The Common Ion Effect

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is an example of LeChatelier's principle

the presence of its conjugate base suppresses the ionization of a weak acid

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Conjugate base suppresses ionization of a weak acid

Consider an aqueous solution containing 1*M* acetic acid (K_a = 1.8 x 10^{-5}).

$$\text{H}-\text{OAc (aq)} \rightleftharpoons \text{H}^+\text{(aq)} + \text{AcO}^-\text{(aq)}$$

$$1.8 \times 10^{-5} = \frac{x^2}{1 - x}$$

$x = [H^+] = 4.2 \times 10^{-3}$ *M* pH = 2.37

Conjugate base suppresses ionization of a weak acid

Consider an aqueous solution containing 1*M* acetic acid (K_a = 1.8 x 10^{-5}).

$$H-OAc\,(aq) \rightleftharpoons H^+\,(aq) + \boxed{AcO^-\,(aq)}$$

LeChatelier's principle (qualitative)

AcO^- increases; position of equilibrium shifts to the left

$$\longleftarrow$$

Conjugate base suppresses ionization of a weak acid

Consider an aqueous solution containing 1*M* acetic acid and 1*M* acetate ion

$$\mathrm{H{-}OAc\,(aq)} \rightleftharpoons \mathrm{H^{+}\,(aq)} + \boxed{\mathrm{AcO^{-}\,(aq)}}$$

$$1.8 \times 10^{-5} = \frac{(x)\,(1 + x)}{1 - x}$$

$$1.8 \times 10^{-5} = x = [H^{+}] \qquad \mathrm{pH} = 4.74$$

Henderson-Hasselbalch Equation

$$HA\,(aq) \rightleftharpoons H^+\,(aq) + A^-(aq)$$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} \qquad K_a = [H^+] \times \frac{[A^-]}{[HA]}$$

$$\log K_a = \log\,[H^+] + \log \frac{[A^-]}{[HA]}$$

$$-\log\,[H^+] = -\log K_a + \log \frac{[A^-]}{[HA]}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

General form of Henderson-Hasselbalch equation

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

$$\boxed{\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{conj.base}]}{[\mathrm{acid}]}}$$

Example

What is the pH of a solution that is 0.30 *M* in HCOOH and 0.52 *M* in HCOOK?

$(K_a = 1.7 \times 10^{-4})$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{c.base}]}{[\text{acid}]}$$

$$-\log[\text{H}^+] = -\log(1.7 \times 10^{-4}) + \log \frac{(0.52)}{(0.30)}$$

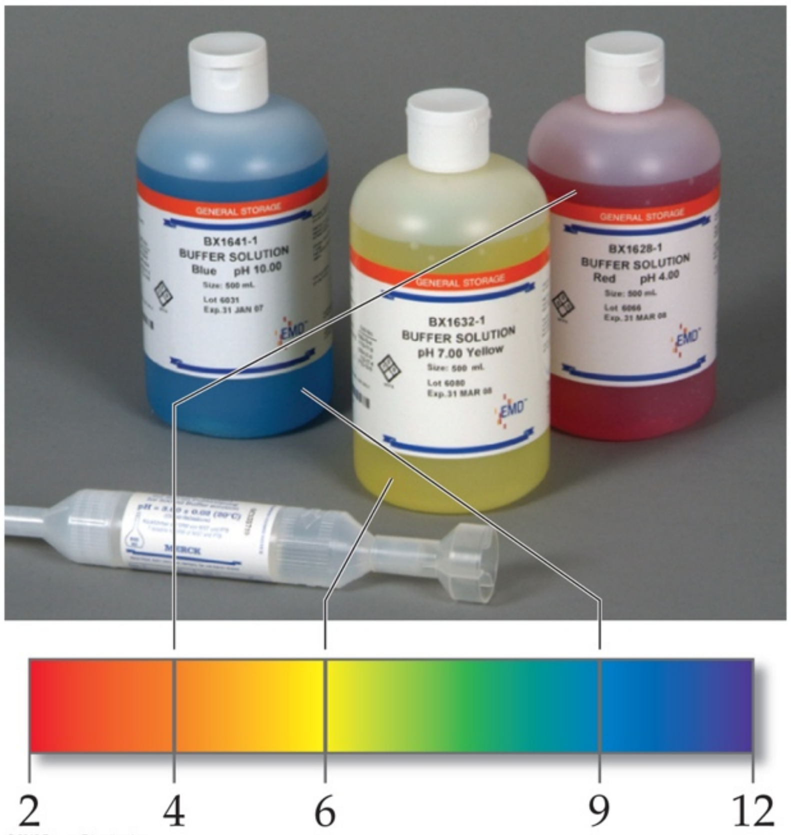
$$\text{pH} = 3.77 + 0.23 = \boxed{4.0}$$

Buffer Solutions

- **resist changes in pH upon the addition of small amounts of either acid or base**

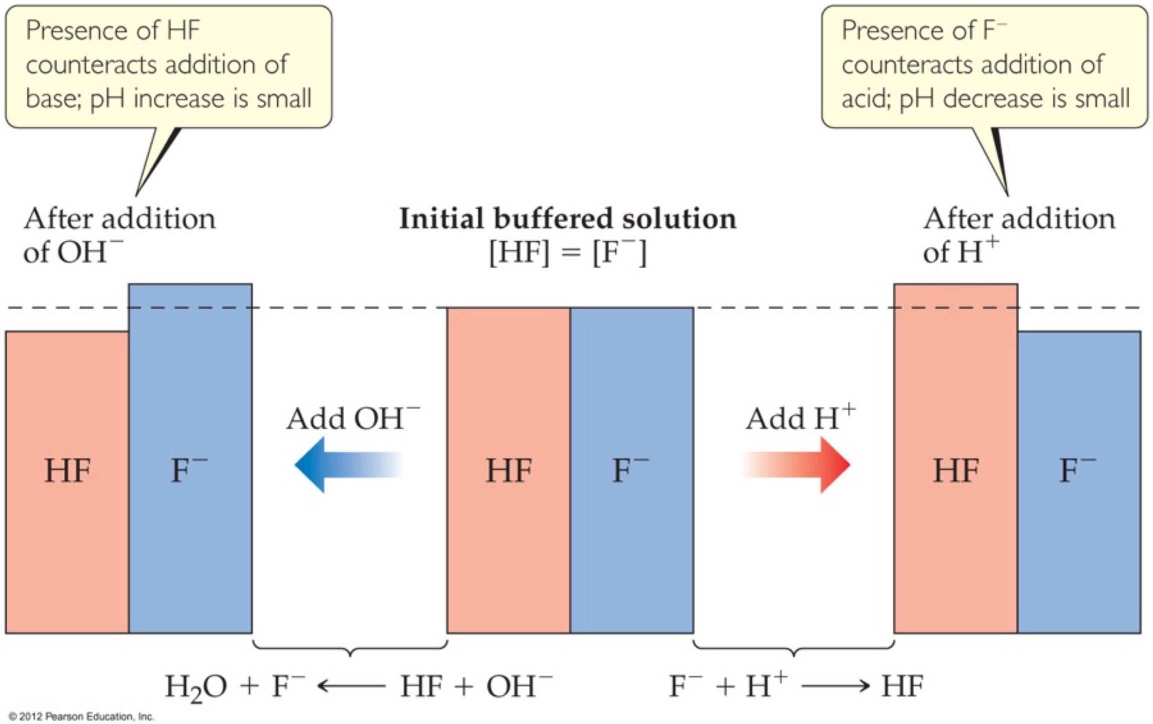
- **contain a weak acid or base and its salt (both must be present)**

