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CEE 680: Water Chemistry

Lecture #7

Acids & Bases: Analytical Solutions with simplifying assumptions I

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Question

- What is the pH of a liter of water to which you add 1 mL of White Vinegar?
  A. 5.89
  B. 4.75
  C. 3.91
  D. 3.00
  E. Impossible to tell
  F. None of the above

Substance	By mass	Molarity
Glacial acetic acid	99.7%	17.4
White Vinegar	5.7%	1.0

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

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

R=1.987 x10^{-3} kcal/mole °K

Acetic Acid Example

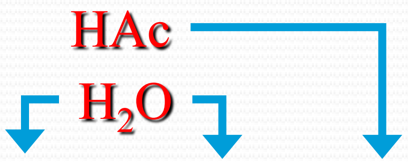
- What is the pH and solution composition when you add 1 mM acetic acid to 1 liter of water
  - The Reaction:
    $$HAc \leftrightarrow H^{+} + Ac^{-}$$
  - The overall Gibbs Free Energy:
    $$\Delta G^{o} = \sum \nu_i \Delta G_f^{o}$$
    $$= \Delta G^{o}_{f-Ac^-} + \Delta G^{o}_{f-H^+} - \Delta G^{o}_{f-HAc}$$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

We will explain this further in Lecture #11

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

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)



- $[H^+] = [OH^-] + [Ac^-]$ 4

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

Exact Solution

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

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

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

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

Exact Solution: Is it really necessary?

- Can we simplify?

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

1.82E-12	2.53E-13	1.22E-18	2.07E-12	1.70E-19	0

- What about the PBE?
  - $[H^+] = [OH^-] + [Ac^-]$

    $[OH^-] \rightarrow \sim 0$

Simplified HAc Example

- 3. Use simplified PBE & solve for H^+
  - (4) $[H^+] = [OH^-] + [Ac^-]$
  - $[H^+] \approx [Ac^-]$ **Assumes $[H^+] >> [OH^-]$**

(1+3+4)
- $[H^+] \approx K_aC/\{K_a+[H^+]\}$
  - $[H^+]^2 \approx K_aC[H^+]/\{K_a+[H^+]\}$
  - $K_a[H^+]^2 + [H^+]^3 \approx K_aC[H^+]$
- $[H^+]^2 + K_a[H^+] - K_aC \approx 0$

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

Simplified solution #1

- Exact solution: pH = 3.9132779
  - $[H^+]$ = 1.22 x 10^{-4}
  - $[OH^-]$ = 8.19 x 10^{-11}
  - $[Ac^-]$ = 1.22 x 10^{-4}
  - $[HAc]$ = 8.78 x 10^{-4}

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

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

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

Same as exact to at least 3 significant figures!

So how do we know when to use a simplified method?

- Use both & Compare answers
  - Exact: pH = 3.9132777
  - Simplified: pH = 3.9132779
- Use simplified equation, and check assumptions!
  - $[OH^-] << [H^+]$
  - $8.19 \times 10^{-11} << 1.22 \times 10^{-4}$
    - yes!

Types of Simplifying Assumptions for Acids

- Basis: one additive term is negligible
  - MBE: C = [HA] + [A]
  - PBE: $[H^+]$ = [A] + [OH]

0 (strong acid)

0 (weak acid)

0 (acidic solution)

- Combinations
  - Acidic Solution: $[OH^-] << [H^+]$
  - Weak Acid: [HA] >> [A]
  - Strong Acid: [A] >> [HA]
  - Weak Acid & Acidic Solution
  - Strong Acid & Acidic Solution

Simplified HAc Example #2

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

- 3. Use simplified PBE & MBE
  - (4) $[H^+] = [OH^-] + [Ac^-]$
  - $[H^+] \approx [Ac^-]$ **Assumes $[H^+] >> [OH^-]$**

(1+3+4)
- $[H^+] \approx K_aC/[H^+]$
  - $[H^+]^2 \approx K_aC$
- $[H^+] \approx (K_aC)^{0.5}$

(3) $C = [HAc]+[Ac^-]$
$[HAc] \approx C$
Assumes $[HAc] >> [Ac^-]$

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

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

- 4. Solve for other species

Simplified solution #2

- Solution: pH = 3.885
  - $[H^+] = 1.3 \times 10^{-4}$
  - $[OH^-] = 7.7 \times 10^{-11}$
  - $[Ac^-] = 1.3 \times 10^{-4}$
  - $[HAc] = 8.7 \times 10^{-4}$

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

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

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

Assumptions

- Use both & Compare answers
  - Exact: pH = 3.9132777
  - Simplified: pH = 3.885
- Use simplified equation, and check assumptions!
  - $[OH^-] << [H^+]$
    - $7.7 \times 10^{-11} << 1.3 \times 10^{-4}$ yes!
  - $[Ac^-] << [HAc]$
    - $1.3 \times 10^{-4} << 8.7 \times 10^{-4}$ probably OK

- To next lecture