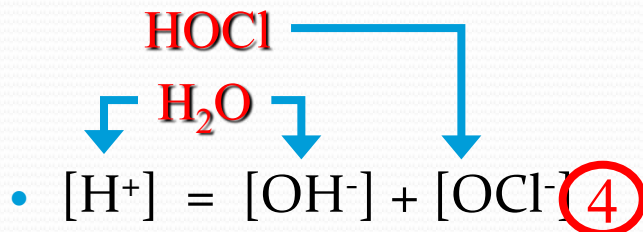
- Check Assumptions

- $[\text{Cl}^-] \approx C = 10^{-7}$
- $[\text{HCl}] = [\text{H}^+] C / K_a$
 - $= 10^{-6.79} 10^{-7} / 10^{+3} = 10^{-16.79}$
- $[\text{Cl}^-] \gg [\text{HCl}]$, yes!

$$\begin{aligned} [\text{H}^+] &= \frac{C \pm \sqrt{C^2 + 4K_w}}{2} \\ &= \frac{10^{-7} \pm \sqrt{10^{-14} + 4 \times 10^{-14}}}{2} \\ &= \frac{1 + \sqrt{5}}{2} 10^{-7} \\ &= 1.62 \times 10^{-7} \end{aligned}$$

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: $\Sigma(\text{proton rich species}) = \Sigma(\text{proton poor species})$



HOCl Example for low C

- 3. Combine equations and solve for H⁺

$$\textcircled{2} \quad K_w = [\text{H}^+][\text{OH}^-]$$

$$[\text{OH}^-] = K_w / [\text{H}^+]$$

$$\textcircled{4} \quad [\text{H}^+] = [\text{OH}^-] + [\text{OCl}^-]$$

$$\textcircled{2+4} \quad [\text{H}^+] = K_w / [\text{H}^+] + [\text{OCl}^-]$$

$$[\text{H}^+] = K_w / [\text{H}^+] + K_a C / [\text{H}^+]$$

$$[\text{H}^+]^2 = K_w + K_a C$$

$$[\text{H}^+] = (K_a C + K_w)^{0.5}$$

- 4. Solve for other species

$$\textcircled{3} \quad C = [\text{HOCl}] + [\text{OCl}^-]$$

$$[\text{HOCl}] \approx C$$

Assumes $[\text{HOCl}] \gg [\text{OCl}^-]$

$$\textcircled{1} \quad K_a = [\text{H}^+][\text{OCl}^-] / [\text{HOCl}]$$

$$K_a = [\text{H}^+][\text{OCl}^-] / C$$

$$\textcircled{1+3}$$

$$[\text{OCl}^-] = K_a C / [\text{H}^+]$$

Calculation for HOCl example

- For a 10^{-6} solution of HOCl

- $\text{pH} = 6.73$

- Check Assumptions

- $[\text{HOCl}] \approx C = 10^{-6}$
- $[\text{OCl}^-] = K_a C / [\text{H}^+]$
 - $= 10^{-7.6} 10^{-6} / 10^{-6.73} = 10^{-6.87}$
- $[\text{HOCl}] \gg [\text{OCl}^-]$, OK

$$\begin{aligned} [\text{H}^+] &= \sqrt{K_a C + K_w} \\ &= \sqrt{10^{-7.6} 10^{-6} + 10^{-14}} \\ &= \sqrt{3.51 \times 10^{-14}} \\ &= 1.87 \times 10^{-7} \end{aligned}$$

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	$\text{HClO}_4 = \text{H}^+ + \text{ClO}_4^-$	-7 STRONG
Hydrochloric acid	$\text{HCl} = \text{H}^+ + \text{Cl}^-$	-3
Sulfuric acid	$\text{H}_2\text{SO}_4 = \text{H}^+ + \text{HSO}_4^-$	-3 (&2) ACIDS
Nitric acid	$\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$	-0
Hydronium ion	$\text{H}_3\text{O}^+ = \text{H}^+ + \text{H}_2\text{O}$	0
Trichloroacetic acid	$\text{CCl}_3\text{COOH} = \text{H}^+ + \text{CCl}_3\text{COO}^-$	0.70
Iodic acid	$\text{HIO}_3 = \text{H}^+ + \text{IO}_3^-$	0.8
Dichloroacetic acid	$\text{CHCl}_2\text{COOH} = \text{H}^+ + \text{CHCl}_2\text{COO}^-$	1.48
Bisulfate ion	$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$	2
Phosphoric acid	$\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$	2.15 (&7.2, 12.3)
Ferric ion	$\text{Fe}(\text{H}_2\text{O})_6^{3+} = \text{H}^+ + \text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}$	2.2 (&4.6)
Chloroacetic acid	$\text{CH}_2\text{ClCOOH} = \text{H}^+ + \text{CH}_2\text{ClCOO}^-$	2.85
o-Phthalic acid	$\text{C}_6\text{H}_4(\text{COOH})_2 = \text{H}^+ + \text{C}_6\text{H}_4(\text{COOH})\text{COO}^-$	2.89 (&5.51)
Citric acid	$\text{C}_3\text{H}_5\text{O}(\text{COOH})_3 = \text{H}^+ + \text{C}_3\text{H}_5\text{O}(\text{COOH})_2\text{COO}^-$	3.14 (&4.77, 6.4)
Hydrofluoric acid	$\text{HF} = \text{H}^+ + \text{F}^-$	3.2
Formic Acid	$\text{HCOOH} = \text{H}^+ + \text{HCOO}^-$	3.75
Aspartic acid	$\text{C}_2\text{H}_6\text{N}(\text{COOH})_2 = \text{H}^+ + \text{C}_2\text{H}_6\text{N}(\text{COOH})\text{COO}^-$	3.86 (&9.82)
m-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COOH} = \text{H}^+ + \text{C}_6\text{H}_4(\text{OH})\text{COO}^-$	4.06 (&9.92)
Succinic acid	$\text{C}_2\text{H}_4(\text{COOH})_2 = \text{H}^+ + \text{C}_2\text{H}_4(\text{COOH})\text{COO}^-$	4.16 (&5.61)
p-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COOH} = \text{H}^+ + \text{C}_6\text{H}_4(\text{OH})\text{COO}^-$	4.48 (&9.32)
Nitrous acid	$\text{HNO}_2 = \text{H}^+ + \text{NO}_2^-$	4.5
Ferric Monohydroxide	$\text{FeOH}(\text{H}_2\text{O})_5^{2+} + \text{H}^+ + \text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4^+$	4.6
Acetic acid	$\text{CH}_3\text{COOH} = \text{H}^+ + \text{CH}_3\text{COO}^-$	4.75
Aluminum ion	$\text{Al}(\text{H}_2\text{O})_6^{3+} = \text{H}^+ + \text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$	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

- To next lecture

DAR