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CEE 680: Water Chemistry

Lecture #11

Acids & Bases: Graphical Solutions I

(Stumm & Morgan, Chapt.3)

(Benjamin, Chapt. 4)

Graphical Approach

- Independent Variable
  - pH: “the master variable”
- Two types of graphs
  - Distribution diagrams
    - alpha values, independent of concentration
  - Log concentration diagrams
    - pC-pH diagrams

Monoprotic acids: calculations

Note: $\alpha_0 + \alpha_1 = 1$

- Start with C and K_a equations

$$C = [HA] + [A^-] \quad (3)$$

$$[A^-] = C - [HA] \quad (1+3)$$

$$[HA] = C - [A^-] \quad (1+3)$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (1)$$

$$K_a = \frac{[H^+]\{C - [HA]\}}{[HA]}$$

$$K_a[HA] = -[HA][H^+] + C[H^+]$$

$$K_a = \frac{[H^+][A^-]}{C - [A^-]}$$

$$K_a C - K_a[A^-] = [A^-][H^+]$$

$$[HA] = \frac{C[H^+]}{K_a + [H^+]}$$

For LogC vs pH diagrams

$$[A^-] = \frac{K_a C}{K_a + [H^+]}$$

α_0

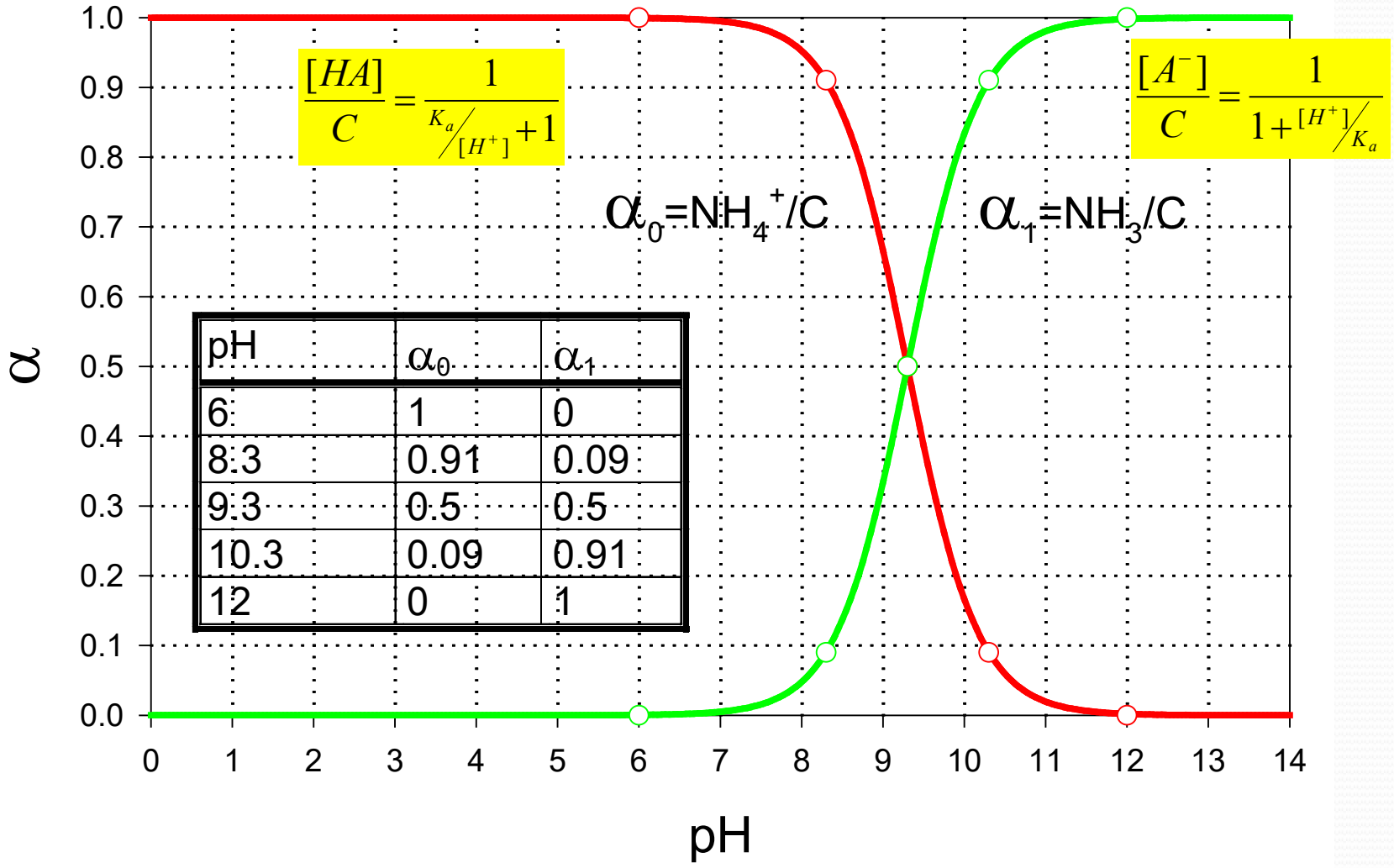
$$\frac{[HA]}{C} = \frac{1}{K_a/[H^+] + 1}$$

