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CEE 680: Water Chemistry

Lecture #14

Acids & Bases: Polyprotics

Benjamin, Chapter 4

(Stumm & Morgan, Chapt.3)

Hydrogen Sulfide example

$$\alpha_0 = \frac{[H_2A]}{C_T} = \frac{1}{1+\frac{K_1}{[H^+]}+\frac{K_1K_2}{[H^+]^2}}$$

- Lines for H_2S
  - Low pH (pH << pK_1, or $[H^+] >> K_1$)
    - $\alpha_0 = 1$ or $[H_2S] = C_T$
    - $\log[H_2S] = \log C_T$
  - Intermediate pH (pK_1 << pH << pK_2, or $K_1 >> [H^+] >> K_2$)
    - $\alpha_0 = [H^+]/K_1$ or $[H_2S] = C_T [H^+]/K_1$
    - $\log[H_2S] = \log C_T + pK_1 - pH$
  - High pH (pK_2,<< pH, or $K_2 >> [H^+]$)
    - $\alpha_0 = [H^+]^2/K_1K_2$ or $[H_2S] = C_T [H^+]^2/K_1K_2$
    - $\log[H_2S] = \log C_T + pK_1 + pK_2 - 2pH$

Slope	Intercept
0	Log C_T
-1	7+log C_T
-2	21+log C_T

$H_2S \rightleftharpoons HS^- \rightleftharpoons S^{-2}$

Hydrogen Sulfide example

$$\alpha_1 \equiv \frac{[HA^-]}{C_T} = \frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}}$$

- Lines for HS^-

	Slope	Intercept
• Low pH (pH << pK_1, or $[H^+] >> K_1$)		
• $\alpha_1 = K_1/[H^+]$ or $[HS^-] = C_T K_1/[H^+]$ $\log[HS^-] = \log C_T - pK_1 + pH$	+1	$-7 + \text{Log } C_T$
• Intermediate pH (pK_1 << pH << pK_2, or $K_1 >> [H^+] >> K_2$)		
• $\alpha_1 = 1$ or $[HS^-] = C_T$	0	$\log C_T$
• $\log[HS^-] = \log C_T$		
• High pH (pK_2,<< pH, or $K_2 >> [H^+]$)		
• $\alpha_1 = [H^+]/K_2$ or $[HS^-] = C_T [H^+]/K_2$	-1	$14 + \log C_T$
• $\log[HS^-] = \log C_T + pK_2 - pH$		

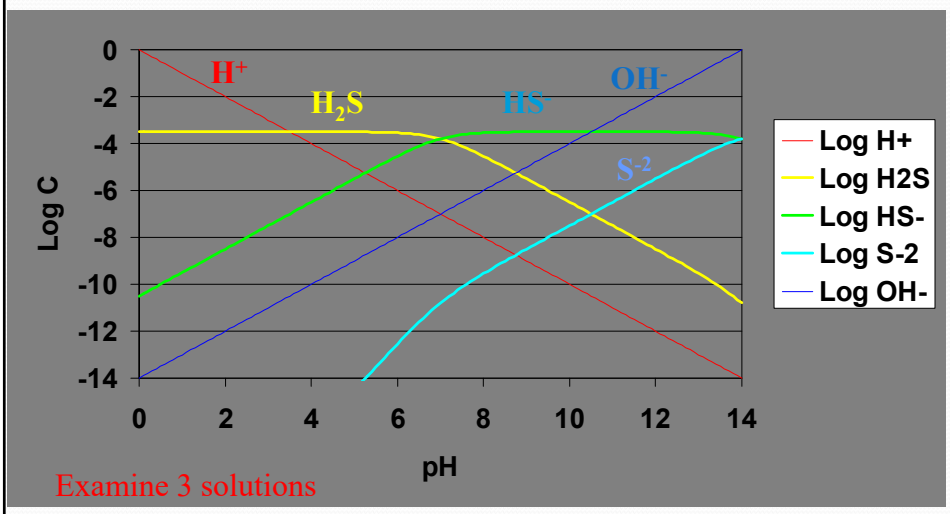
Hydrogen Sulfide example

$$\alpha_2 \equiv \frac{[A^{-2}]}{C_T} = \frac{1}{\frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1}$$