Buffers



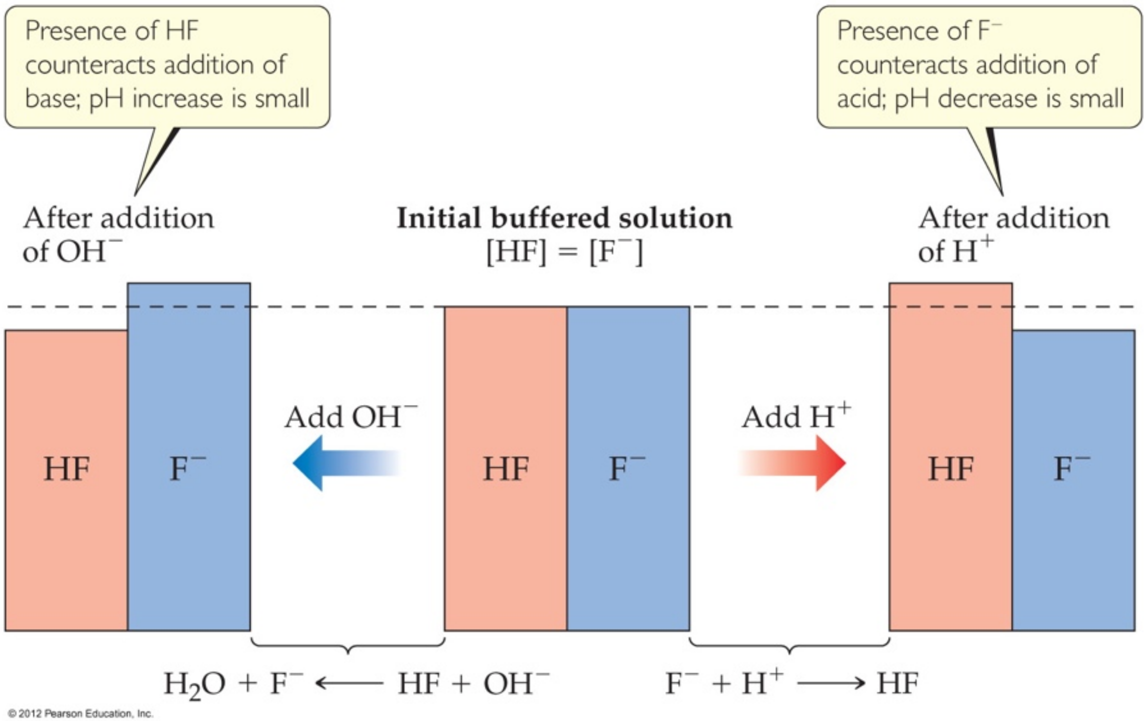
- Buffers are solutions of a weak conjugate acid–base pair.
- They are particularly resistant to pH changes, even when strong acid or base is added.

Buffers



If a small amount of hydroxide is added to an equimolar solution of HF in NaF, for example, the HF reacts with the OH^- to make F^- and water.

Buffers



Similarly, if acid is added, the F^- reacts with it to form HF and water.

