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CEE 680: Water Chemistry

Lecture #12

Acids & Bases: Graphical Solutions II

Benjamin, Chapter 4

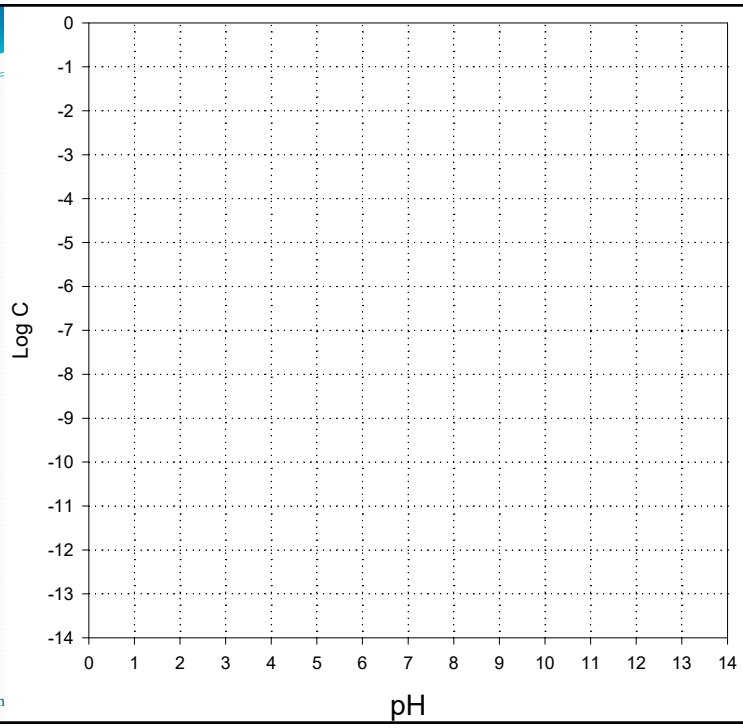
(Stumm & Morgan, Chapt.3)