- Lines for S^{-2}

	Slope	Intercept
• Low pH (pH << pK_1, or $[H^+] >> K_1$)		
• $\alpha_2 = K_1K_2/[H^+]^2$ or $[S^{-2}] = C_T K_1K_2/[H^+]^2$	+2	$-21 + \text{Log } C_T$
• $\log[S^{-2}] = \log C_T - pK_1 - pK_2 + 2pH$		
• Intermediate pH (pK_1 << pH << pK_2, or $K_1 >> [H^+] >> K_2$)		
• $\alpha_2 = K_2/[H^+]$ or $[S^{-2}] = C_T K_2/[H^+]$	+1	$-14 + \log C_T$
• $\log[S^{-2}] = \log C_T - pK_2 + pH$		
• High pH (pK_2,<< pH, or $K_2 >> [H^+]$)		
• $\alpha_2 = 1$ or $[S^{-2}] = C_T$	0	$\log C_T$
• $\log[S^{-2}] = \log C_T$		

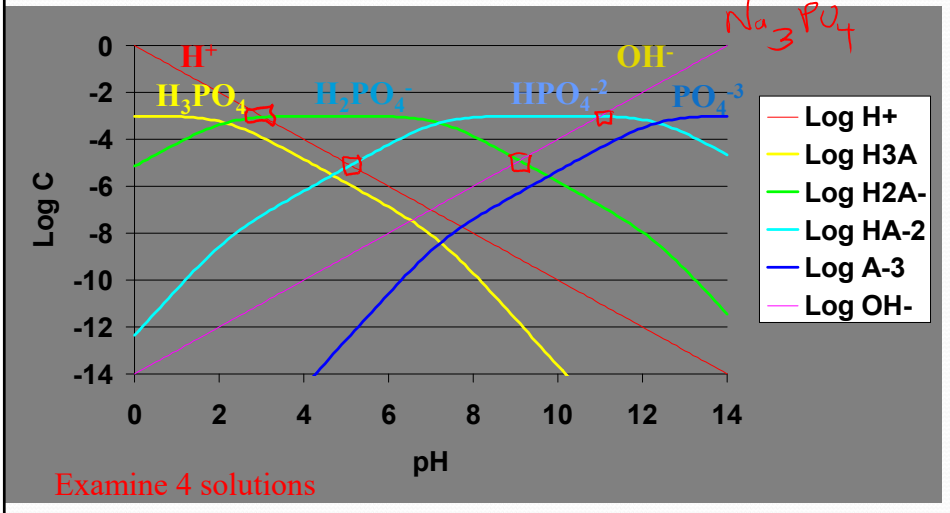
Hydrogen Sulfide ($C_T=10^{-3.5}$)



Examine 3 solutions

Phosphate System ($C_T=10^{-3}$)

H_3PO_4 NaH_2PO_4 Na_2HPO_4 Na_3PO_4



Examine 4 solutions

Alpha summary

	α_o	α_1	α_2	α_3
Monoprotic	$\frac{1}{1+\frac{K_a}{[H^+]}}$	$\frac{1}{\frac{[H^+]}{K_a}+1}$		
Diprotic	$\frac{1}{1+\frac{K_1}{[H^+]}+\frac{K_1K_2}{[H^+]^2}}$	$\frac{1}{\frac{[H^+]}{K_1}+1+\frac{K_2}{[H^+]}}$	$\frac{1}{\frac{[H^+]^2}{K_1K_2}+\frac{[H^+]}{K_2}+1}$	
Triprotic	$\frac{1}{1+\frac{K_1}{[H^+]}+\frac{K_1K_2}{[H^+]^2}+\frac{K_1K_2K_3}{[H^+]^3}} = \alpha_0$			

In-class Practice

- 10^{-4} M $NaHCO_3$
- 10^{-3} M $NaKHPO_4$
- 10^{-3} M H_2S + 10^{-4} M NaOCl
- 10^{-2} M H_2CO_3 + 10^{-2} M Na_2S
- 10^{-2} M NaHS + 10^{-3} M Na_2S

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

Multiple acids

- Solve problems in class
- Two different acids?
  - e.g., 10^{-5} HF and 10^{-4} NH_4Cl
  - e.g., 10^{-3} acetic acid and 10^{-2} hypochlorous
- Acid and conjugate base pair?
  - e.g., carbonic acid and bicarbonate
  - e.g., $9x10^{-3}$ HNO_2 + 10^{-3} $NaNO_2$
  - don't try to use the PBE, it won't work very well. Use the ENE (CBE) instead

- To next lecture

DAR