



Unit 8

Acids & Bases

8.1 Introduction to Acids & Bases

8.2 pH & pOH of Strong Acids & Bases

- Autoionization of Water
- pH of Strong Acids
- pOH & pH of Strong Bases

Terminology

Arrhenius *(what you learned last year)*

- Acid: substances that dissolve in water to form H^+
- Base: substances that dissolve in water to form OH^-

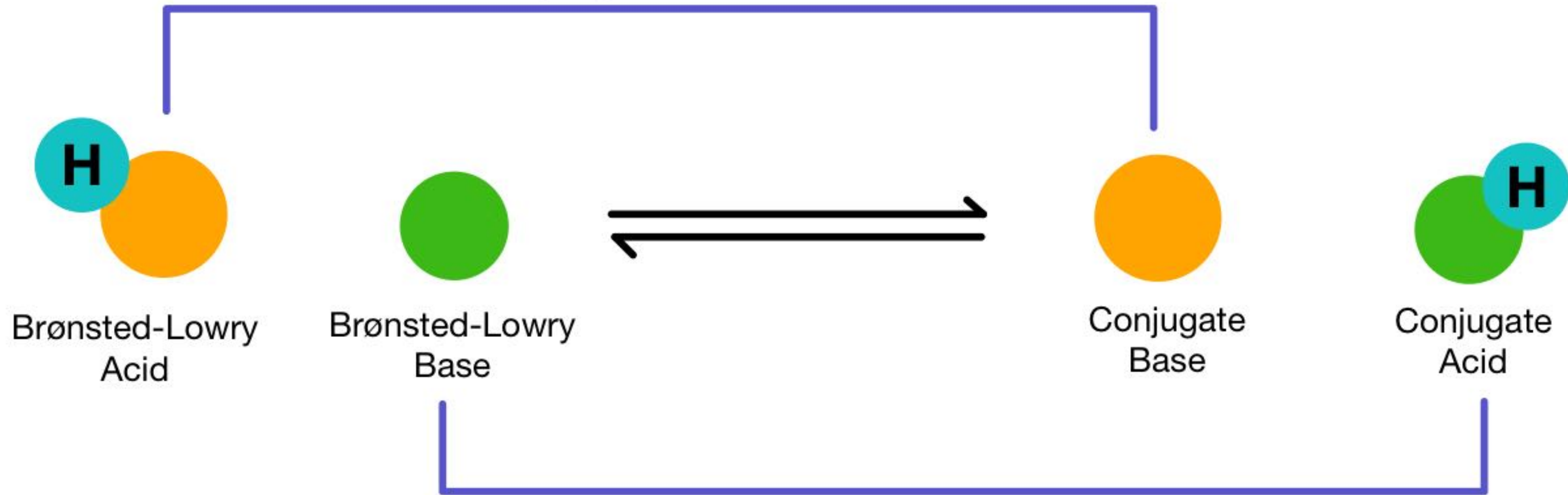
Brønsted-Lowry *(transfer of H^+ during an acid-base reaction)*