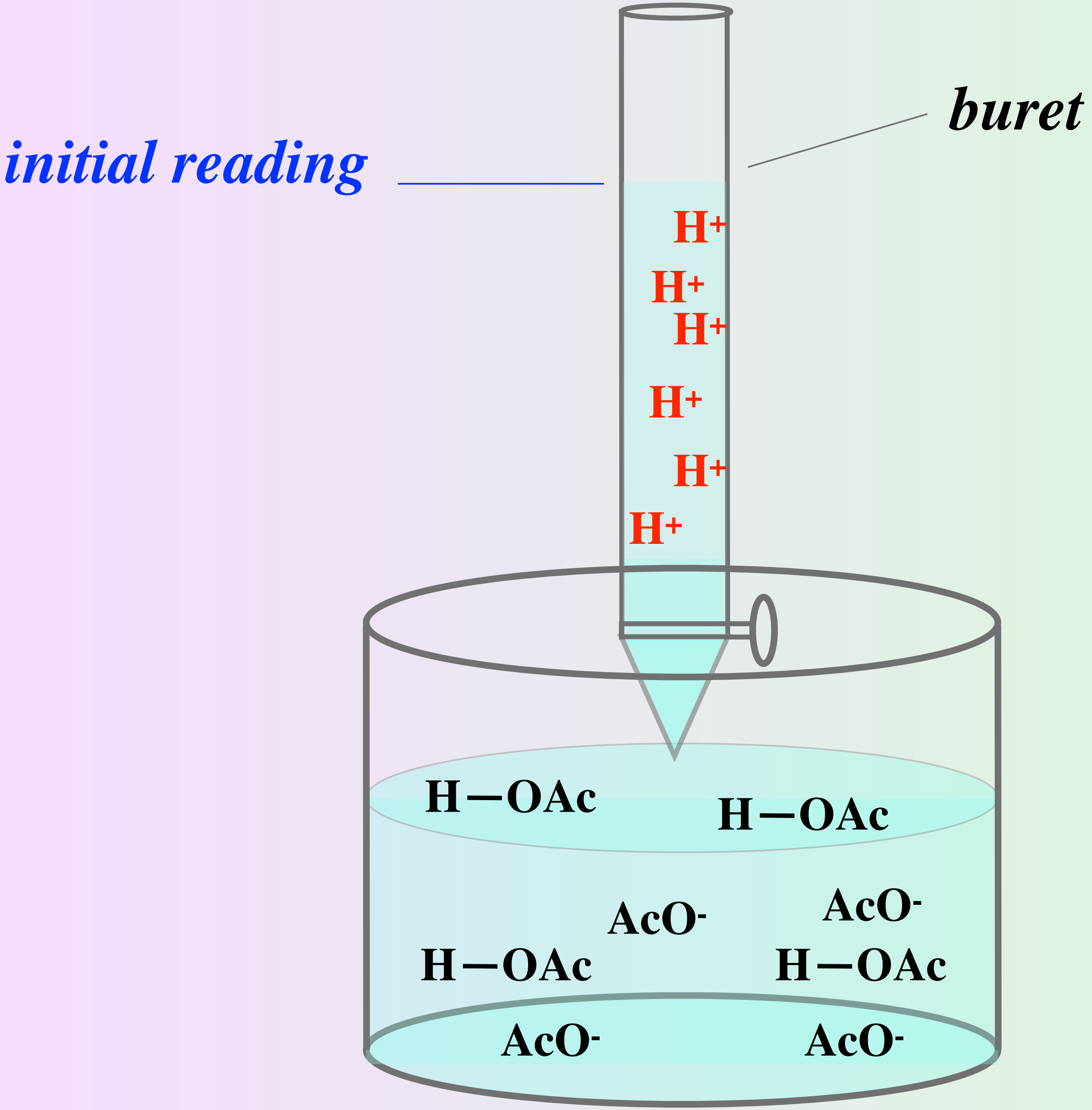
Aqueous Equilibria

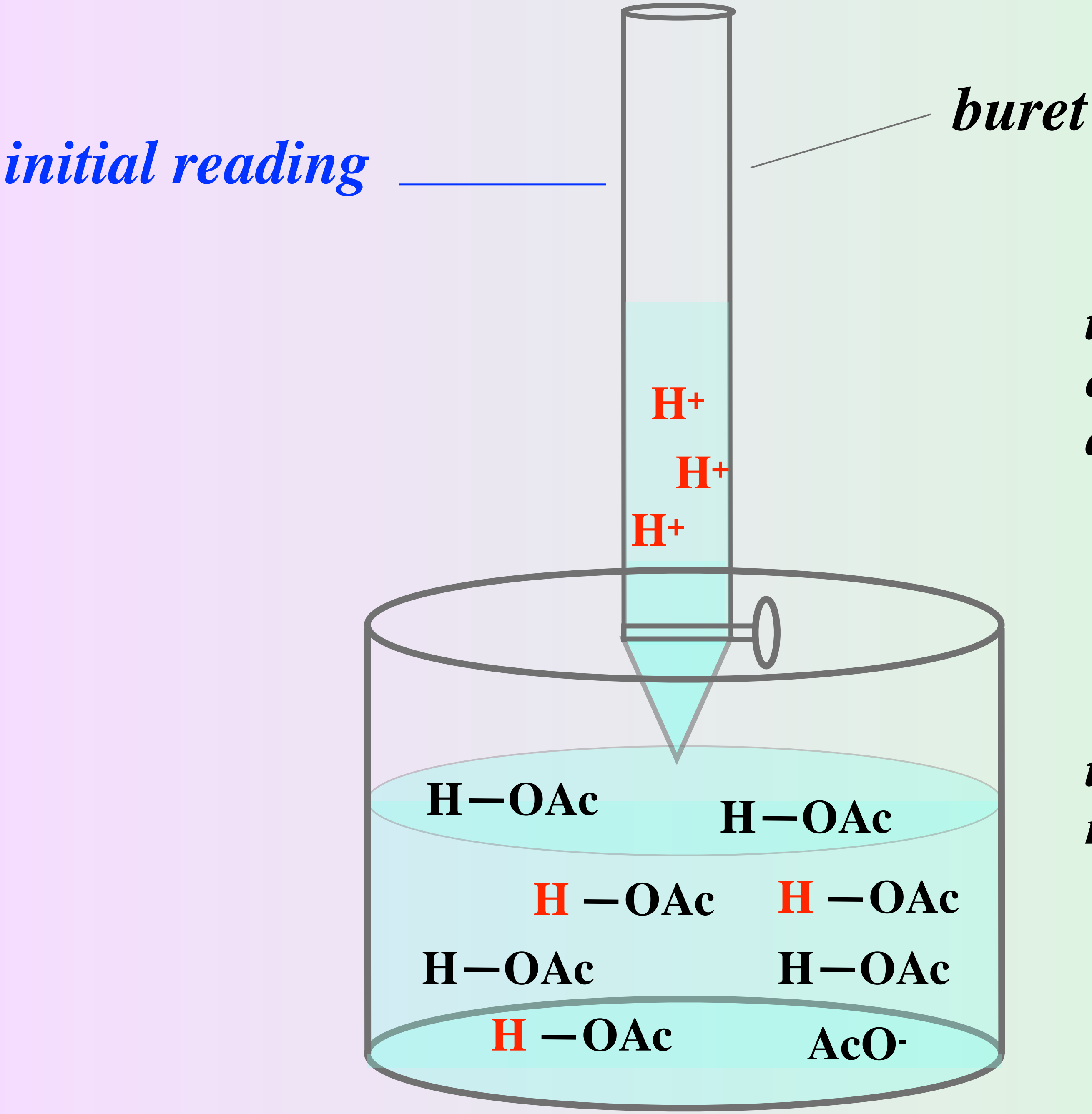
How a sodium acetate/ acetic acid buffer buffers

the chemistry

$$H-OAc \qquad\qquad AcO^{-}$$

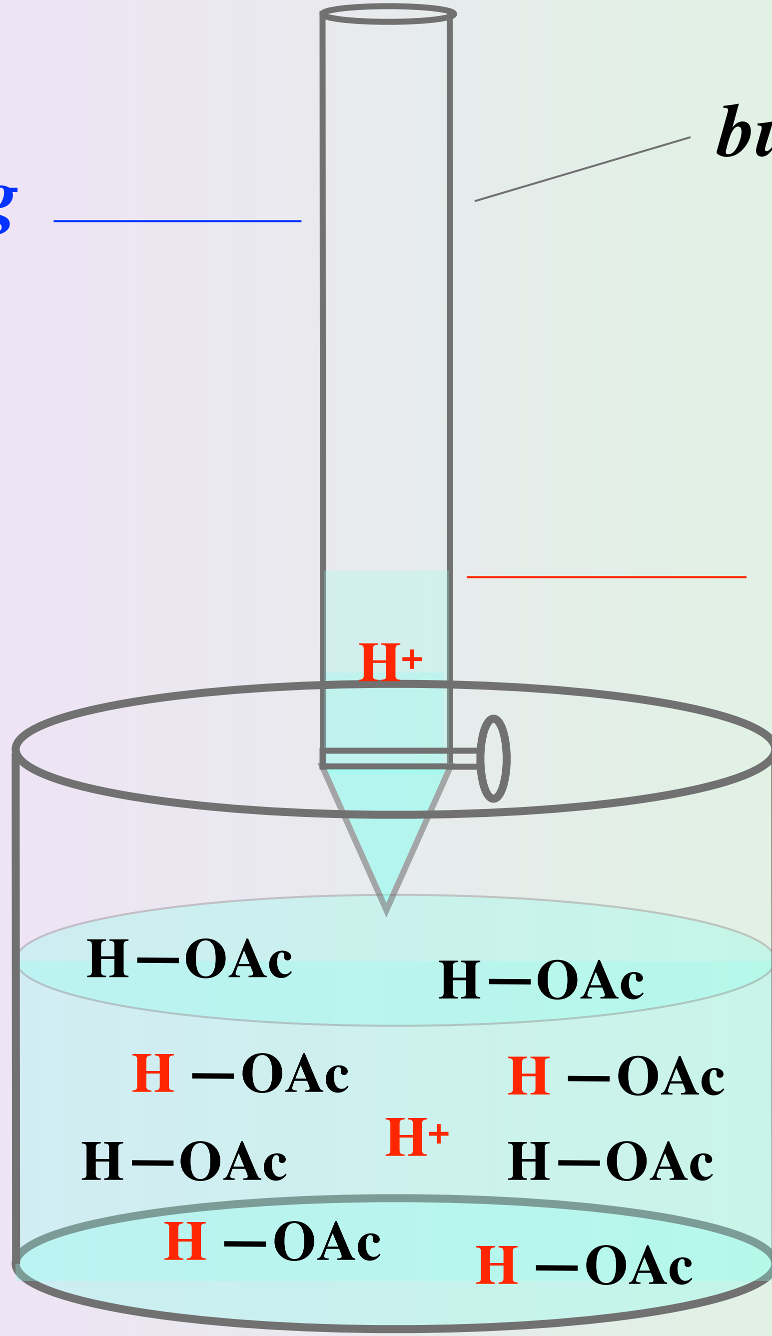
$$AcO^{-} \xrightarrow{H^{+}} H-OAc$$


initial reading
buret
H+
H+
H+
H+
H+
H+
H—OAc
H—OAc
AcO-
AcO-
H—OAc
H—OAc
AcO-
AcO-

