Acid-base systems I

Weak acids & bases

- Many of the important properties of natural waters and wastewaters are due to the presence of weak acid, weak bases, and their salts
  - Carbonate species (HCO_3^- & CO_3^{2-}) in natural waters and their buffering effect
  - Ammonia speciation (NH_3 & NH_4^+) in water
  - Speciation of hypochlorous acid ($HOCl$ & OCl^-) in chlorine disinfection

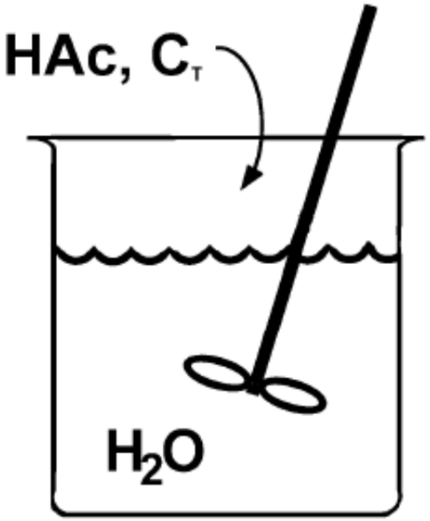
- Monoprotic vs. polyprotic acids
  - Monoprotic: contains only one exchangeable H^+ ion

    ex: HCl, $HOCl$, CH_3COOH
  - Polyprotic: contains two or more exchangeable H^+ ions

    ex: H_2SO_4, H_2CO_3, H_3PO_4

Analyzing monoprotic weak acid/base system

- 10^{-3} M CH_3COOH (HAc) is added in pure water at 25°C. What will be the pH of the water? What will be the HAc and Ac^- concentrations?



Reaction: $HAc + H_2O = H_3O^+ + Ac^-$

$C_T = 10^{-3}$ M, $pK_a = 4.75$ (at 25°C)

Species involved (4):

H^+ (H_3O^+), OH^-, HAc, Ac^-

➡ **Need 4 equations!**

Analyzing monoprotic weak acid/base system

Equilibrium constants:

Mass balance:

Charge balance (electroneutrality):

Analyzing monoprotic weak acid/base system

Assuming $[H^+] >> [OH^-]$ (acidic), we can solve the equation to get

$$[H^+] = \frac{-K_a + \sqrt{{K_a}^2 + 4K_aC_T}}{2}$$

As $K_a = 10^{-4.75}$ & $K_w = 10^{-14}$ at 25°C,

$$[H^+] = 1.25 \times 10^{-4}\ M$$ (pH=3.9)

$$[OH^-] = 8.00 \times 10^{-11}\ M$$ (assumption holds)

$$[Ac^-] = 1.25 \times 10^{-4}\ M$$

(A weak acid → partial dissociation)