- Acid: donates H^+
- Base: accepts H^+



Conjugate Pairs

Conjugate Pair



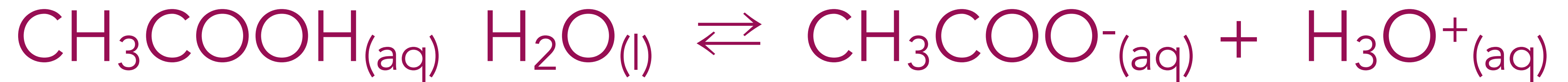
Conjugate Pair



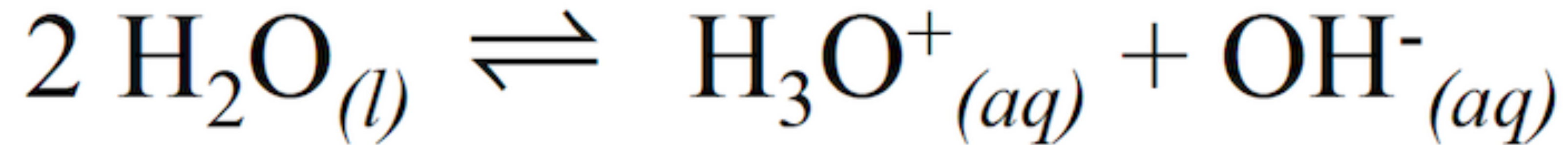
Example: Conjugate Pairs

Label the conjugate acid-base pairs in the reaction.

In a conjugate pair, the acid will always have one more proton than its conjugate base - making it easier to predict formulas



Autoionization of Water



In pure water at 25°C,

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ and } [\text{OH}^-] = 1.0 \times 10^{-7}.$$

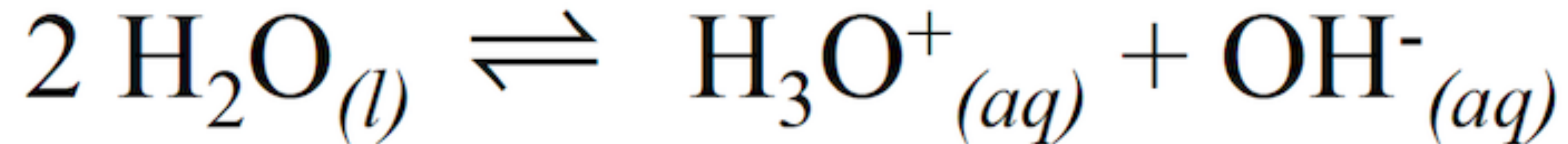
As $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ the solution is neutral.

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-]$$

$$K_w = (1.0 \times 10^{-7}) (1.0 \times 10^{-7})$$

$$K_w = 1.0 \times 10^{-14} \quad (\text{at } 25 \text{ }^\circ\text{C})$$

Autoionization of Water



$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 1.0 \times 10^{-14} \quad (\text{at } 25 \text{ }^\circ\text{C})$$

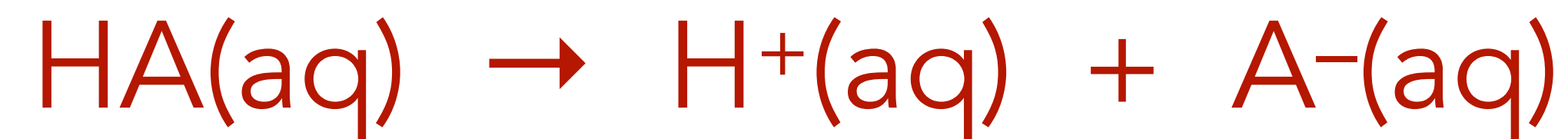
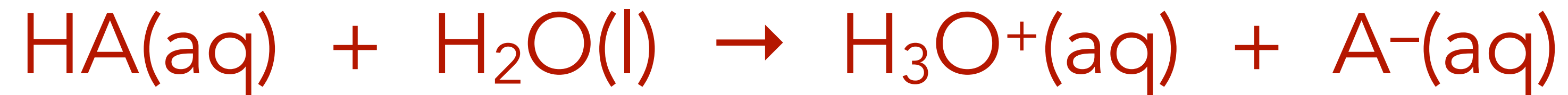
- This is a constant.
- If you know the concentration of $[\text{H}_3\text{O}^+]$ you can calculate the concentration of $[\text{OH}^-]$ or vice versa.
- Memorize this constant! It's very useful.