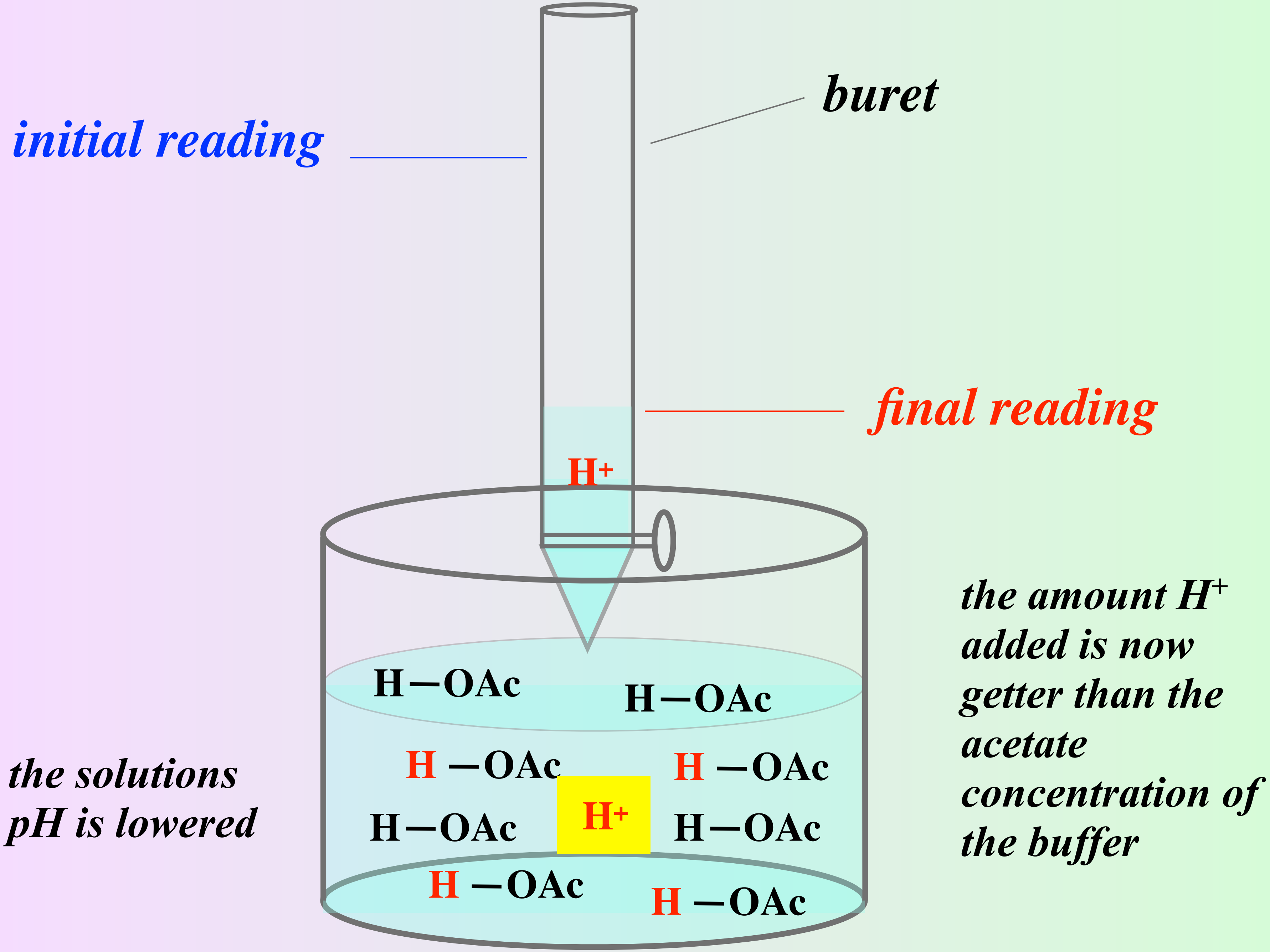


the H$^+$ added gets consumed by the acetate

the solutions pH is not lower by much



the amount H^+ added is now getter than the acetate concentration of the buffer



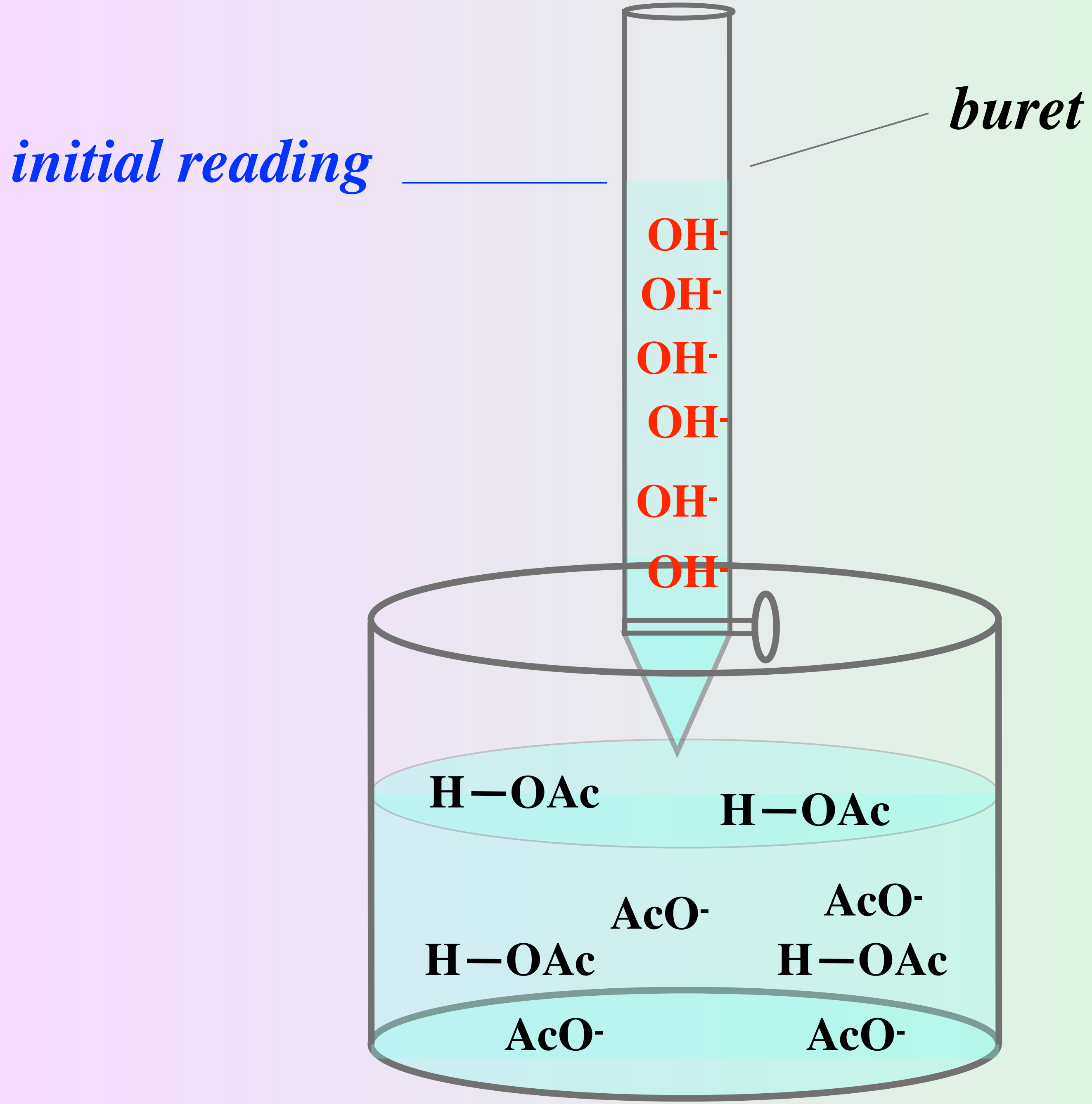
initial reading
buret
final reading
H+
H—OAc
H—OAc
H —OAc
H —OAc
H+
H—OAc
H—OAc
H —OAc
H —OAc
the solutions pH is lowered
the amount H+ added is now getter than the acetate concentration of the buffer