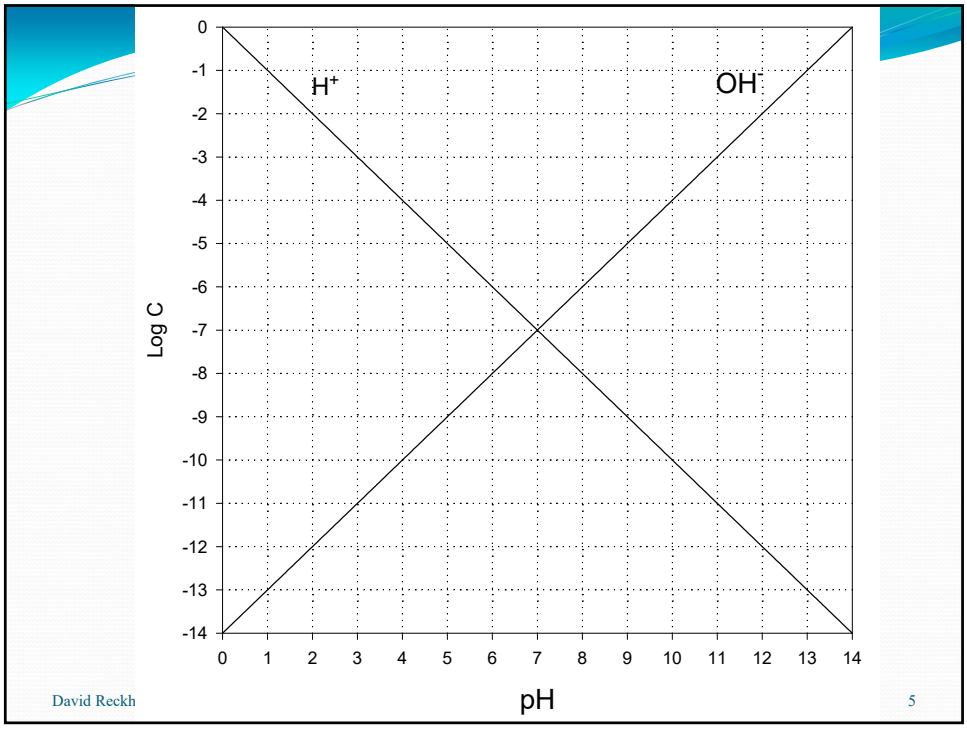
Rapid Method for Log C vs. pH Graph

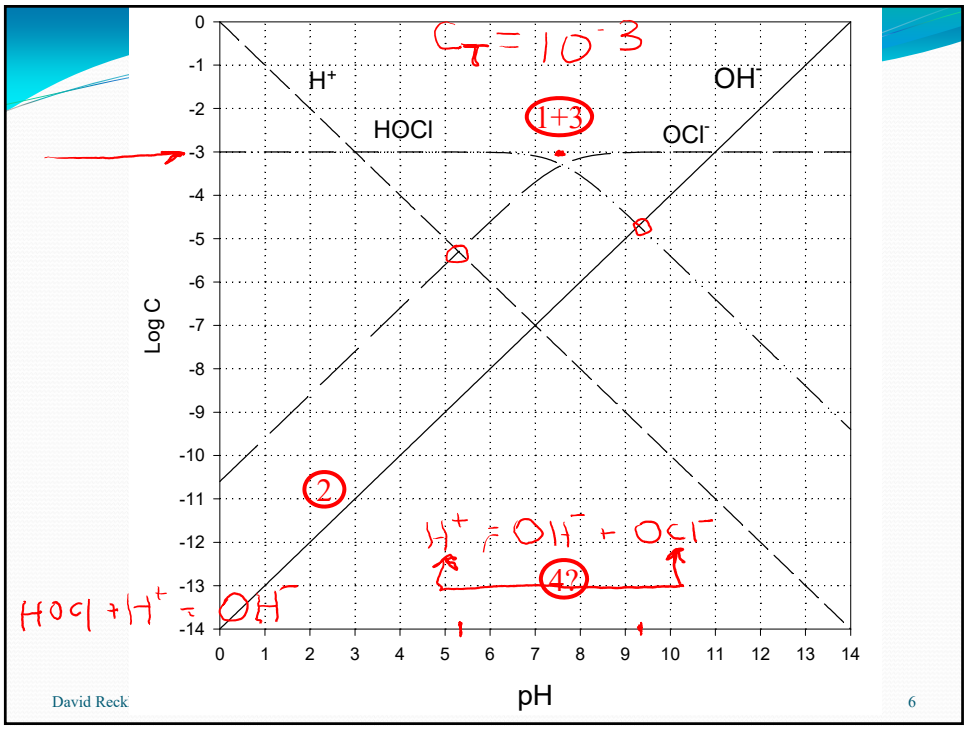
- 1. Plot diagonal $[H^+]$ and $[OH^-]$ lines
- 2. Draw a light horizontal line corresponding to log C_T
- 3. Locate System Point
  - i.e., pH = pK_a, log C = log C_T
  - make a mark 0.3 units below system point
- 4. Draw 45º lines (slope = ±1) below log C_T line, and aimed at system point
- 5. Approximate curved sections of species lines ±1 pH unit around system point
- 6. Repeat steps as necessary for more complex graphs
  - #3-#5 for additional pK_as of polyprotic acids
  - #2-#5 for other acid/base pairs

Example problems

- Hypochlorous Acid System at $C_T = 10^{-3}$
  - HOCl
    - $[H^+]=[OCl^-]$ (5.3)
  - NaOCl
    - $[HOCl]=[OH^-]$ (9.3)
  - mix: 99% HOCl, 1% NaOCl
    - use CBE ($[Na^+]=[OCl^-]$) (5.6)
- How does composition change when:
  - $C_T = 10^{-2}$?
    - 5.8, 9.8, 5.6




H+
OH-
Log C
pH
David Reckh
5


H+
OH-
HOCl
OCl-
Log C
pH
David Reck
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In-Class Practice

- List species, equations, graph species, then solve using PBE
  - 10^{-3} M NH_3
  - 10^{-4} M HF
  - 10^{-4} M HF + 10^{-3} M HAc
  - 10^{-3} M HAc
  - 10^{-3} M NaAc
  - 10^{-3} M NaOCl + 10^{-4} M HAc

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

See pgs. 110-112

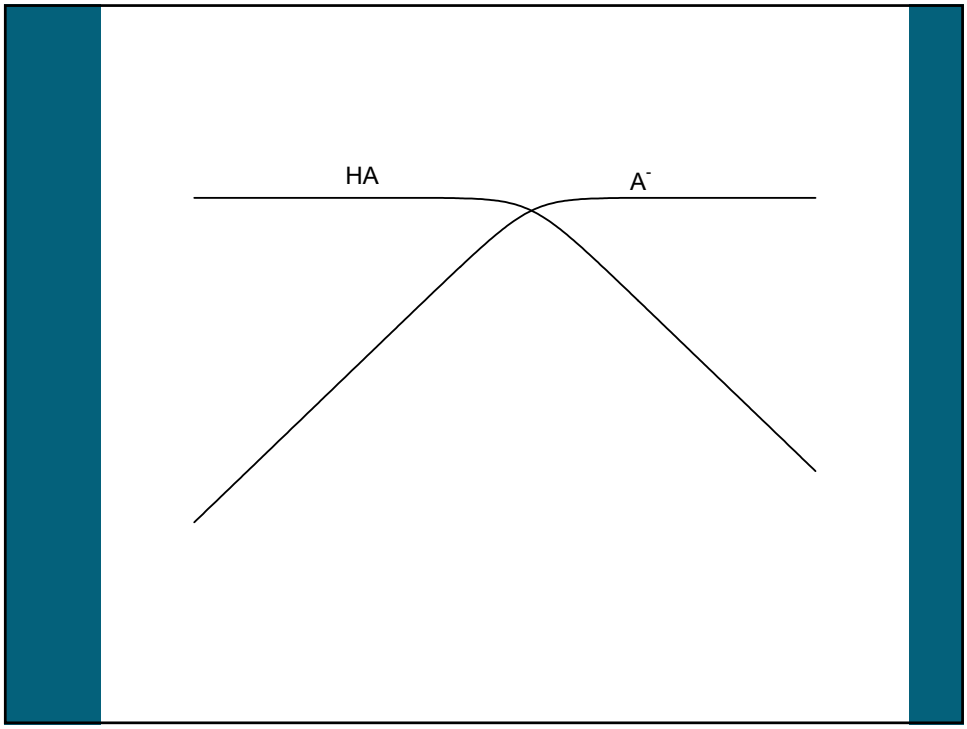
Tableaux

	Components	HOCl	H^+	H_2O	Log K
Species	OCl^-	1	-1	0	-7.6
	H_2O	0	0	1	0
	OH^-	0	-1	1	-14
	H^+	0	1	0	0
	Total	10^{-3}	0	55.4	

$$10^{-7.6} = \frac{[OCl^-][H^+]}{[HOCl]}$$

$$[OCl^-] = [HOCl]^1[H^+]^{-1}[H_2O]^0 10^{-7.6}$$

- A means of summarizing the necessary equations



- To next lecture