Example: Autoionization of Water

- The concentration of OH^- in a solution is found to be $1.4 \times 10^{-11} \text{ M}$ at 25°C .
Find $[\text{H}_3\text{O}^+]$

H⁺ and H₃O⁺

- Equations for acids can be written as:



Hydrogen ion, H⁺, and hydronium ion, H₃O⁺, are used interchangeably for the aqueous ion of hydrogen.

pH = $-\log[\text{H}^+]$ and pOH = $-\log[\text{OH}^-]$

$$[\text{H}^+] = 10^{-\text{pH}} \text{ M}$$

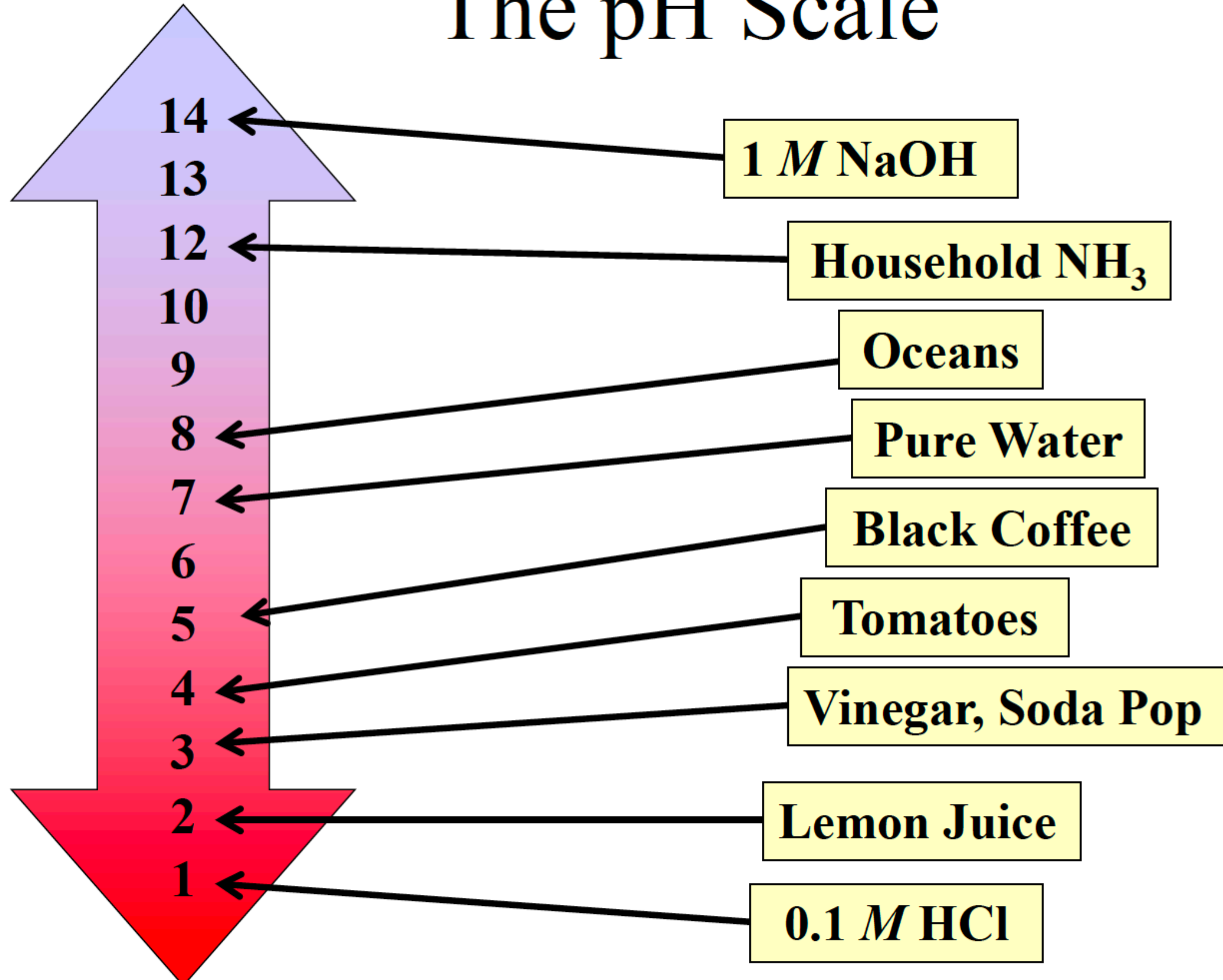
$$[\text{OH}^-] = 10^{-\text{pOH}} \text{ M}$$