How a sodium acetate/ acetic acid buffer buffers

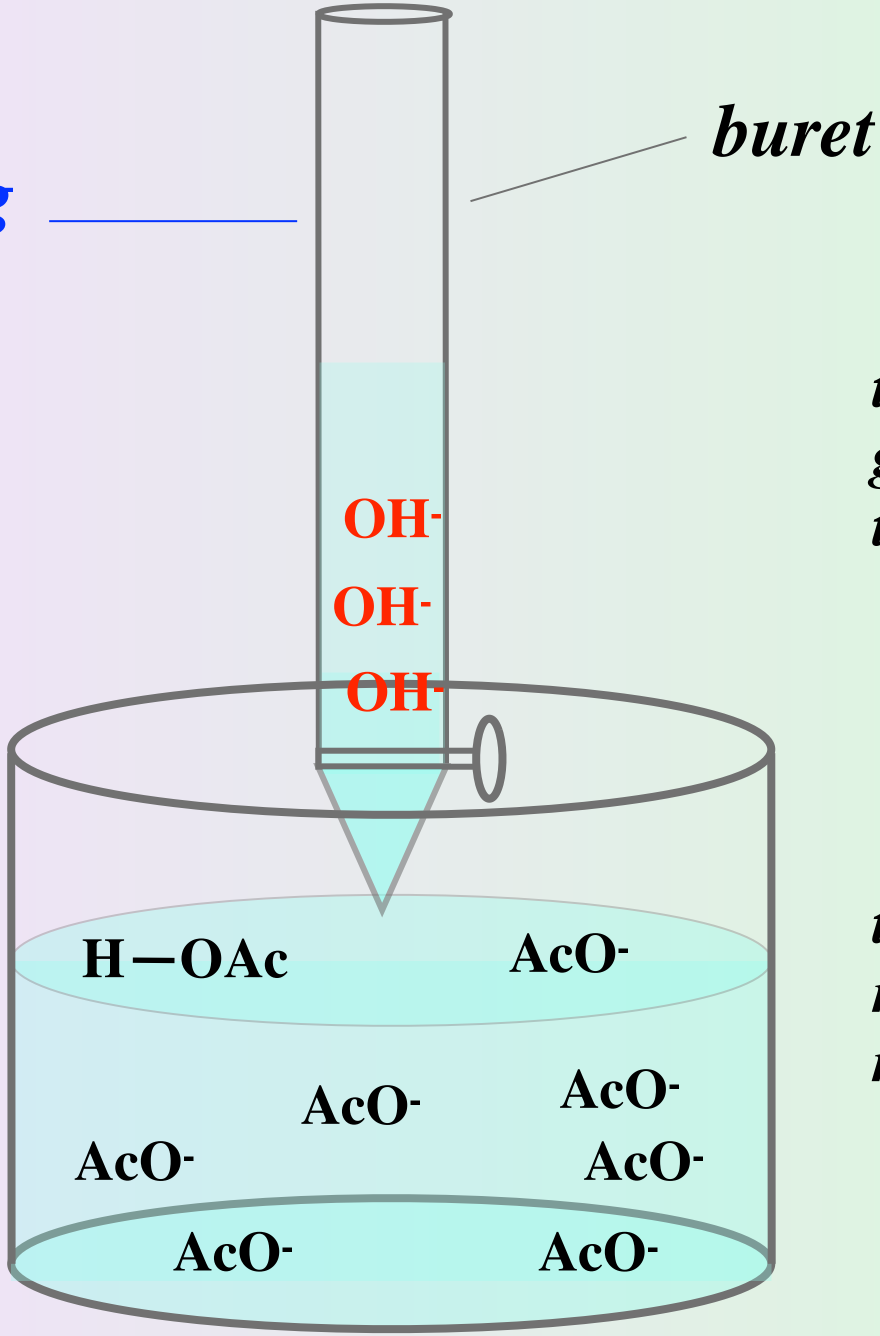
the chemistry

H − OAc AcO$^-$

$$\text{H}-\text{OAc} \xrightarrow{\text{HO}^-} \text{AcO}^-$$

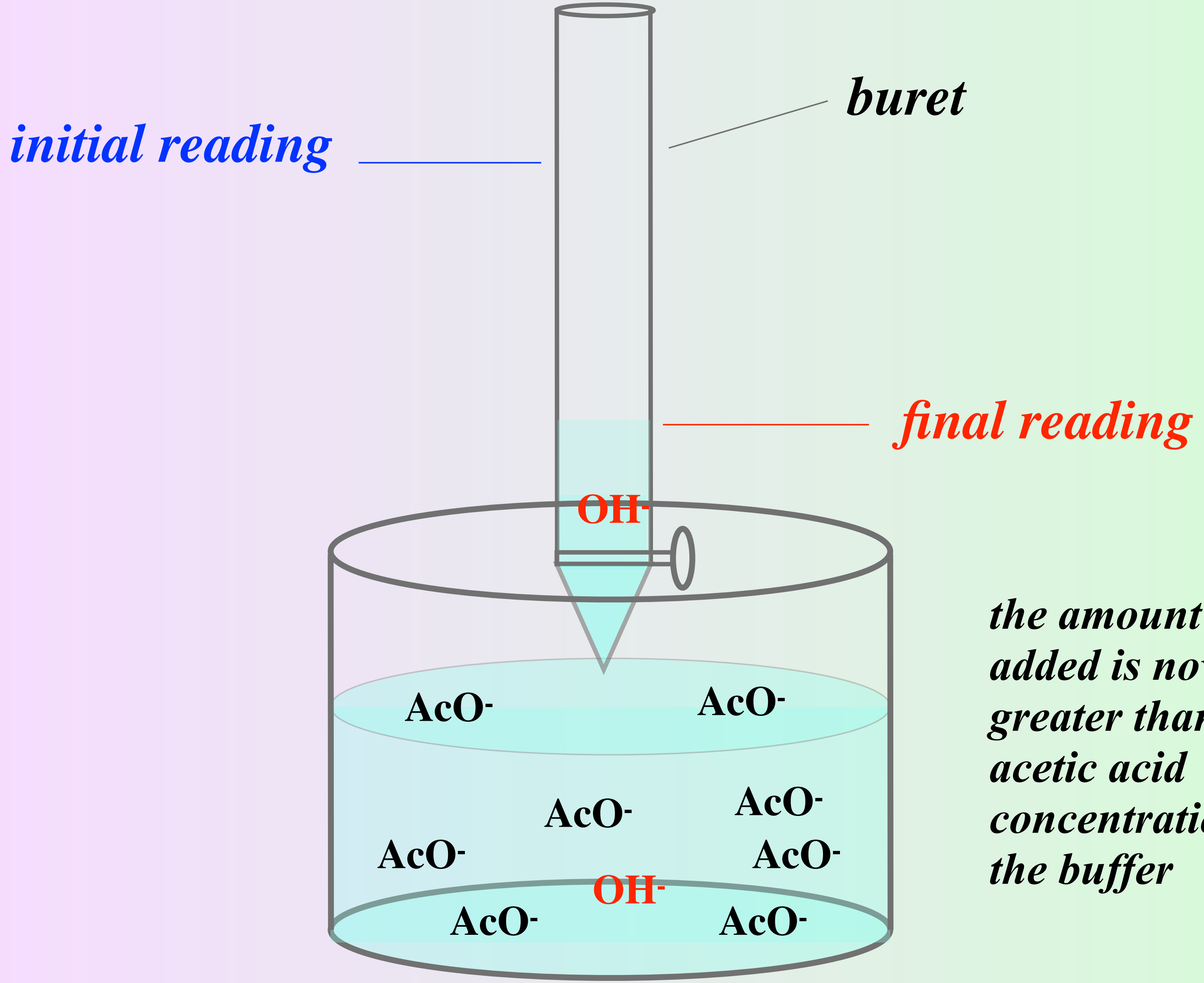

initial reading
buret
OH-
OH-
OH-
OH-
OH-
OH-
H—OAc
H—OAc
AcO-
AcO-
H—OAc
H—OAc
AcO-
AcO-