$$[HAc] = 8.75 \times 10^{-4}\ M$$

Analyzing monoprotic weak acid/base system

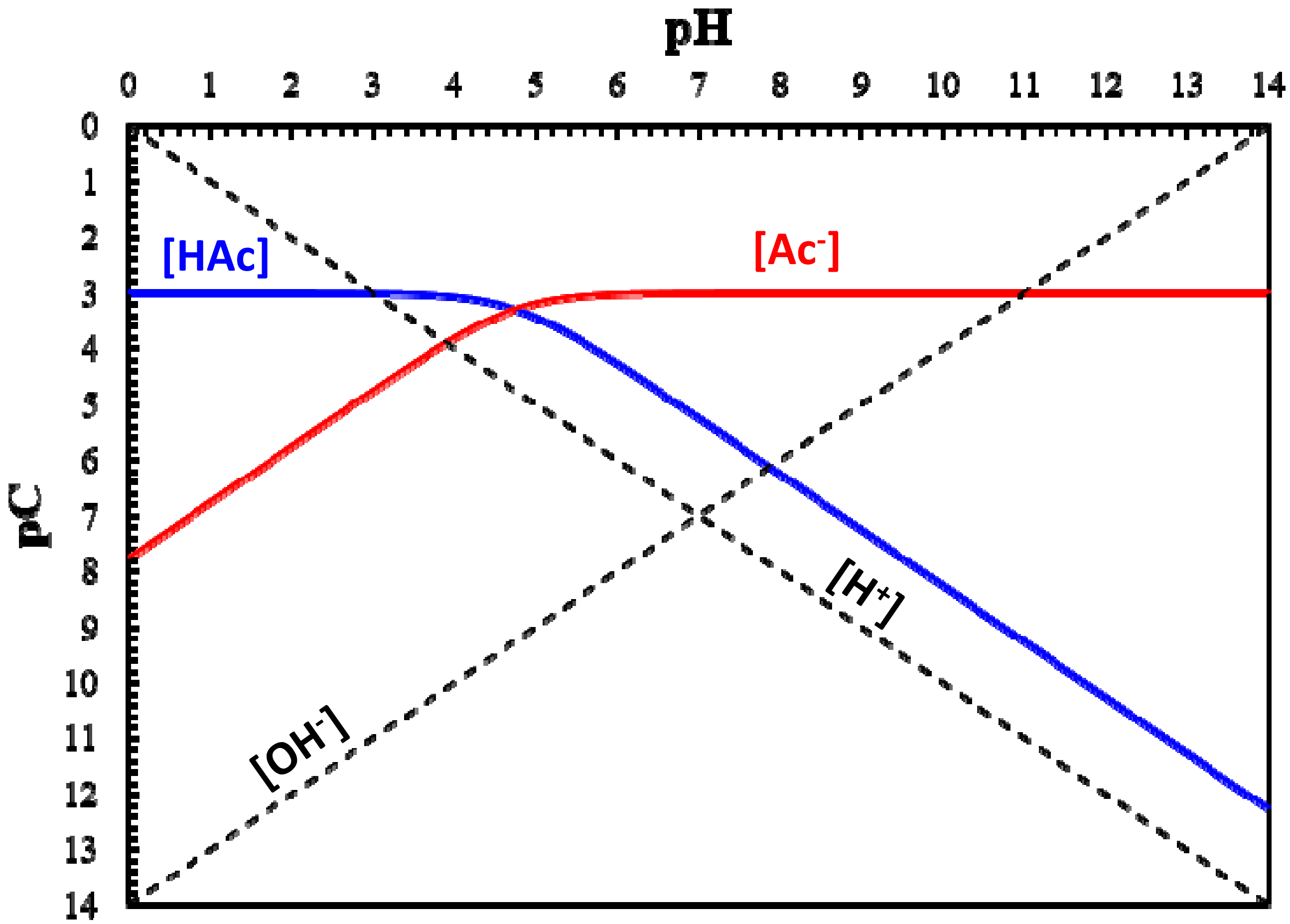
The question can be solved using **[H⁺]** as a major variable:

(2) + (3): $$[Ac^-] = \frac{C_T K_a}{K_a + [H^+]} \qquad (5)$$

(3) + (5): $$[HAc] = \frac{C_T [H^+]}{K_a + [H^+]} \qquad (6)$$

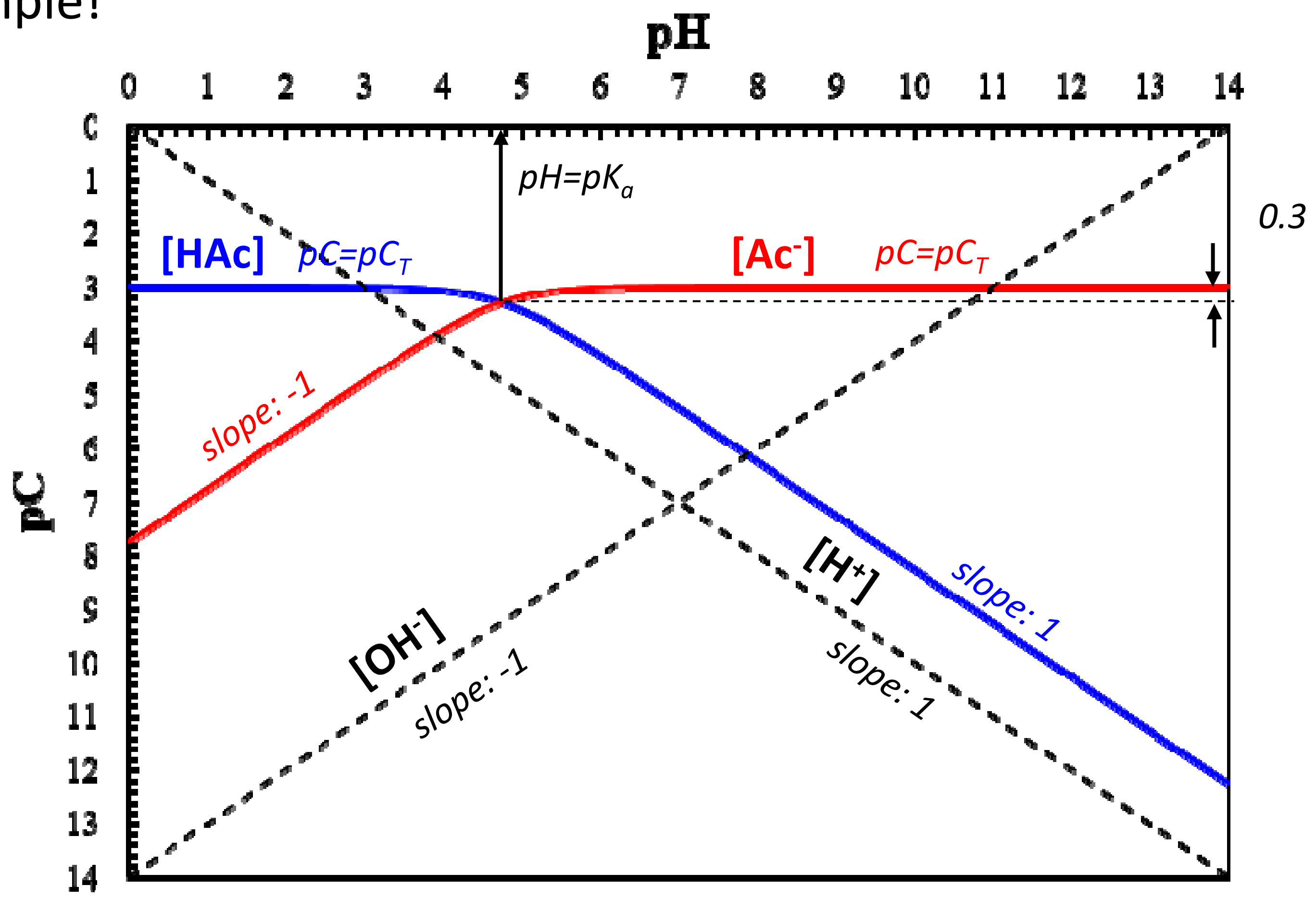
(1): $$[OH^-] = \frac{K_w}{[H^+]} \qquad (7)$$