- Expresses the negative power of 10 for the concentration of H^+
- A solution with $[\text{H}_3\text{O}^+] = 10^{-4}$ has a pH of 4

Find the pH of pure water at 25°C , remembering that $K_w = 1.0 \times 10^{-14}$ at 25°C .

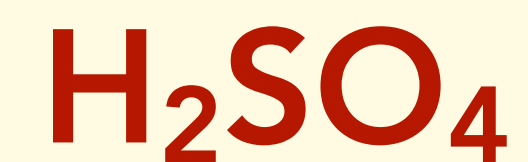
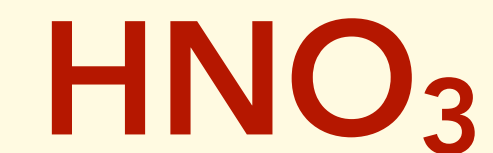
If a solution has a pH of 5.63, find the $[\text{H}^+]$.

The pH Scale



The 'Big Six' Strong Acids

- These are the only acids that completely ionize (dissociate) in aqueous solution to produce hydronium ions, H_3O^+ .

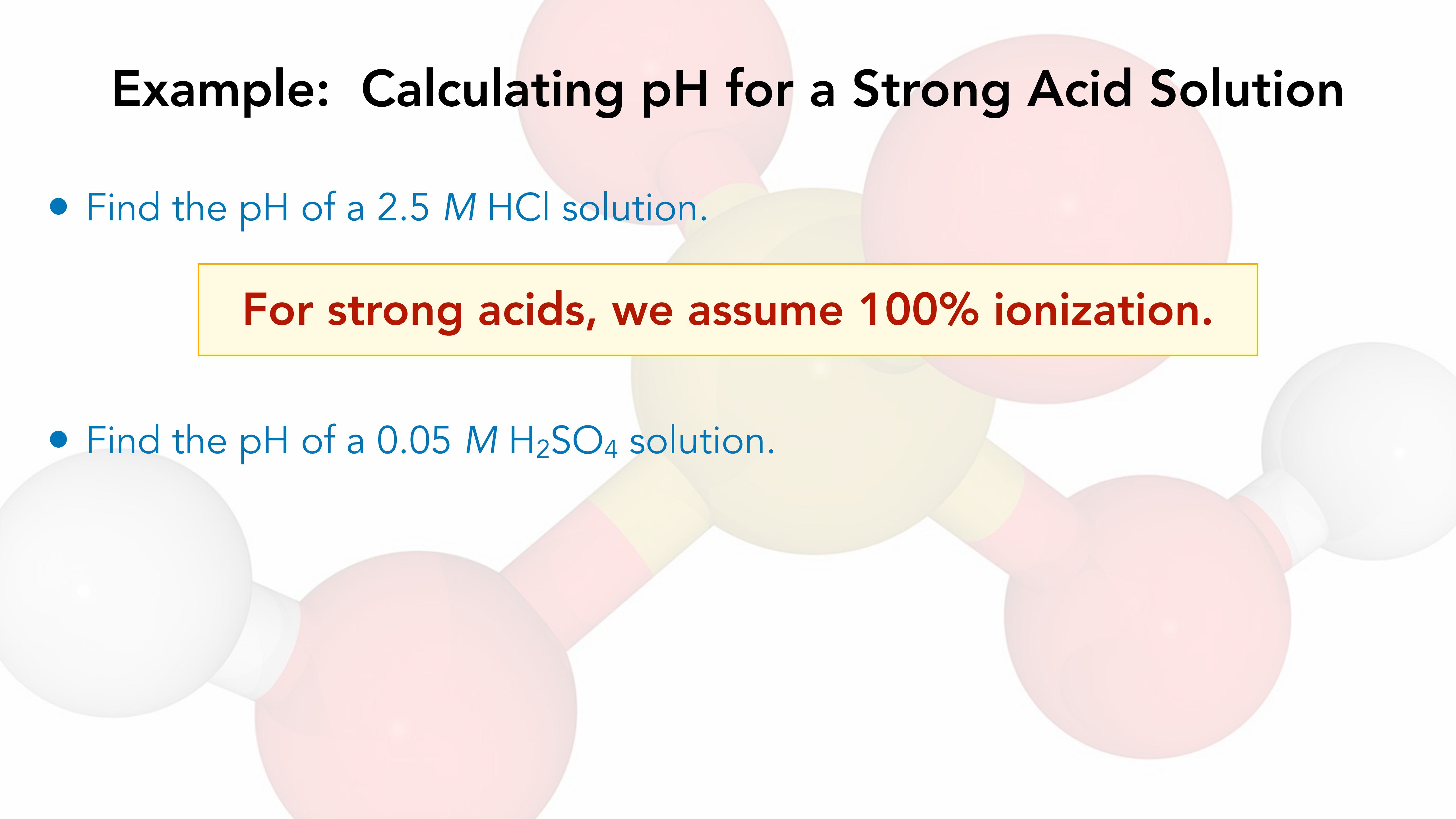


Example: Calculating pH for a Strong Acid Solution

- Find the pH of a 2.5 *M* HCl solution.

For strong acids, we assume 100% ionization.

- Find the pH of a 0.05 *M* H₂SO₄ solution.



Example: Calculating pH for a Strong Acid Solution

Find the pH of a solution that was created by mixing 500.0 mL of 0.15 M HBr with 250.0 mL of 0.20 M HNO₃. Assume the volumes are additive.

Step 1: Find the concentration of H₃O⁺.

Step 2: Find the final pH.