initial reading

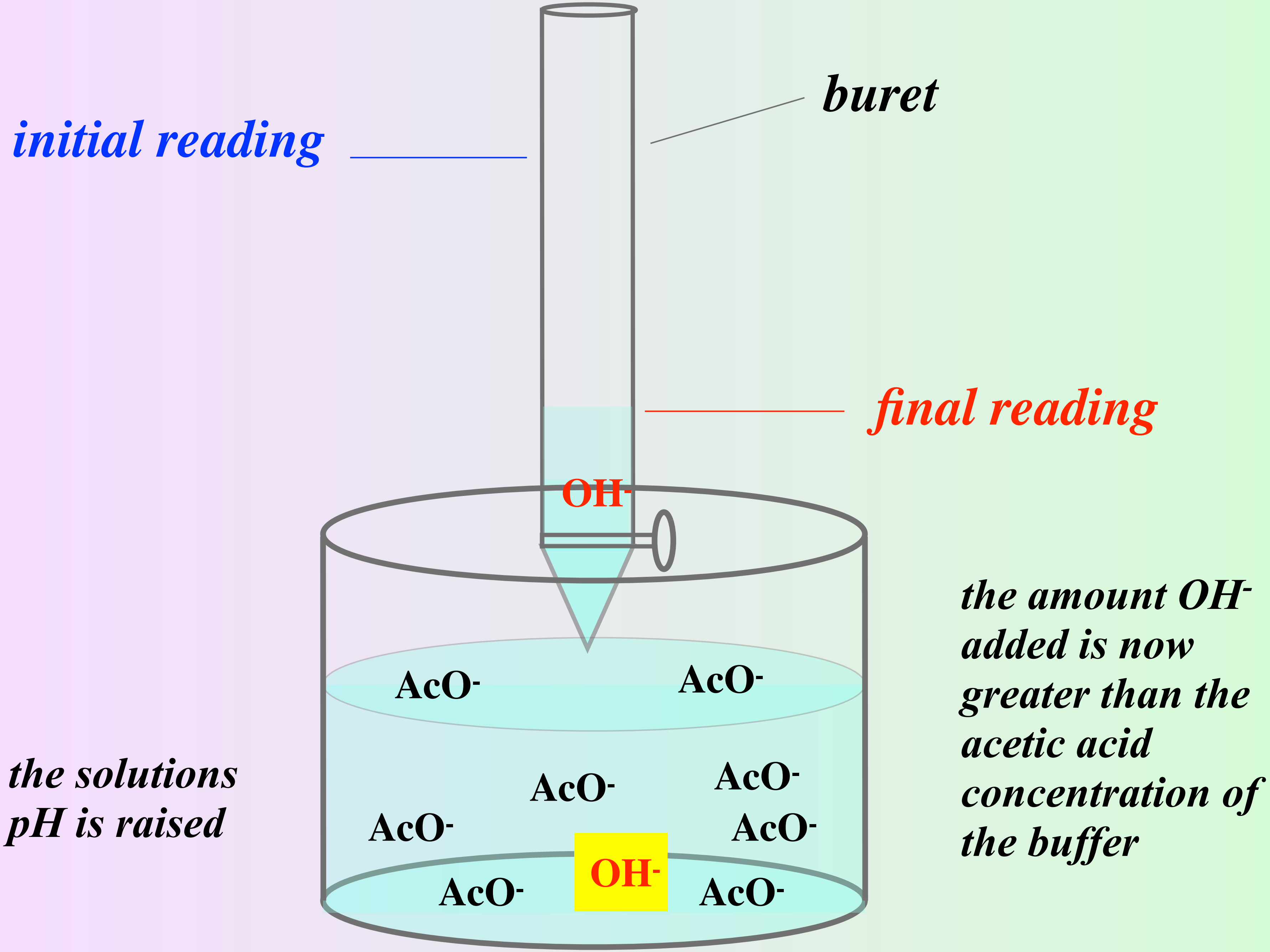


the OH^- added gets consumed by the acetic acid

the solutions pH is not raised by much



the amount OH^- added is now greater than the acetic acid concentration of the buffer



initial reading
buret
final reading
OH-
AcO-
AcO-
AcO-
AcO-
AcO-
AcO-
OH-
AcO-
AcO-
the amount OH- added is now greater than the acetic acid concentration of the buffer
the solutions pH is raised

How a sodium acetate/ acetic acid buffer buffers

the mathematics

$$K_a = \frac{[H^+]\ [AcO^-]}{[HOAc]}$$

$$K_a \times \frac{[HOAc]}{[AcO^-]} = [H^+]$$

$$K_a \times \frac{[HOAc]}{[AcO^-]} = [H^+]$$

$$-\log [H^+] = -\log K_a - \log \frac{[HOAc]}{[AcO^-]}$$

$$pH = pK_a - \log \frac{[HOAc]}{[AcO^-]}$$

or

$$pH = pK_a + \log \frac{[AcO^-]}{[HOAc]}$$

Example

Which of the following are buffer systems?

(a) KF / HF — **yes; HF is a weak acid and F- is its conjugate base**

(b) KBr/ HBr — **no; HBr is a strong acid**

(c) Na_2CO_3/ $NaHCO_3$ — **yes; HCO_3^- is a weak acid and CO_3^{2-} is its conjugate base**

Calculate the pH of a buffer containing 1.0 *M* acetic acid and 1.0 *M* sodium acetate.

$$\mathrm{H{-}OAc\,(aq)} \rightleftharpoons \mathrm{H^+\,(aq)} + \mathrm{AcO^-\,(aq)}$$

$$1.0\ \mathrm{M}\ \ -x \qquad\qquad x \qquad\qquad 1.0\ \mathrm{M}\ \ +x$$

$$K_a = \frac{[\mathrm{H^+}]\,[\mathrm{AcO^-}]}{[\mathrm{HOAc}]}$$

$$1.8 \times 10^{-5} = \frac{[\mathrm{H^+}](1.0 + x)}{(1.0 - x)}$$

$$1.8 \times 10^{-5} = \frac{[\mathrm{H^+}]\cancel{(1.0)}}{\cancel{(1.0)}}$$

$$1.8 \times 10^{-5} = x = [\mathrm{H^+}]$$

$$\boxed{\mathrm{pH} = 4.74}$$

Calculate the pH of a buffer containing 1.0 *M* acetic acid and 1.0 *M* sodium acetate.

pH = 4.7

What happens when 0.10 mol of gaseous HCl is added to 1.0 L of this solution?

add 0.10 mol of HCl(g) to 1.0 L of a solution that is 1.0 *M* in NaOAc and HOAc

$$H^{+}(aq) \quad + \quad AcO^{-}(aq) \longrightarrow H-OAc(aq)$$

0.1 mol	**1.0 mol**	**1.0 mol**
↓	↓	↓
≅ 0.0 mol	**0.9 mol**	**1.1 mol**

$$H^+(aq) + AcO^-(aq) \rightleftharpoons H-OAc(aq)$$

$\cong$ 0.0 mol   0.9 mol   1.1 mol

$$H-OAc(aq) \rightleftharpoons AcO^-(aq) + H^+(aq)$$

$$\frac{1.1\text{ mol}}{1\text{L}} \qquad \frac{0.9\text{ mol}}{1\text{L}}$$

$$K_a = \frac{[H^+]\,[AcO^-]}{[HOAc]} \qquad 1.8 \times 10^{-5} = \frac{[H^+]\,(0.9)}{(1.1)}$$

$$[H^+] = 2.2 \times 10^{-5}\text{ M}$$

pH = 4.66

Same calculation using the Henderson-Hasselbalch equation

$$H-OAc\,(aq) \rightleftharpoons AcO^-\,(aq) + H^+(aq)$$

1.1 mol　　　　　　　　0.9 mol

$$pH = pK_a + \log \frac{[\text{c.base}]}{[\text{acid}]}$$

$$pH = -\log K_a + \log \frac{(0.9)}{(1.1)}$$

$$pH = 4.74 - 0.09 = \boxed{4.65}$$

Calculate the pH of a buffer containing 1.0 *M* acetic acid and 1.0 *M* sodium acetate.

pH = 4.7

What happens when 0.10 mol of gaseous HCl is added to 1.0 L of this solution?

pH = 4.66

What happens when 0.10 mol of solid NaOH is added to 1.0 L of this solution?

add 0.10 mol of NaOH(s) to 1.0 L of a solution that is 1.0 *M* in NaOAc and HOAc

$$OH^- + H-OAc \longrightarrow H_2O + AcO^-$$

0.1 mol	1.0 mol	1.0 mol
↓	↓	↓
≅ 0.0 mol	0.9 mol	1.1 mol

$$OH^- + H-OAc \rightleftharpoons H_2O + AcO^-$$

$\cong$ 0.0 mol   0.9 mol   1.1 mol

$$H-OAc \rightleftharpoons H^+ + AcO^-$$

$$\frac{0.9\text{ mol}}{1L} \qquad x \qquad \frac{1.1\text{ mol}}{1L}$$

$$K_a = \frac{[H^+]\,[AcO^-]}{[HOAc]} \qquad 1.8 \times 10^{-5} = \frac{[H^+]\,(1.1)}{(0.9)}$$

$$[H^+] = 1.47 \times 10^{-5}\text{ M}$$

pH = 4.83

Same calculation using the Henderson-Hasselbalch equation

$$\text{H}-\text{OAc} \rightleftharpoons \text{H}^+ + \text{AcO}^-$$

0.9 mol x 1.1 mol

$$\text{pH} = \text{p}K_a + \log \frac{[\text{c.base}]}{[\text{acid}]}$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) + \log \frac{(1.1)}{(0.9)}$$

$$\text{pH} = 4.74 + 0.09 = \boxed{4.83}$$

Calculate the pH of a buffer containing 1.0 M acetic acid and 1.0 M sodium acetate.

pH = 4.7

What happens when 0.10 mol of gaseous HCl is added to 1.0 L of this solution?

pH = 4.66

What happens when 0.10 mol of solid NaOH is added to 1.0 L of this solution?

pH = 4.83

Example

Calculate the pH of the 0.30 *M* NH_3/0.36 M NH_4Cl buffer system.

$$NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$$

$$K_a = \frac{[H^+][NH_3]}{[NH_4^+]}$$

$$5.6 \times 10^{-10} = \frac{[H^+](0.30)}{(0.36)}$$

$$[H^+] = 6.72 \times 10^{-10}$$

pH = 9.17

Same calculation using the Henderson-Hasselbalch equation

$$NH_4^+ (aq) \rightleftharpoons H^+(aq) + NH_3 (aq)$$

$$pH = pK_a + \log \frac{[\text{c.base}]}{[\text{acid}]}$$

$$pH = -\log (5.6 \times 10^{-10}) + \log \frac{(0.30)}{(0.36)}$$

$$pH = 9.25 - 0.08 = \boxed{9.17}$$

Example (cont.)

