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

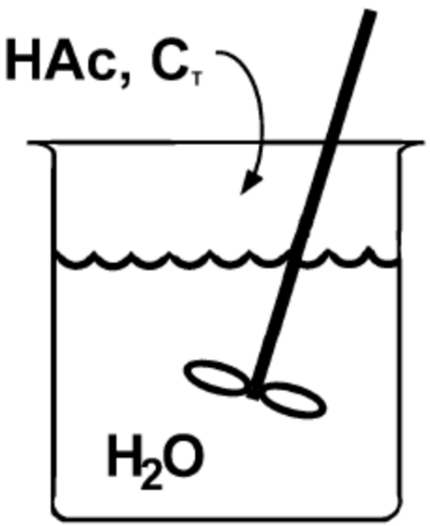
- Monoprotic vs. polyprotic acids
  - Monoprotic: contains only one exchangeable H^+ ion

    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

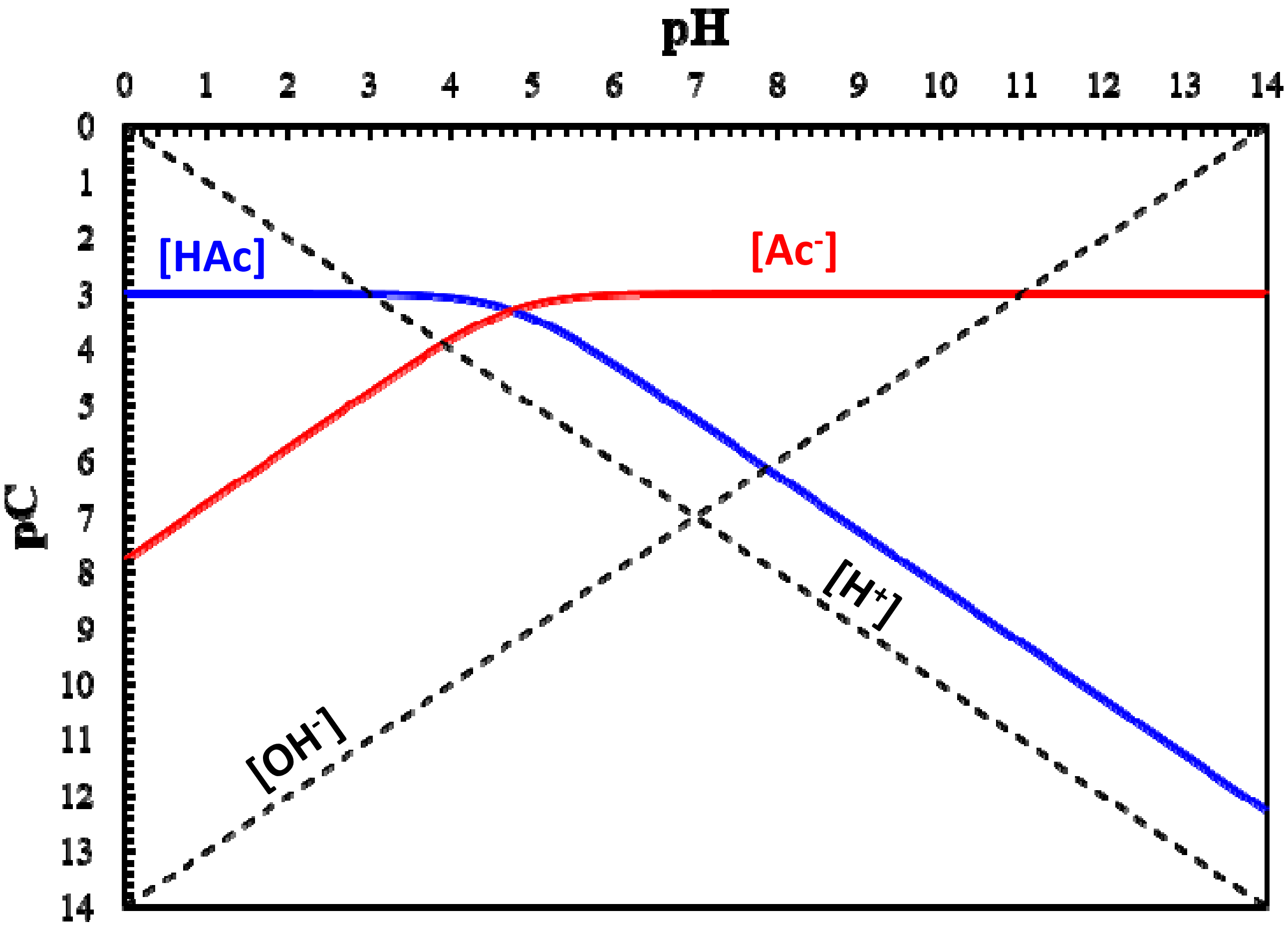
The question can be solved using **[H⁺]** as a major variable:

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

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

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

Analyzing monoprotic weak acid/base system



from (4):

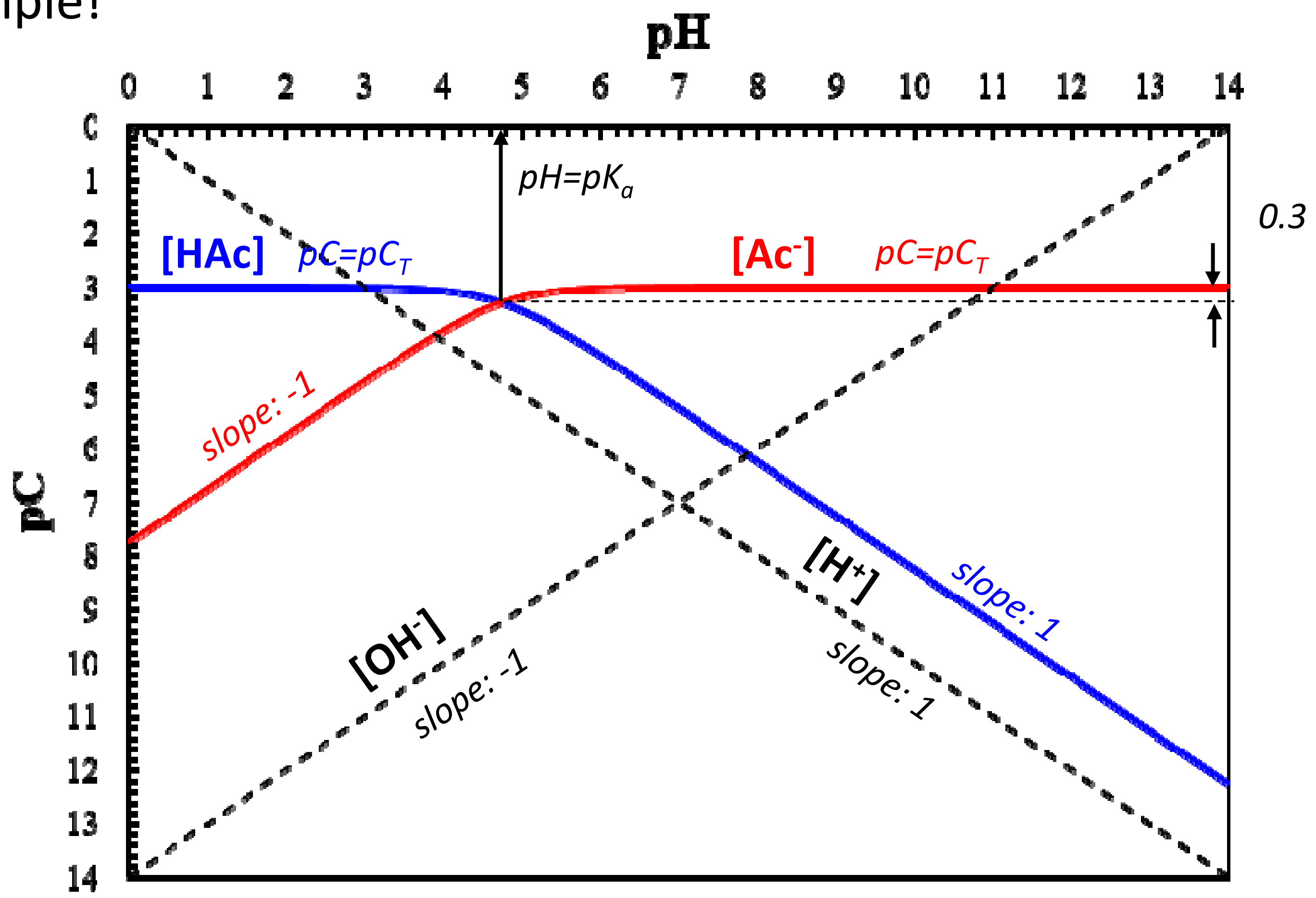
$$[H^+] = [Ac^-] + [OH^-]$$

$$\cong [Ac^-]$$

This is called a **"pH-pC diagram"**

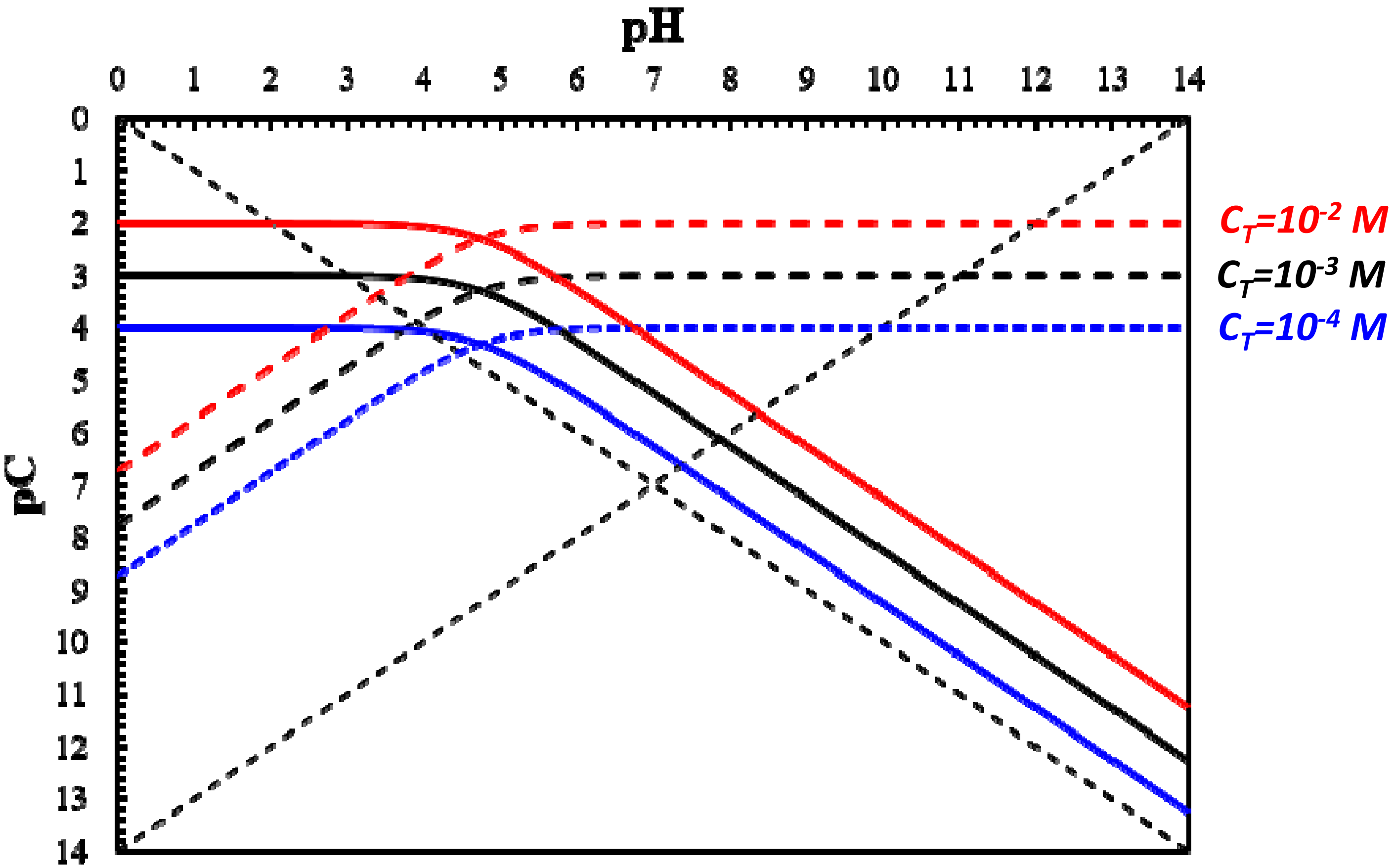
Analyzing monoprotic weak acid/base system