Analyzing monoprotic weak acid/base system



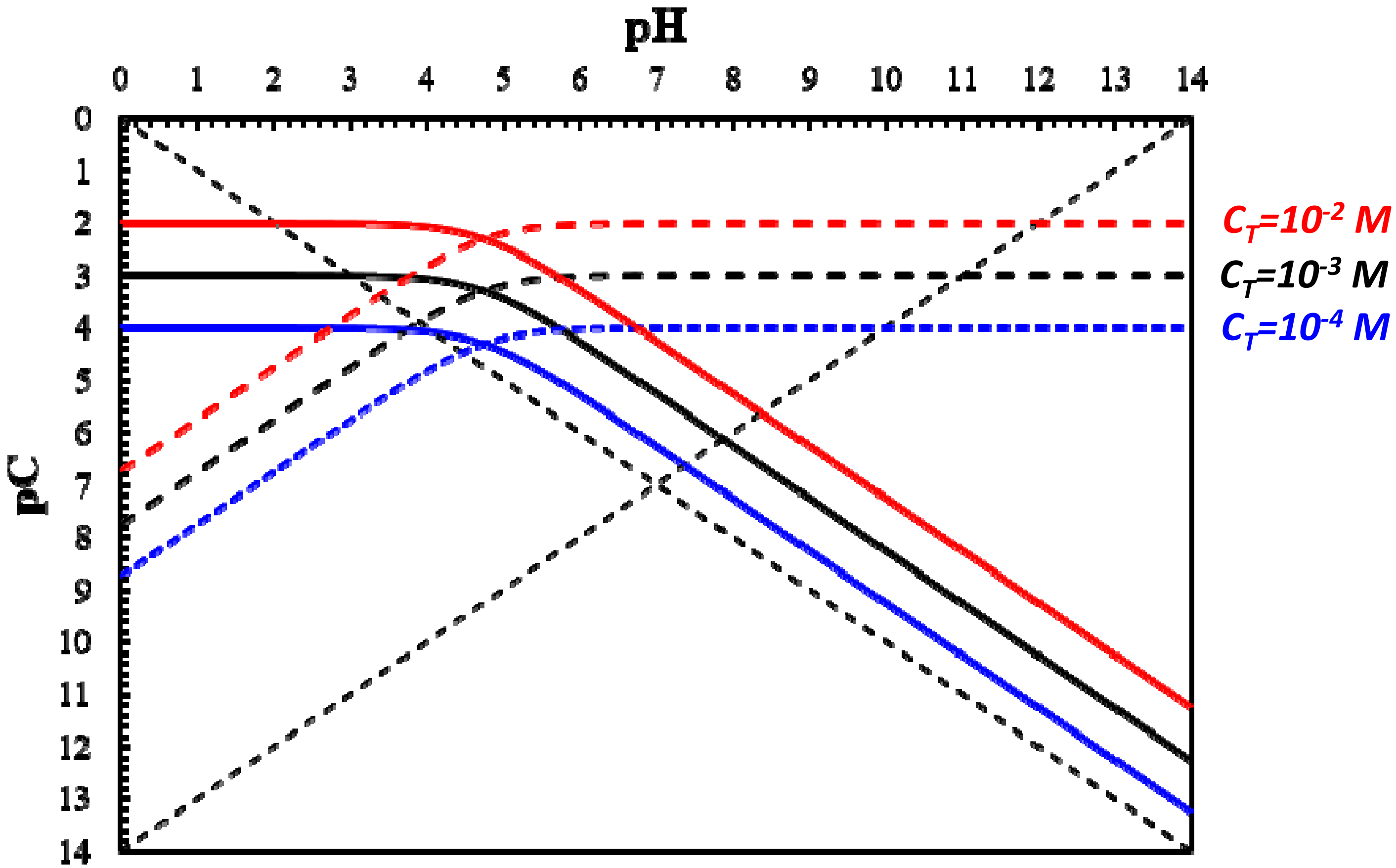
Analyzing monoprotic weak acid/base system

Actually drawing the pH-pC diagram for a monoprotic acid is quite simple!