Calculate the pH after adding 20.0ml of 0.05 *M* NaOH to 80.0 ml of the 0.30*M* NH_3/0.36 M NH_4Cl buffer system.

$$NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$$

$$.080\ L \times \frac{0.30\ mol\ NH_3}{1L} = 0.0240 mol$$

$$.080\ L \times \frac{0.36\ mol\ NH_4^+}{1L} = 0.0288 mol$$

$$.020\ L \times \frac{0.05\ mol\ HO^-}{1L} = 0.001 mol$$

Example (cont.)

Calculate the pH after adding 20.0ml of 0.050 *M* NaOH to 80.0 ml of the 0.30*M* NH_3/0.36 M NH_4Cl buffer system.

$$NH_4^+ (aq) + OH^- (aq) \rightleftharpoons H_2O (aq) + NH_3 (aq)$$

0.0288mol	0.001 mol	0.0240mol
↓	↓	↓
0.0278 mol	0.000 mol	0.0250 mol

Example (cont.)

Calculate the pH after adding 20.0ml of 0.050 *M* NaOH to 80.0 ml of the 0.30*M* NH_3/0.36 M NH_4Cl buffer system.

$$NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$$

0.0278 mol 0.025 mol

$$pH = pK_a + \log \frac{[\text{c.base}]}{[\text{acid}]}$$

$$pH = -\log(5.6 \times 10^{-10}) + \log \frac{\dfrac{(0.025\text{ mol})}{0.10\text{ L}}}{\dfrac{(0.0278\text{ mol})}{0.10\text{L}}}$$

Example (cont.)

Calculate the pH after adding 20.0ml of 0.050 *M* NaOH to 80.0 ml of the 0.30*M* NH_3/0.36 M NH_4Cl buffer system.