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



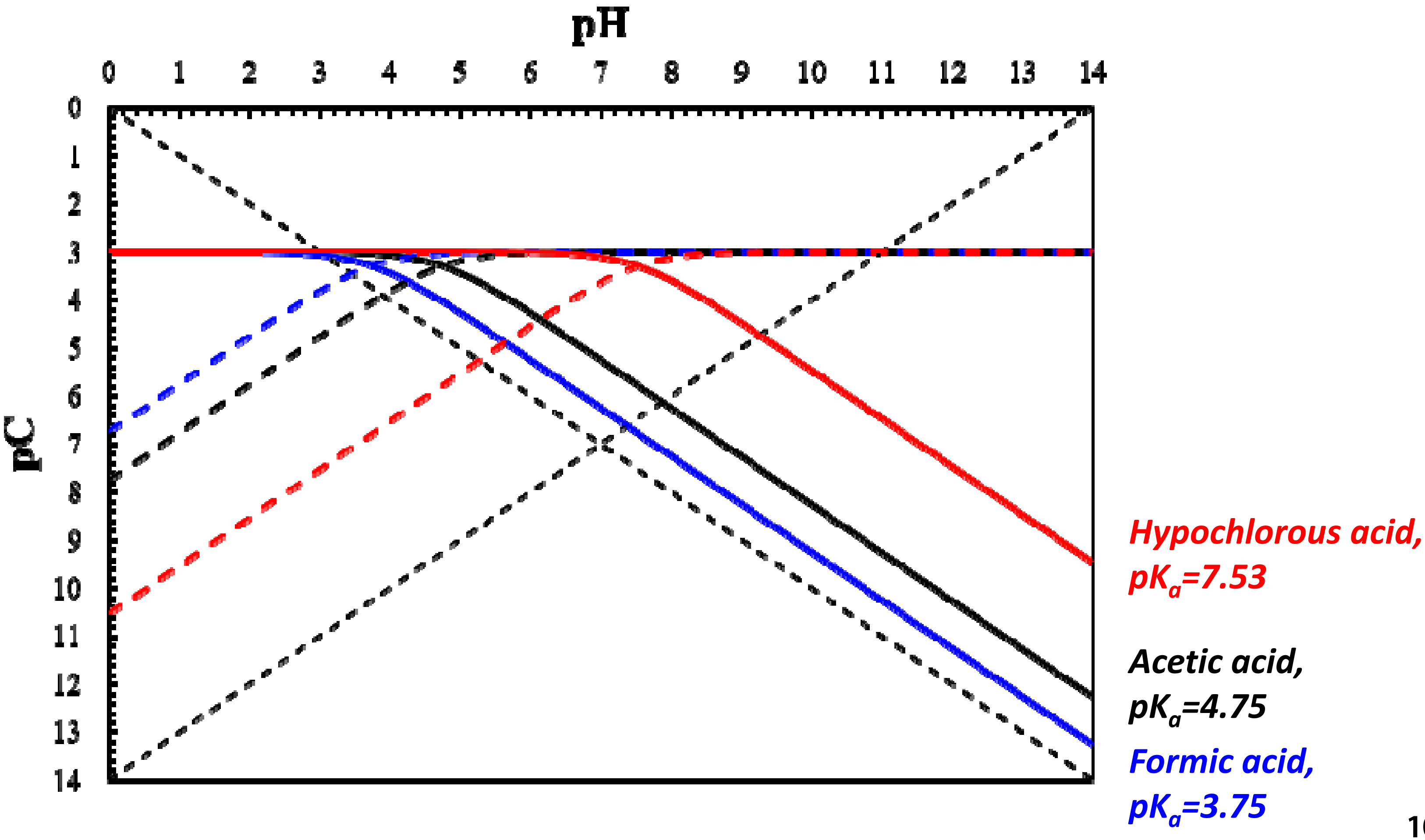
Analyzing monoprotic weak acid/base system

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):