Strong Bases

- Soluble compounds containing the hydroxide ion.

Possible Cations:

- All Group 1A Cations
- Ca^{2+} , Sr^{2+} , or Ba^{2+}

Example: Calculating the pOH for Strong Base Solutions

Find the pOH of a 1.5 M KOH solution.

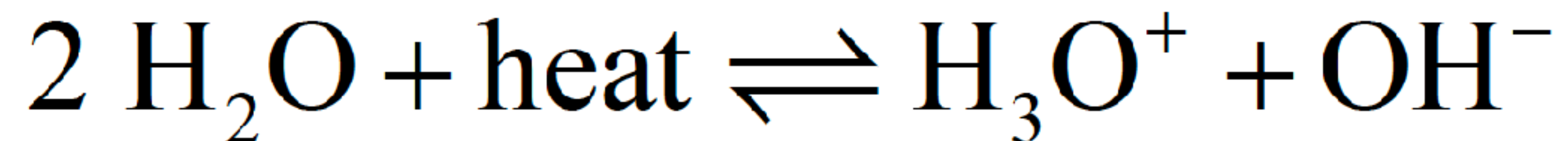
- *This is a strong base, so we assume complete dissociation.*

Example: Calculating pH for Strong Base Solutions

Find the pH of a 3.5 M NaOH solution at 25°C.

- *This is a strong base, so we assume complete dissociation again.*

K_w at Temperatures Other than 25°C



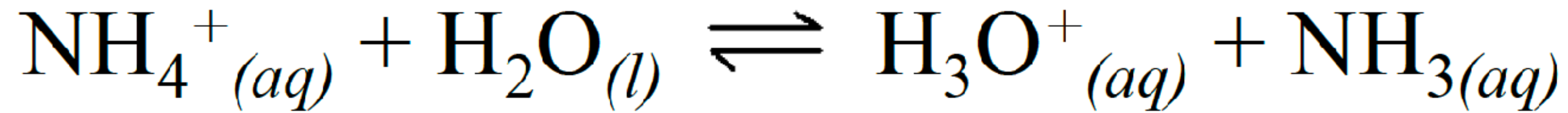
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

- The auto-dissociation of water is an endothermic process.
- When temperature increases, the equilibrium shifts to the right, so $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$ and K_w increase.
- When the temperature decreases, the equilibrium shifts to the left so $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$ and K_w decrease.