For distribution diagrams

$$\frac{[A^-]}{C} = \frac{1}{1 + [H^+]/K_a}$$

α_1

Distribution Diagram for Ammonia



pH	α_0	α_1
6	1	0
8.3	0.91	0.09
9.3	0.5	0.5
10.3	0.09	0.91
12	0	1

Preparing log C vs. pH Diagrams

- 1. Draw $[H^+]$ line
  - $pH \equiv -\log[H^+]$
  - $\log[H^+] = -pH$ ⇐
- 2. Draw $[OH^-]$ line
  - $K_w=[H^+][OH^-]$ ②
  - $\log K_w = \log[H^+] + \log[OH^-]$
  - $\log [OH^-] = -\log [H^+] + \log K_w$
  - $\log [OH^-] = pH - pK_w$ ⇐
- 3. Draw $[HA]$ and $[A^-]$ lines
  - see next slide

Calculations for log [HA] and log [A$^-$] lines

$$[HA] = \frac{C[H^+]}{K_a + [H^+]}$$

$$[A^-] = \frac{K_a C}{K_a + [H^+]}$$

1+3

1+3

If pH << pK_a, or $[H^+]$ >> K_a

Log [HA]=log C

Log [A$^-$]=log C + pH - pK_a

If pH >> pK_a, or $[H^+]$ << K_a

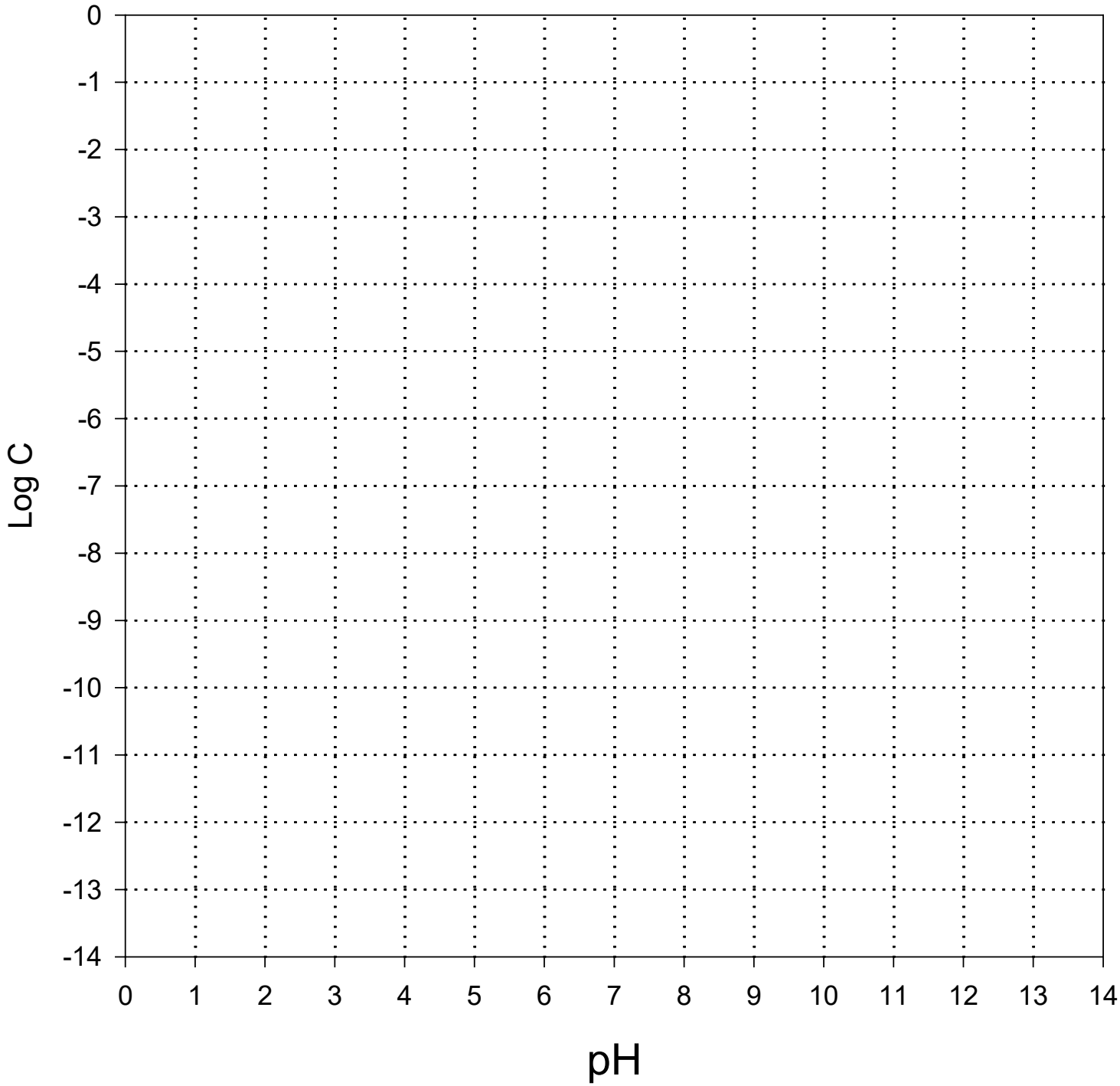
Log [HA]=log C - pH + pK_a

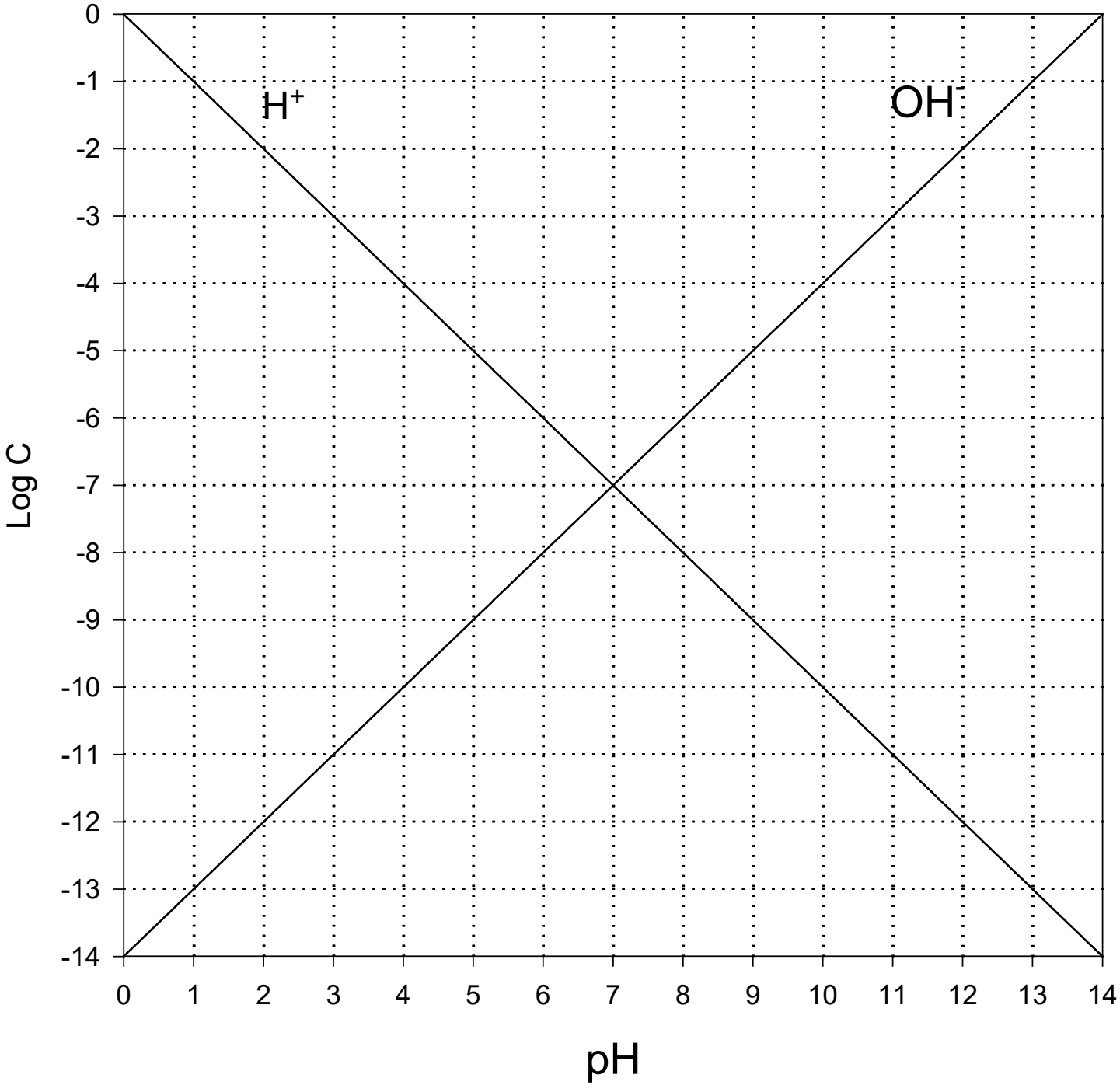
Log [A$^-$]=log C