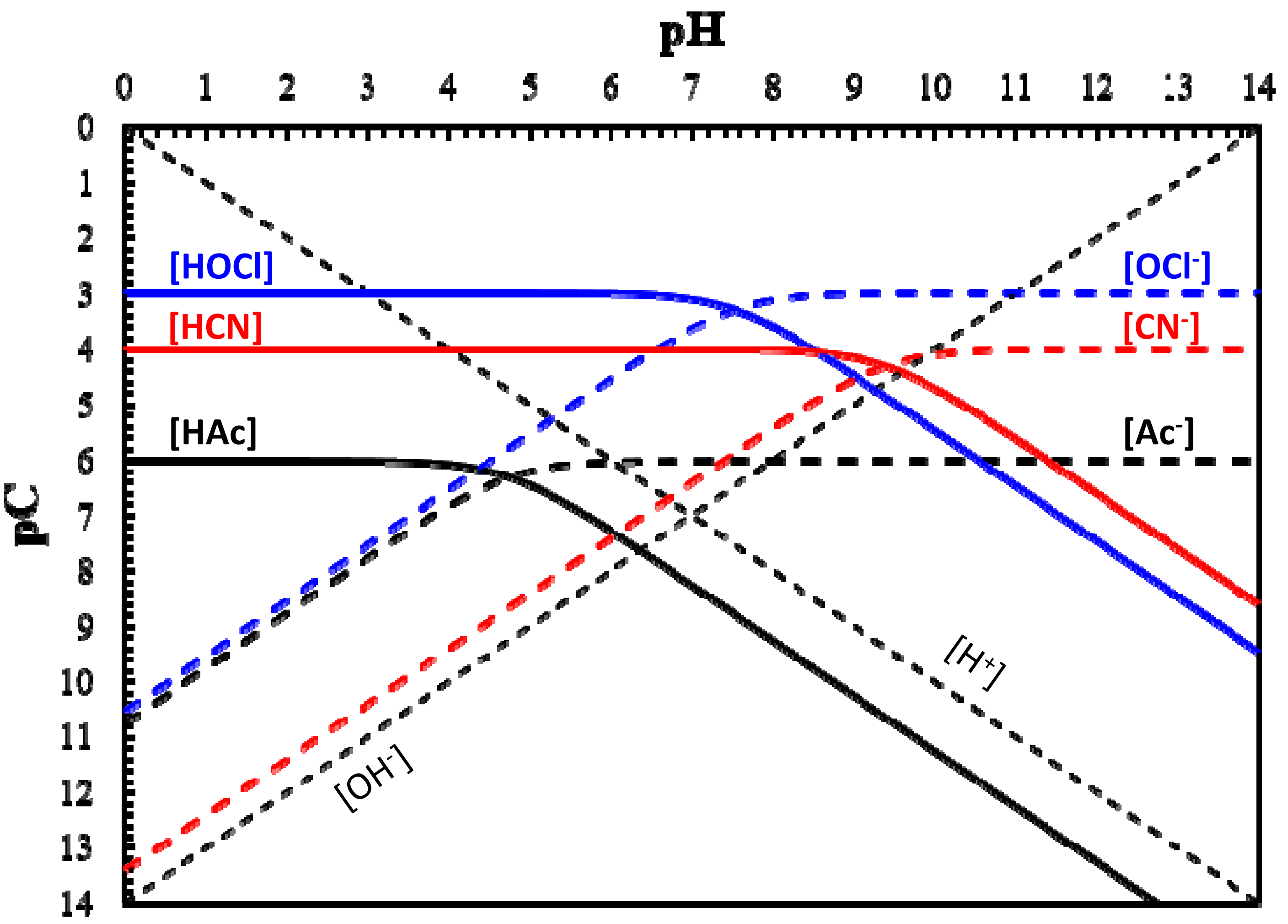
Analyzing monoprotic weak acid/base system

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?