$$NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$$

0.0278 mol 0.025 mol

$$pH = pK_a + \log \frac{[\text{c.base}]}{[\text{acid}]}$$

$$pH = -\log(5.6 \times 10^{-10}) + \log \frac{0.0025}{0.00278}$$

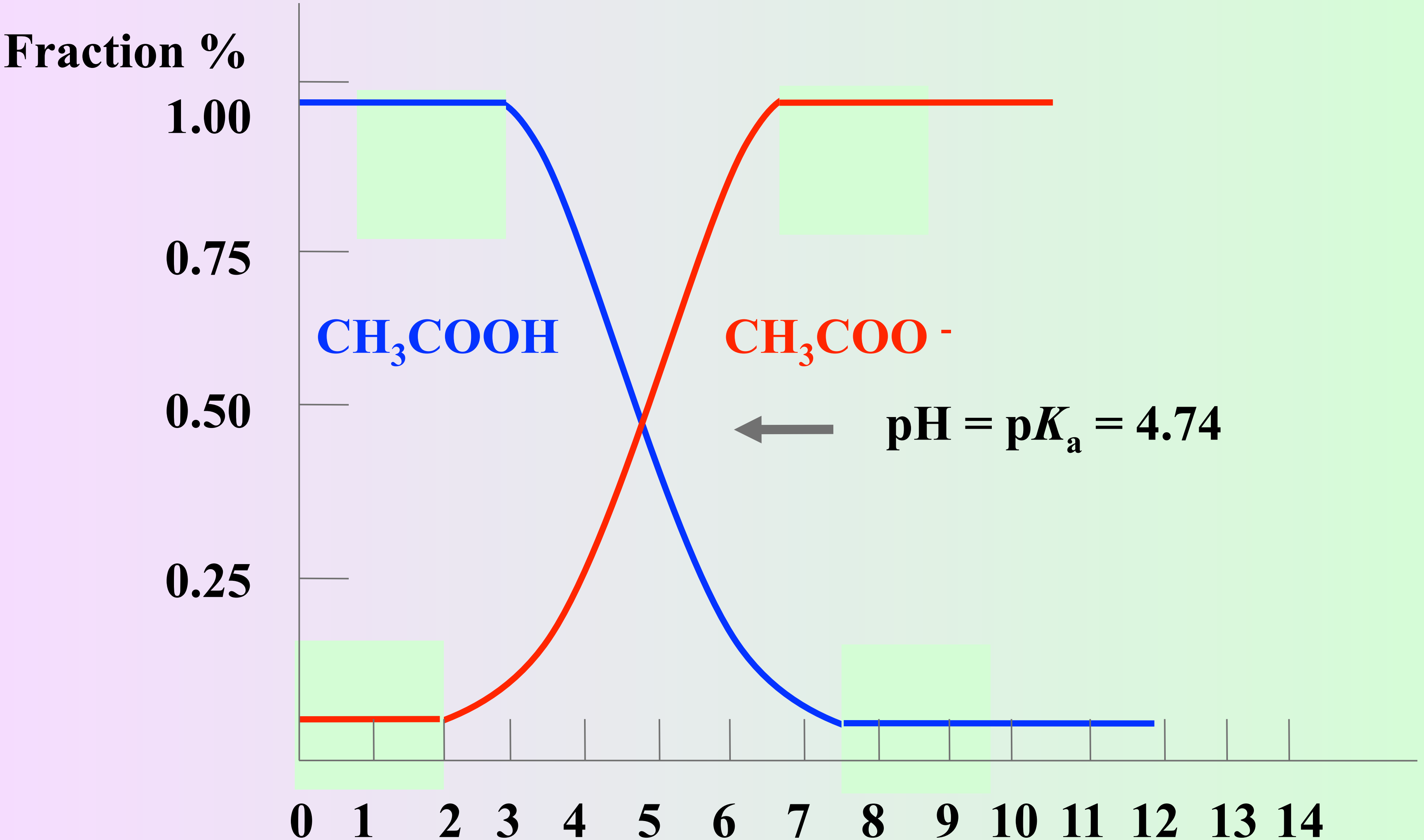
$$pH = 9.25 - 0.05 = \boxed{9.20}$$

Distribution Curves

Show the fraction of each species present as a function of pH

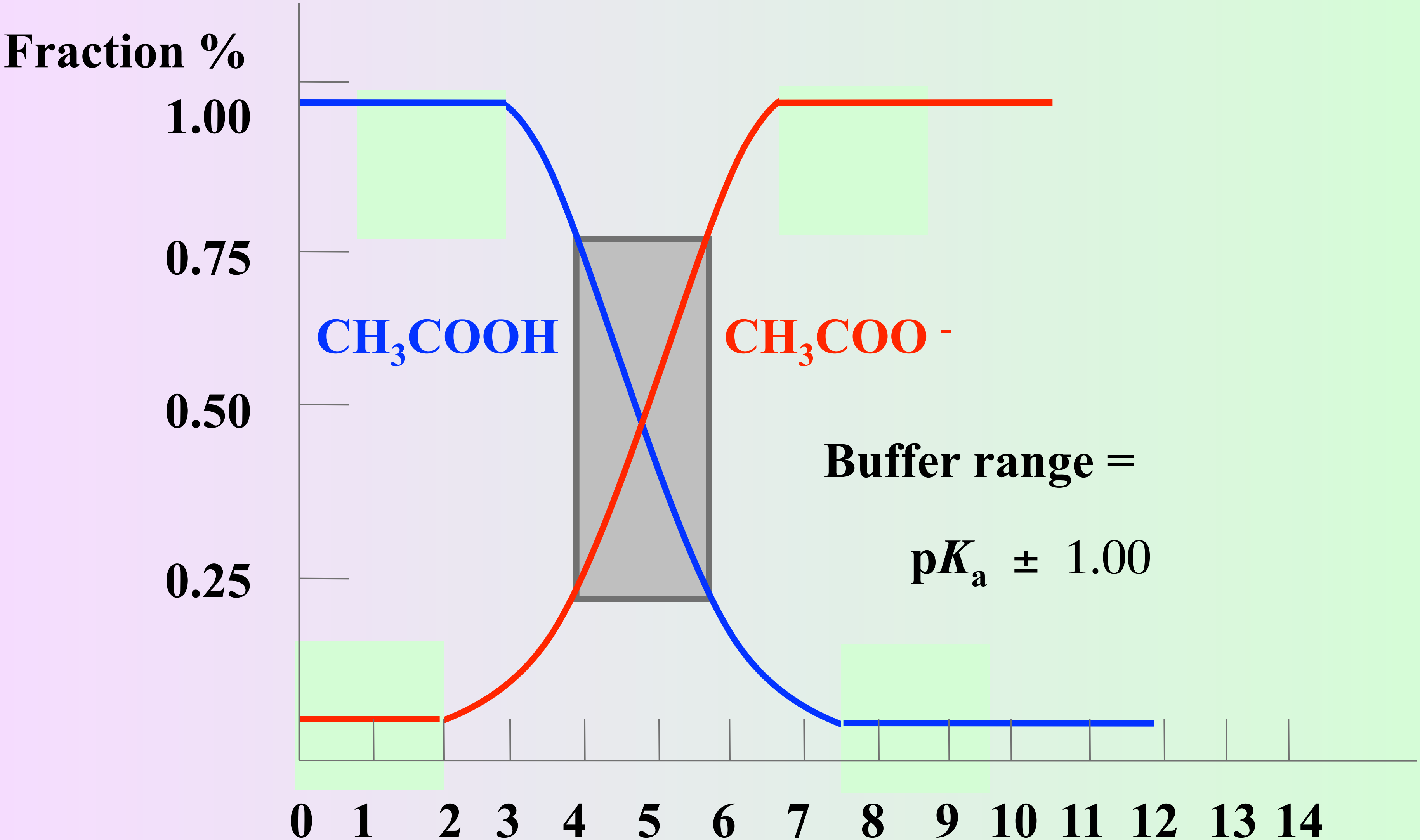
acid and conjugate base

base and conjugate acid



distribution curves for acidic acid and acetate ion as a function of pH

pH

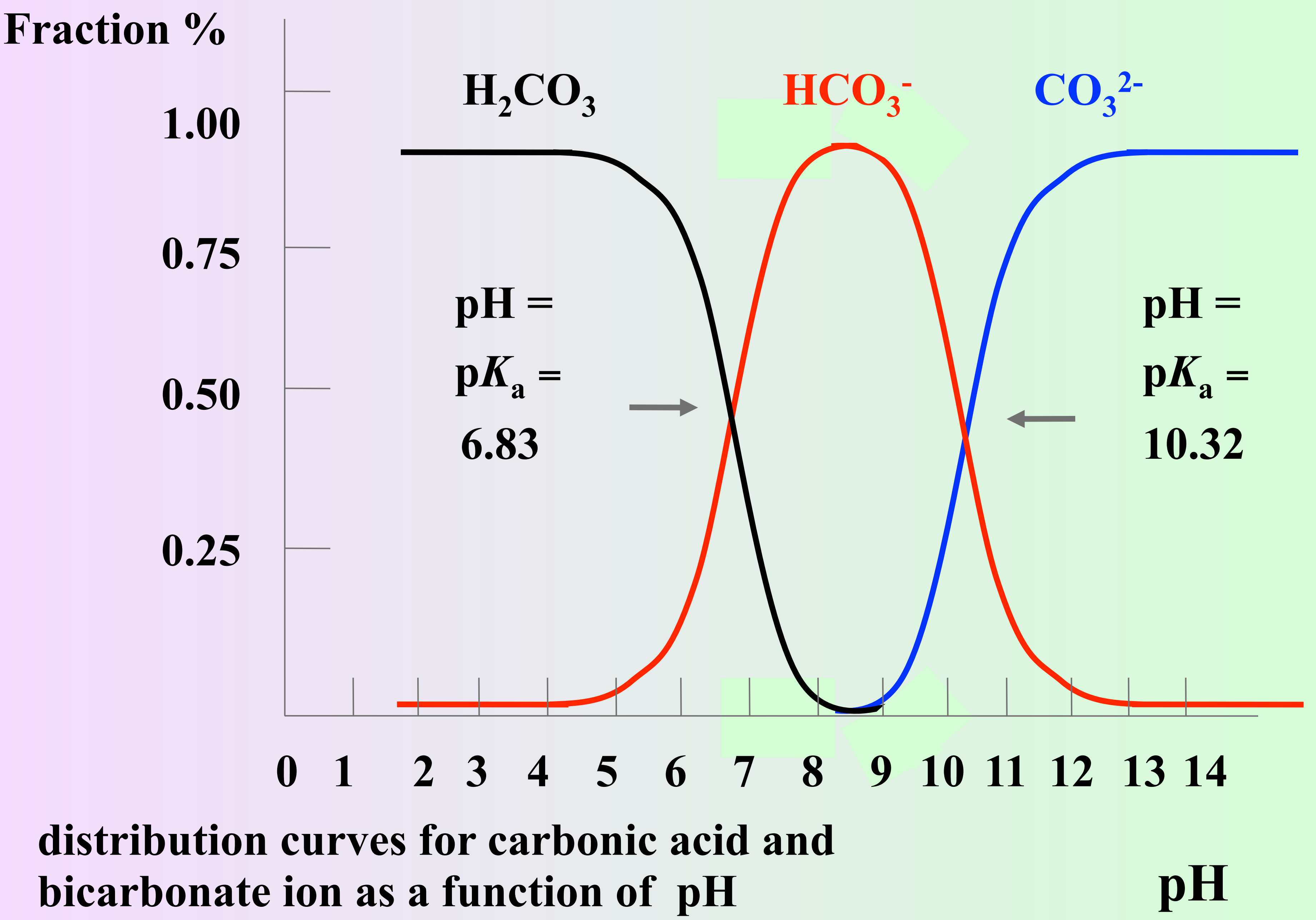


distribution curves for acidic acid and acetate ion as a function of pH

pH

The bicarbonate/carbonate acid buffer is more complicated because carbonic acid is a diprotic acid.

It is important because it contributes to controlling the pH of blood at 7.4.



distribution curves for carbonic acid and bicarbonate ion as a function of pH

Preparing a Buffer Solution with a Specific pH

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\text{c.base}]}{[\text{acid}]}$$

- center of buffer range: [acid] = [base] and pH = pK_a

- choose a weak acid/conjugate base combination where the pK_a of the acid corresponds to the pH at which you want the solution buffered

How would you prepare a liter of "carbonate buffer" at a pH of 10.10 ?

you have available:

H_2CO_3	pK_a 6.38
$\boxed{NaHCO_3}$	$\boxed{pK_a\ 10.32}$
Na_2CO_3	

Pick $NaHCO_3$ and its conjugate base.

How would you prepare a liter of "carbonate buffer" at a pH of 10.10 ?

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{c.base}]}{[\mathrm{acid}]}$$

$$10.10 = 10.32 + \log \frac{[\mathrm{Na_2CO_3}]}{[\mathrm{NaHCO_3}]}$$

$$\frac{[\mathrm{Na_2CO_3}]}{[\mathrm{NaHCO_3}]} = 10^{-0.22} = 0.60$$

The shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance is called the common ion effect.