8.3 Weak Acid & Base Equilibria

- K_a and K_b
- pH of Weak Acids & Bases
- Polyprotic Acids

Acid Ionization Constant (K_a)

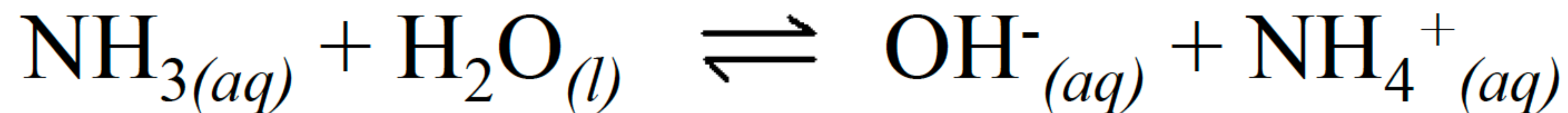


$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$

Acid	K_a
HCl	2×10^6
HNO ₃	30
HSO ₄ ⁻	0.011
C ₉ H ₈ O ₄	6.6×10^{-4}
CH ₃ COOH	1.8×10^{-5}
HCN	4.9×10^{-10}

The stronger the acid, the larger the K_a

Base Ionization Constant (K_b)



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

Base	K_b
NaOH	Very Large Number
NH_3	1.8×10^{-5}
ClO^-	3.3×10^{-7}
H_2NOH	1.1×10^{-8}
$\text{C}_5\text{H}_5\text{N}$	1.7×10^{-9}

The stronger the base, the larger the K_b

pK_a and pK_b Values are Often Given

$$pK_a = -\log_{10}(K_a)$$

$$pK_b = -\log_{10}(K_b)$$

$$K_a = 10^{-pK_a}$$

$$K_b = 10^{-pK_b}$$

pK_a for HCN is 9.31 at 25°C. Find K_a at 25°C.

pK_a

Acid	K_a	pK _a
HCl	2×10^6	-6.3
HNO ₃	30	-1.5
HSO ₄ ⁻	0.011	1.96
C ₉ H ₈ O ₄	6.6×10^{-4}	3.18
CH ₃ COOH	1.8×10^{-5}	4.74
HCN	4.9×10^{-10}	9.31

The stronger the acid, the smaller the pK_a

pK_b

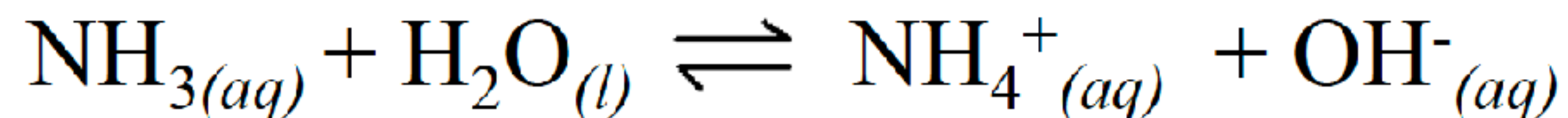
Base	K _b	pK _b
NaOH	Very Large Number	Negative Number
NH ₃	1.8 x 10 ⁻⁵	4.74
ClO ⁻	3.3 x 10 ⁻⁷	6.48
H ₂ NOH	1.1 x 10 ⁻⁸	7.96
C ₅ H ₅ N	1.7 x 10 ⁻⁹	8.77