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

HAc	H₂O	H₃O⁺	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

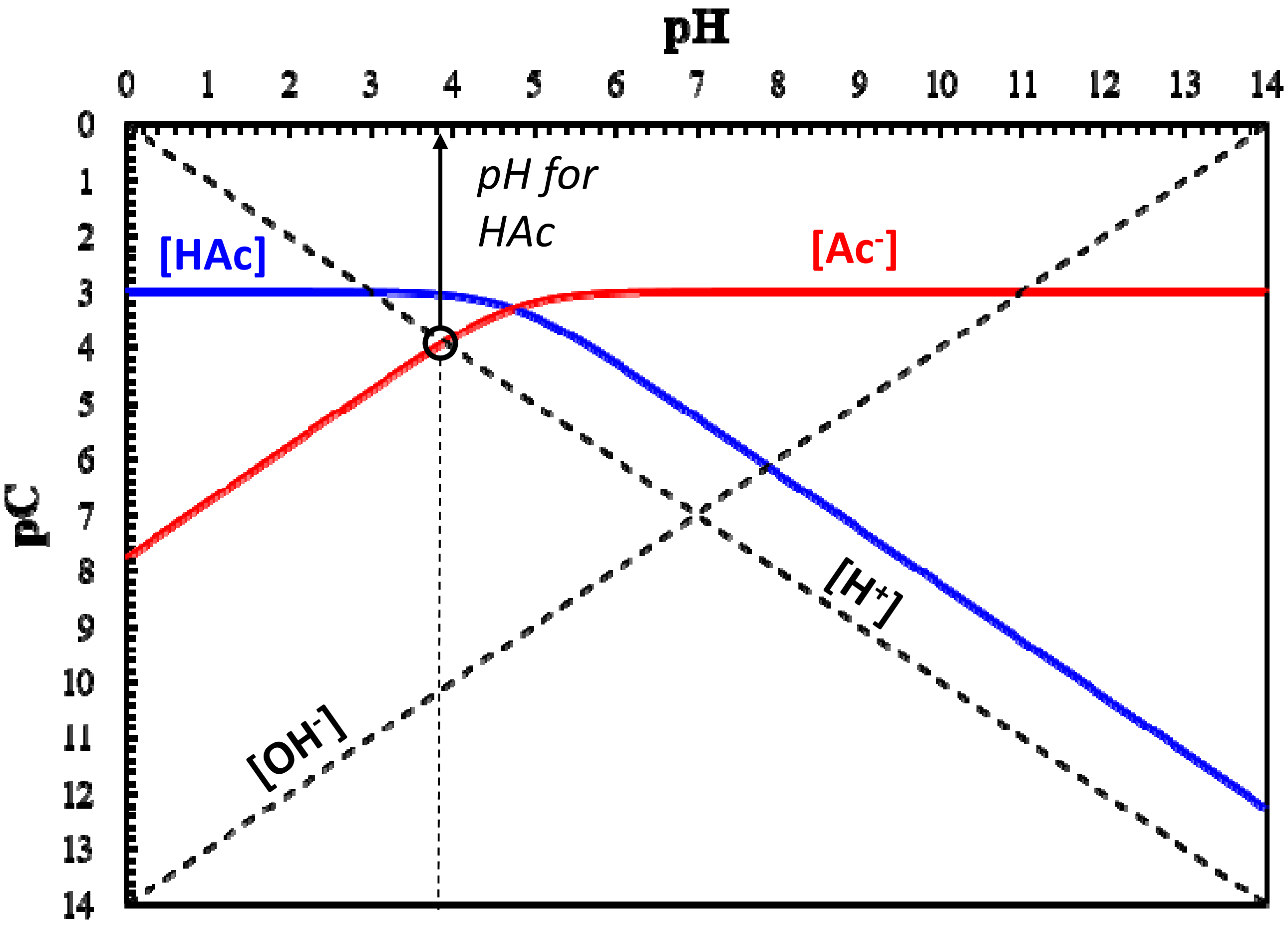
$$K_w = [H^+][OH^-]$$

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

Mass balance

Charge balance

Analyzing monoprotic weak acid/base system



$C_T = 10^{-3}$ M

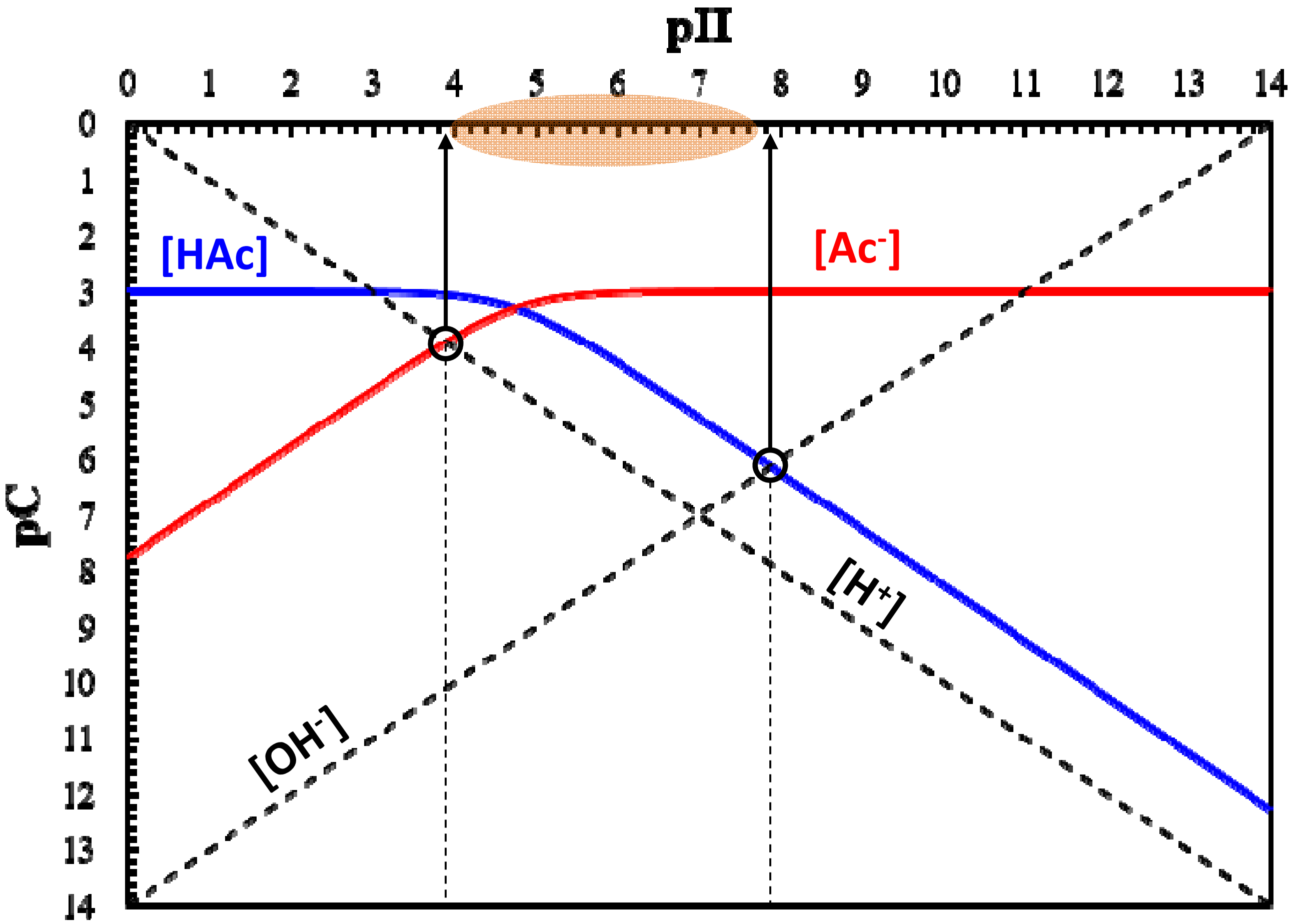
$pK_a = 4.75$

Mass balance + charge balance:

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

pH buffer

Weak acid + salt of its conjugate base



Microorganism growth medium example

Bushnell Haas Broth

M350

Bushnell Haas Broth is recommended for the examination of fuels for microbial contamination and for studying microbial hydrocarbon deterioration.

Composition**

Ingredients	Gms / Litre
Magnesium sulphate	0.200
Calcium chloride	0.020
Monopotassium phosphate	1.000
Dipotassium phosphate	1.000
Ammonium nitrate	1.000
Ferric chloride	0.050
Final pH (at 25°C)	7.0±0.2

**Formula adjusted, standardized to suit performance parameters

pH buffer

A slightly more complicated system:

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?