

CEE 680: Water Chemistry

Lecture #12

Acids & Bases: Graphical Solutions II

Benjamin, Chapter 4

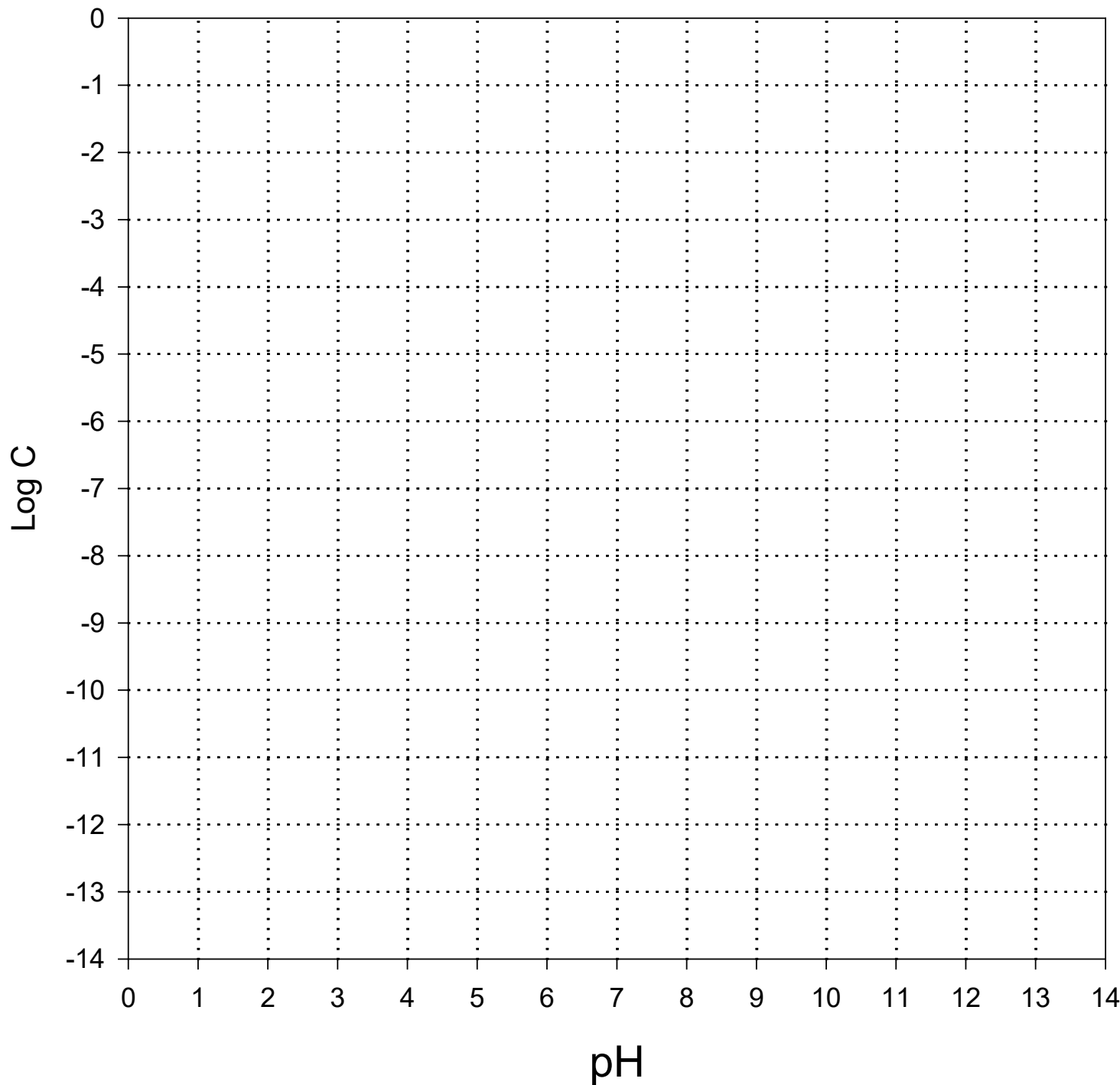
(Stumm & Morgan, Chapt.3)