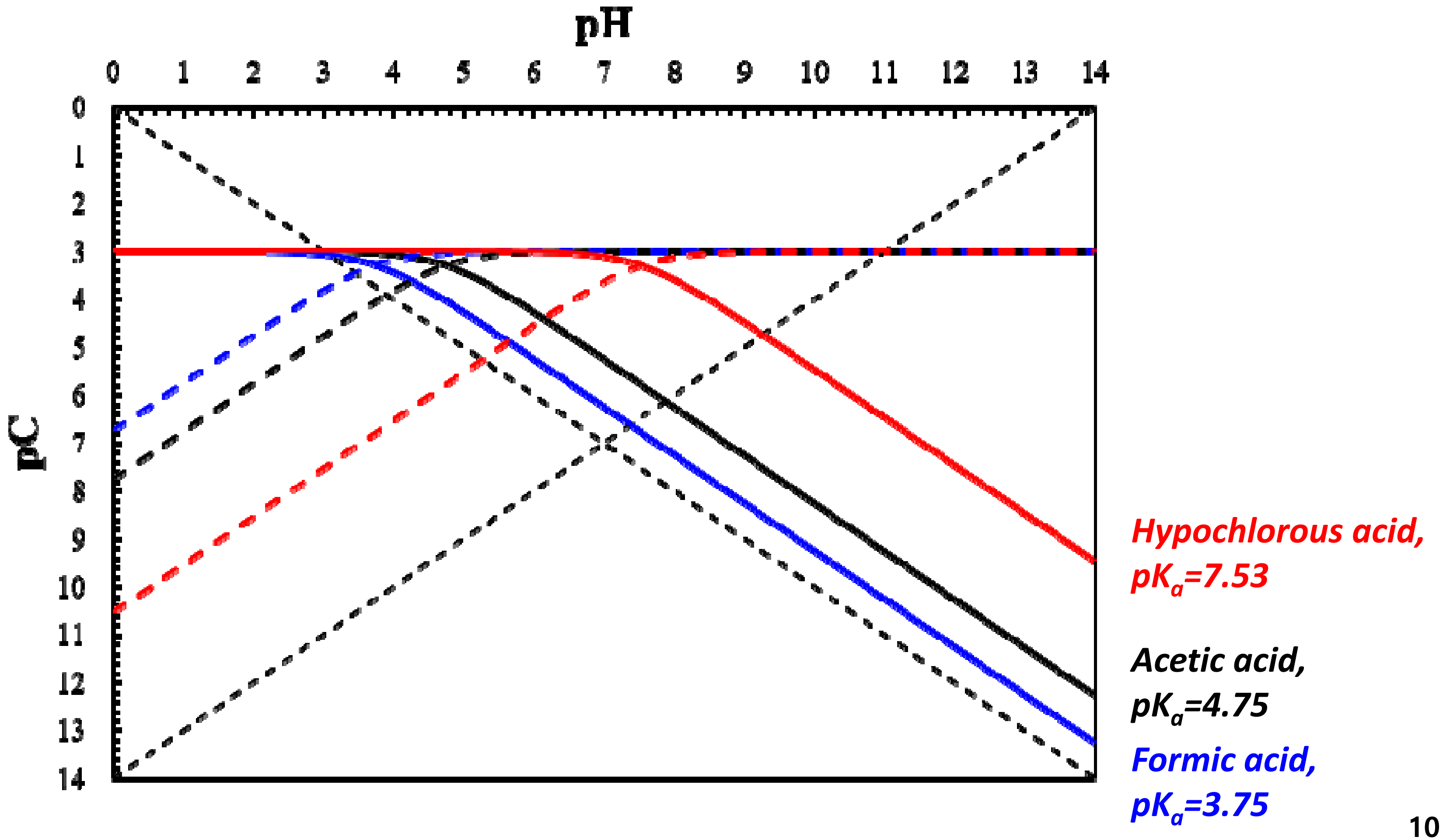
Analyzing monoprotic weak acid/base system

For different C_T (acetic acid, pK_a=4.75):



Analyzing monoprotic weak acid/base system

For different K_a ($C_T=10^{-3}$ M):