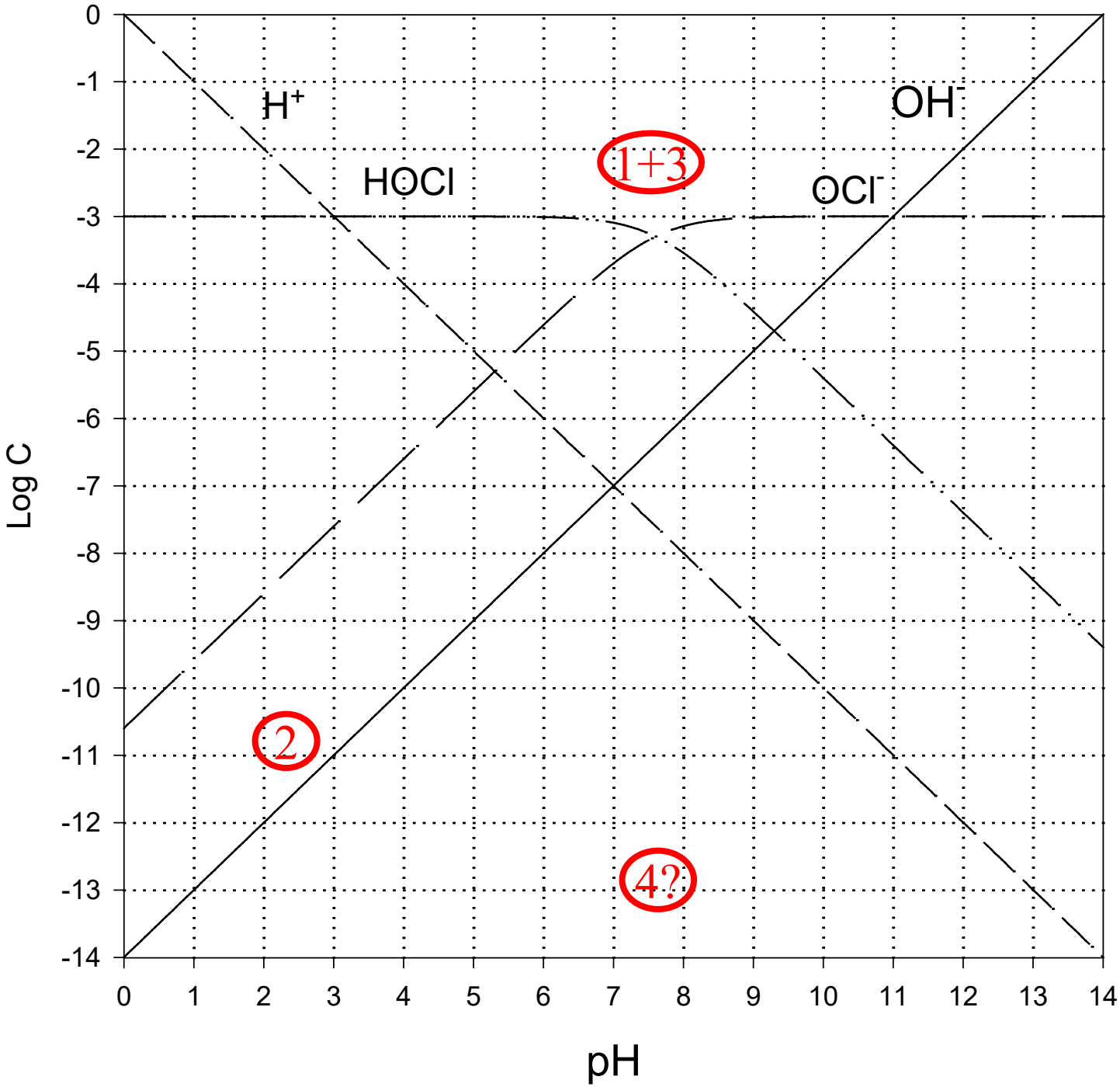
If pH = pK_a, or $[H^+]$ = K_a

Log [HA]=log C - 0.3

Log [A$^-$]=log C - 0.3


0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
Log C
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH


H+
OH-
Log C
pH
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14


0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
Log C
H+
HOCl
OH-
OCl-
1+3
2
4?
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH

- To next lecture