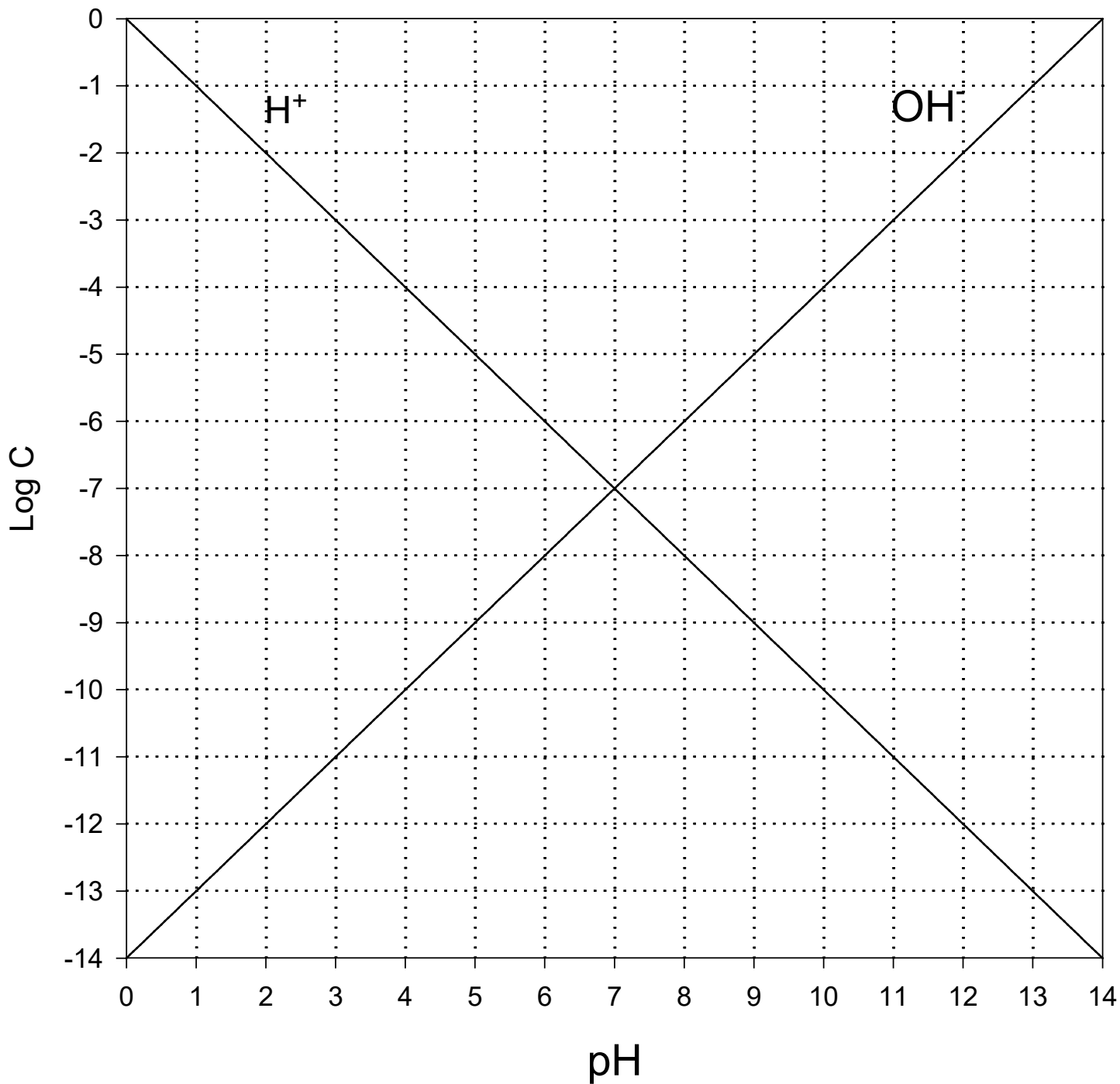
Rapid Method for Log C vs. pH Graph

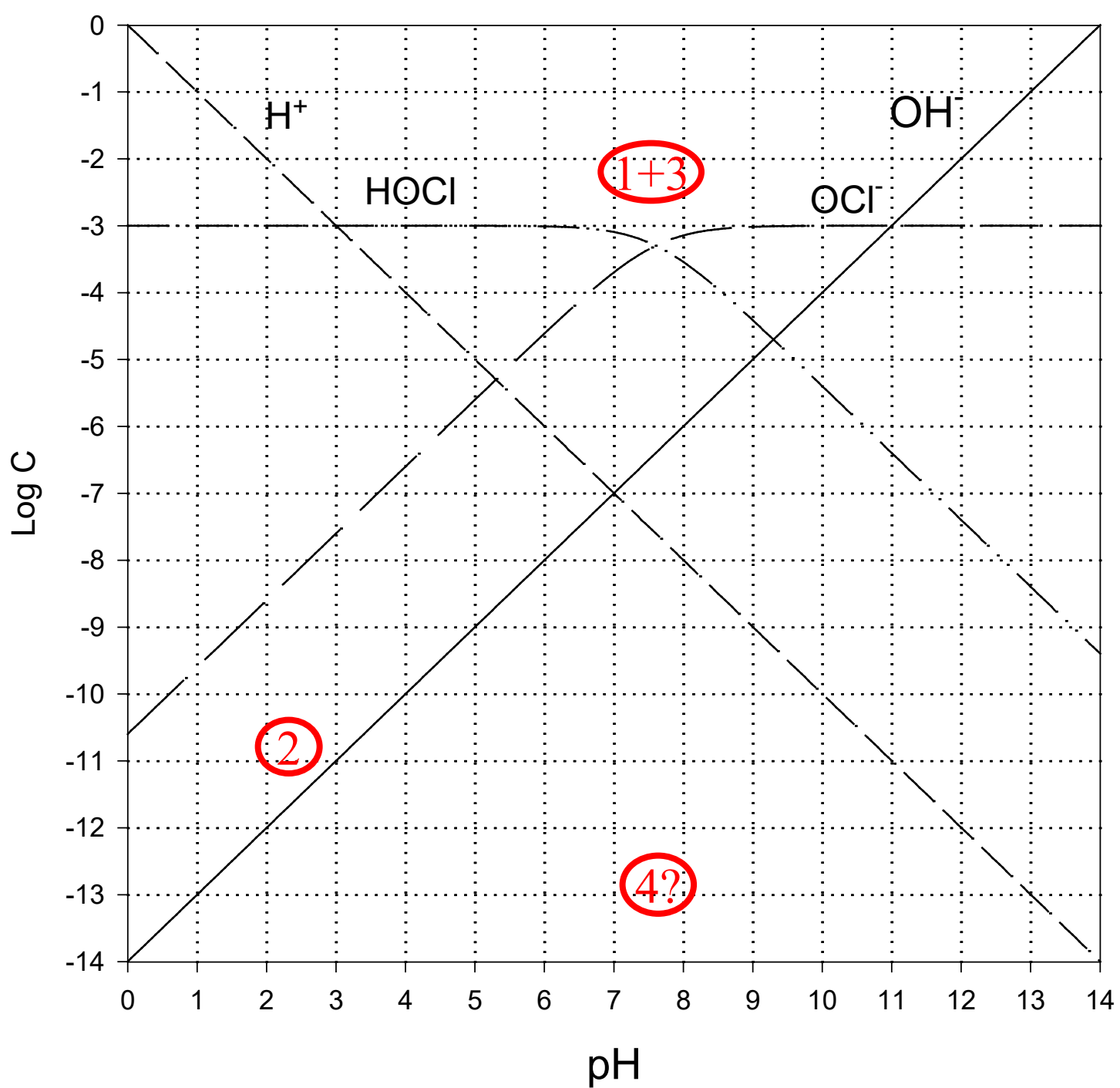
- 1. Plot diagonal $[H^+]$ and $[OH^-]$ lines
- 2. Draw a light horizontal line corresponding to $\log C_T$
- 3. Locate System Point
 - i.e., $pH = pK_a$, $\log C = \log C_T$
 - make a mark 0.3 units below system point
- 4. Draw 45° lines (slope = ± 1) below $\log C_T$ line, and aimed at system point
- 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_a s 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