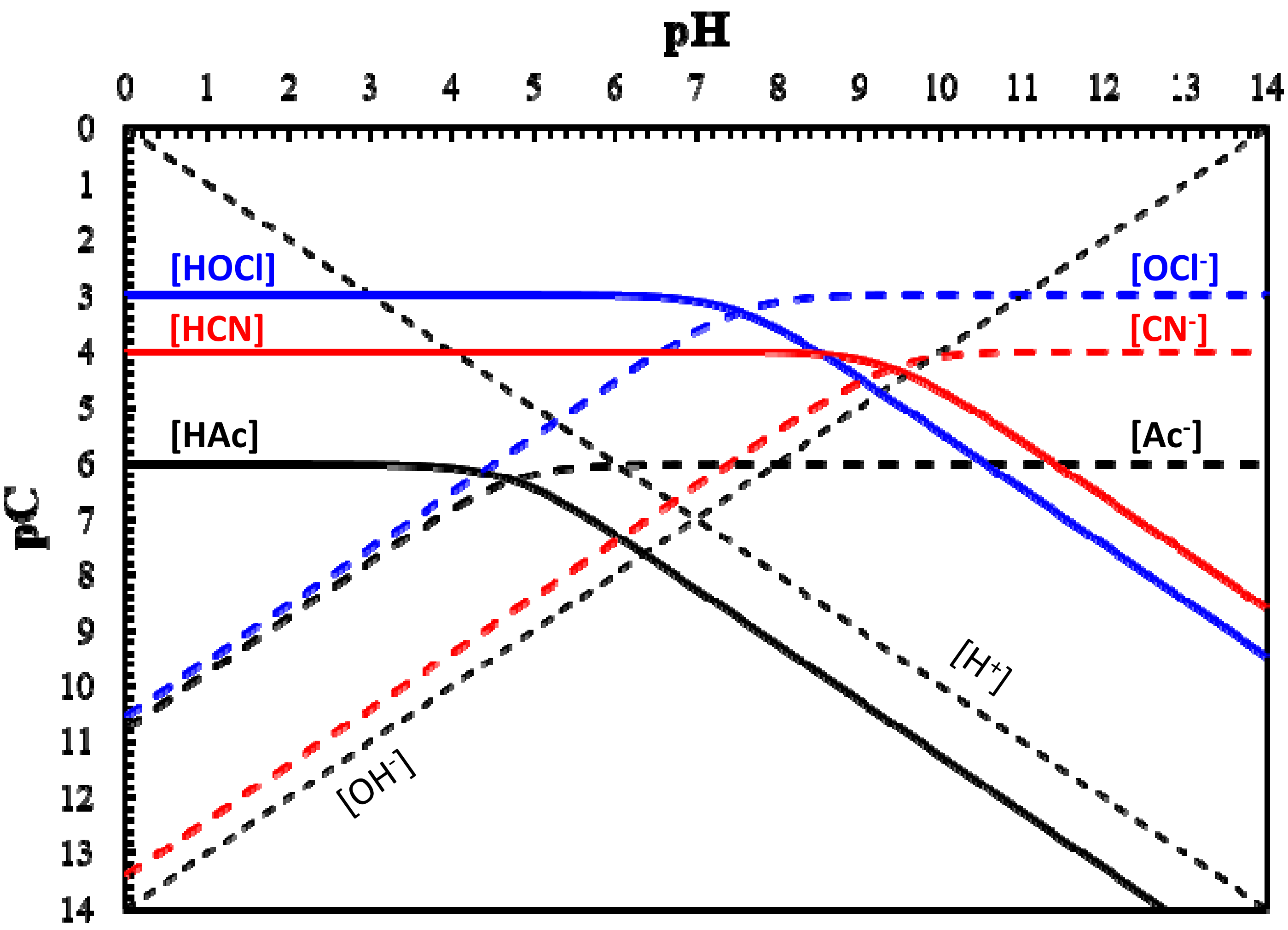
Analyzing monoprotic weak acid/base system

Q: What if there are multiple acids in water?

ex)

Acids	**C_T (M)**	**pK_a**
HAc	10^{-6}	4.75
HOCl	10^{-3}	7.53
HCN	10^{-4}	9.40

Analyzing monoprotic weak acid/base system



Dominant vs. Trace acid/base systems

So:

- Usually one or two acid/base systems dominate a system, setting the pH value
- All other trace acid/base systems will adjust to the pH value

  (dissociated according to the pH value set by

  the dominant acid/base systems)

Analyzing monoprotic weak acid/base system

What about a "salt" of a "conjugate base" of a weak acid?

HAc	+	H_2O	=	H_3O^+	+	Ac^-
Acid		Base		Conjugate acid		Conjugate base

- **Brønsted-Lowry acid & base**
  - Brønsted-Lowry acid: any substance that can donates a proton (i.e., proton donor)
  - Brønsted-Lowry base: any substance that can accepts a proton (i.e., proton acceptor)

Analyzing monoprotic weak acid/base system

NaAc as an example:

Equilibrium constants

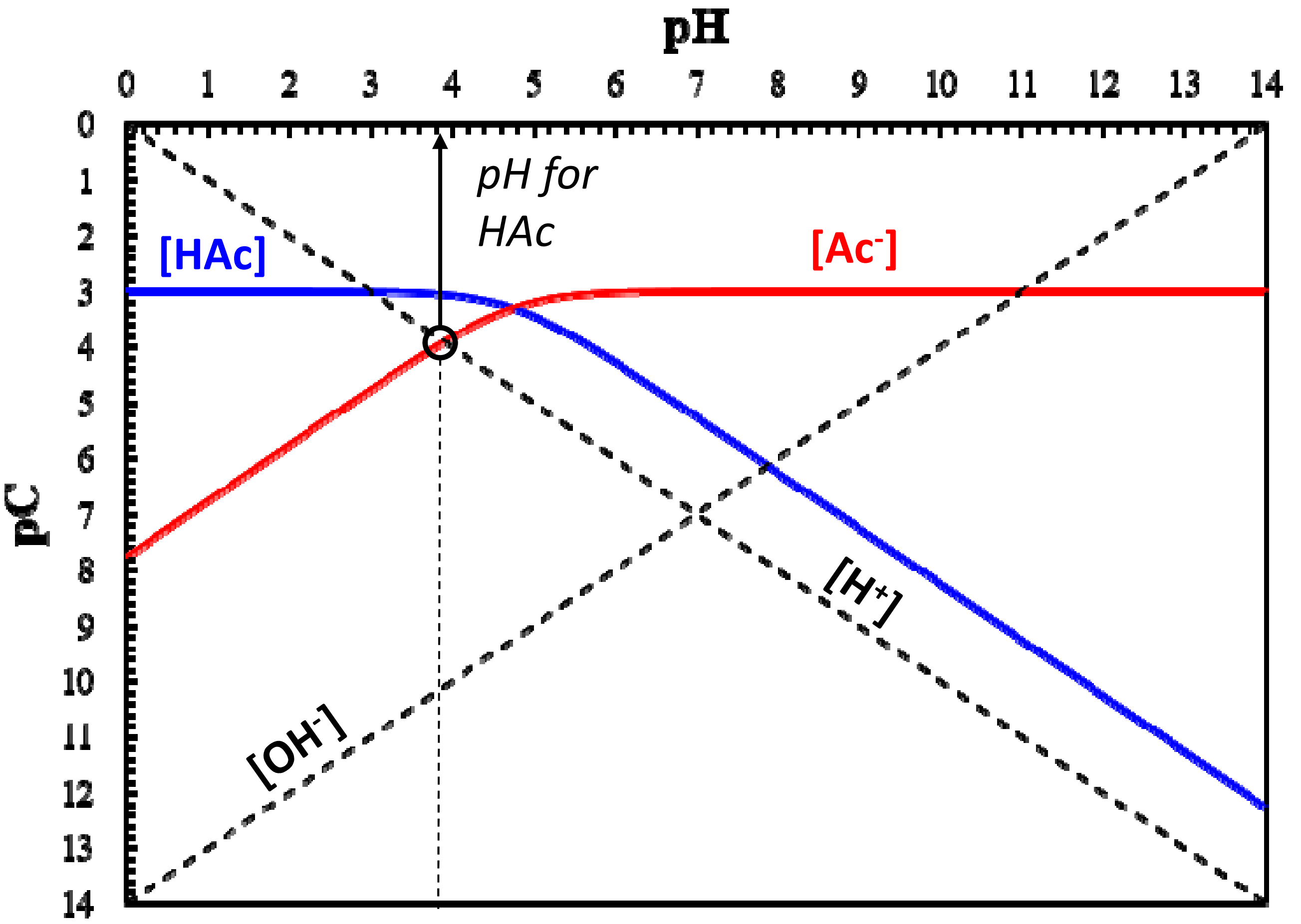
$$K_w = [H^+][OH^-]$$

$$K_a = \frac{[H^+][Ac^-]}{[HAc]}$$

Mass balance

Charge balance

Analyzing monoprotic weak acid/base system

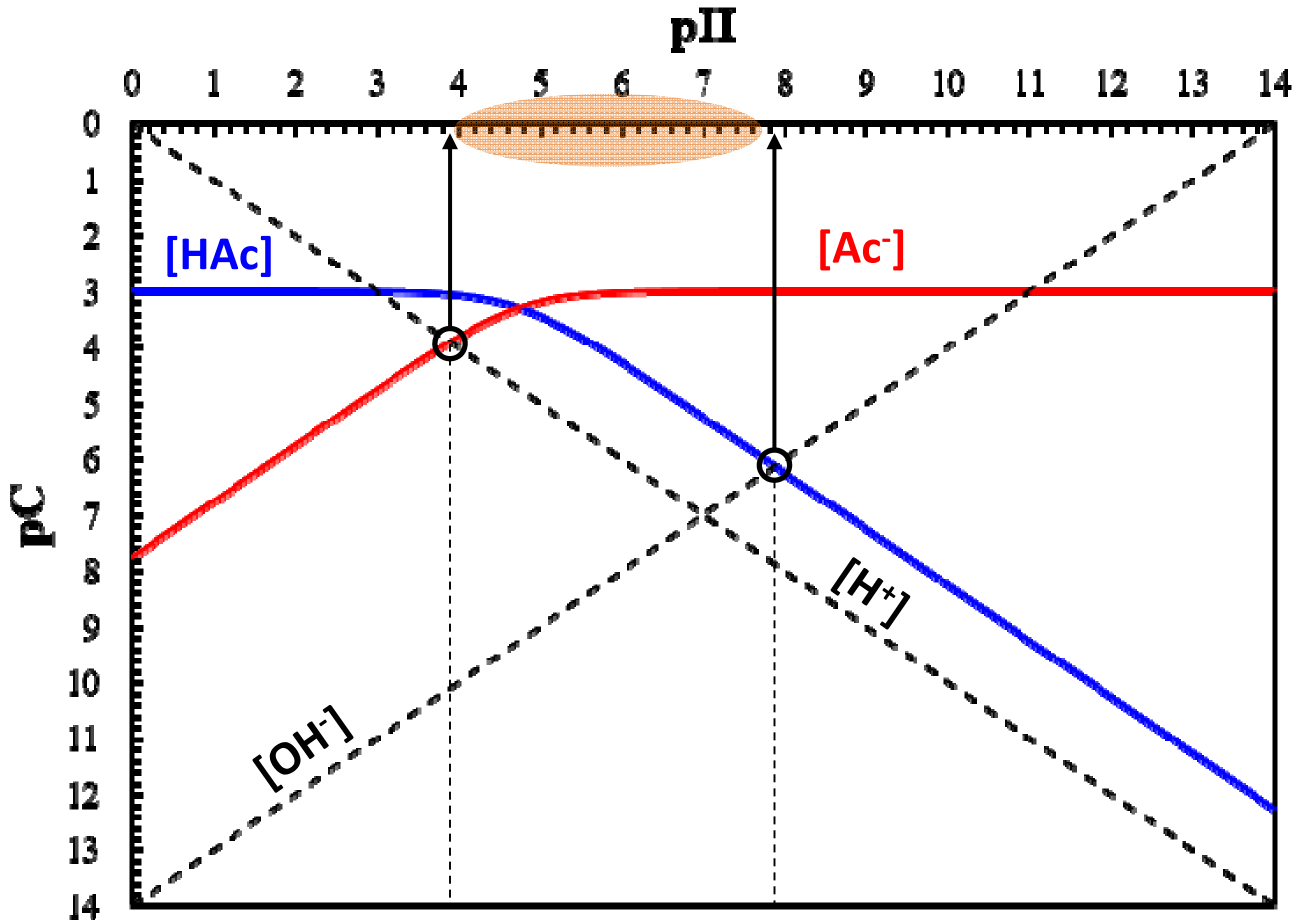


$C_T = 10^{-3}$ M

$pK_a = 4.75$

pH buffer

Weak acid + salt of its conjugate base



pH buffer

Homework:

5×10^{-4} M NaAc and 5×10^{-4} M HAc is added in pure water to make a buffer solution with $C_T = 10^{-3}$ M.

What is the pH of the buffer?