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	$\text{HClO}_4 = \text{H}^+ + \text{ClO}_4^-$	-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

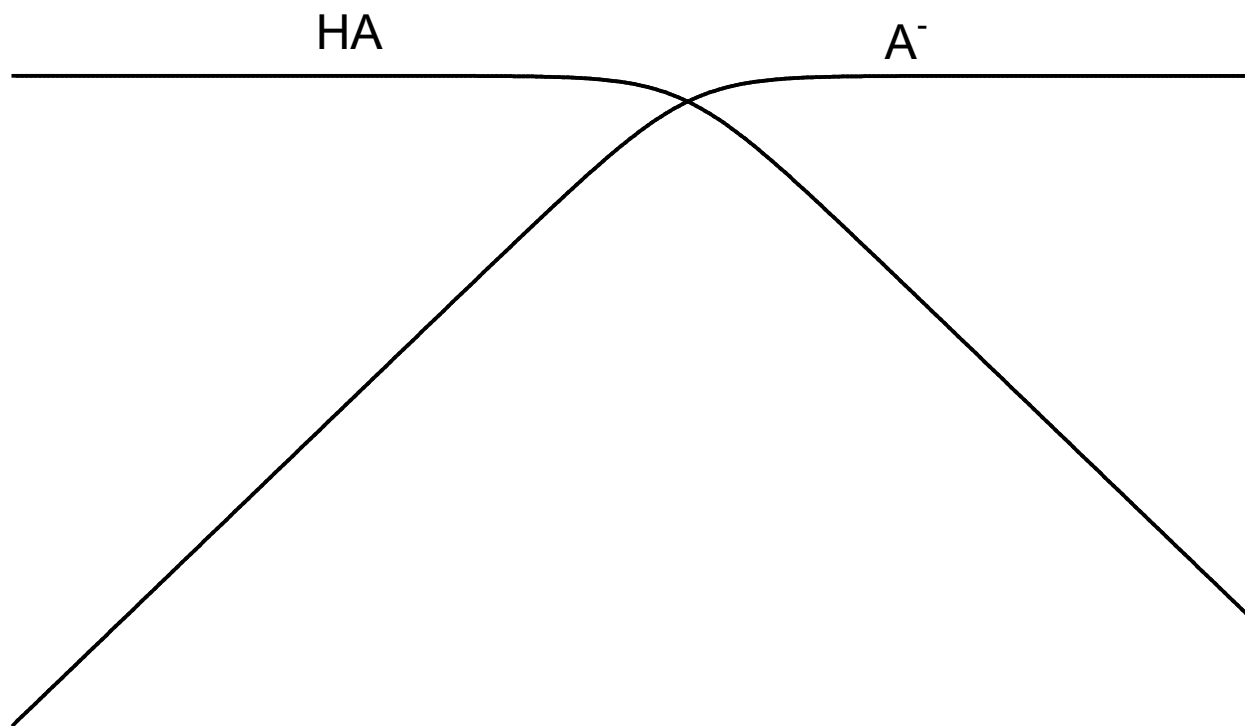
Tableaux

Components		HOCl	H ⁺	H ₂ O	Log K
Species	OCl ⁻	1	-1	0	-7.6
	H ₂ O	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