The stronger the base, the smaller the pK_b

Relationship Between K_a and K_b

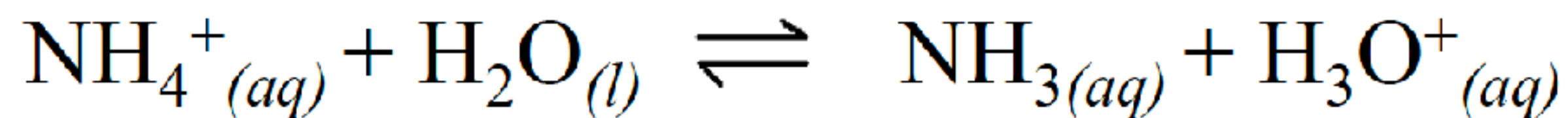
$$K_w = K_a \times K_b$$

Basic Reaction



$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

Acidic Reaction



$$K_a = 5.6 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

Relationship Between K_a and K_b

$$K_w = K_a \times K_b$$

$$\left(\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \right) \left(\frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \right) = [\text{OH}^-][\text{H}_3\text{O}^+] = K_w$$

$$\text{p}K_w = \text{p}K_a + \text{p}K_b \text{ (@}25^\circ\text{C)}$$

Example: pK_a & pK_b

$$pK_w = pK_a + pK_b (@25^\circ\text{C})$$

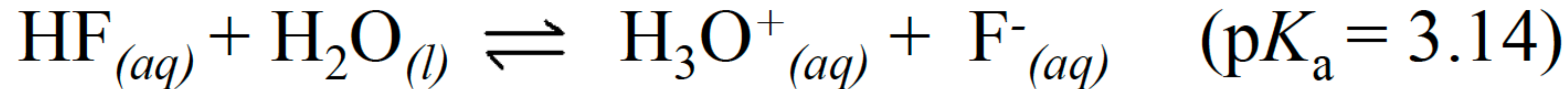
An acid was dissolved in water and the pK_b value associated with its conjugate base was found to be 15.5 at 25°C.

1. What is the pK_a value for the acid? $pK_a = -1.5$
2. Is the solution acidic or basic? Acidic
3. Is the conjugate base a stronger or a weaker base than water?

The conjugate base is a weaker base than water. Water and the conjugate base compete for protons and water wins every time (strong acid - HNO_3).

Example: Calculating pH for a Weak Acid Solution

Find the pH of a 2.5 M solution of HF.



Step 1: Find K_a

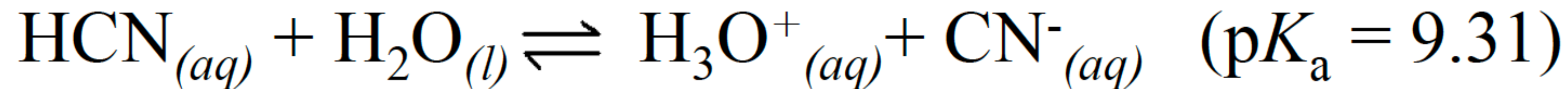
Step 3: Find pH using $[\text{H}_3\text{O}^+]$

Step 2: Find $[\text{H}_3\text{O}^+]$ using an ICE chart

	[HF]	[H ₃ O ⁺]	[F ⁻]
I			
C			
E			

Example: Calculating pH for a Weak Acid Solution

Find the pH and % ionization of a 1.5 M HCN solution.



Step 1: Find K_a

Step 3: Find pH using $[\text{H}_3\text{O}^+]$

Step 2: Find $[\text{H}_3\text{O}^+]$ using an ICE chart

Step 4: Find % ionization.

	[HCN]	[H ₃ O ⁺]	[CN ⁻]
I			
C			
E			

Example: K_a and pH with % Ionization

Acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, experiences 0.767% ionization in a 0.300 M solution at 25°C . Find K_a for acetic acid at 25°C and the pH of the solution.

Step 1: Find K_a

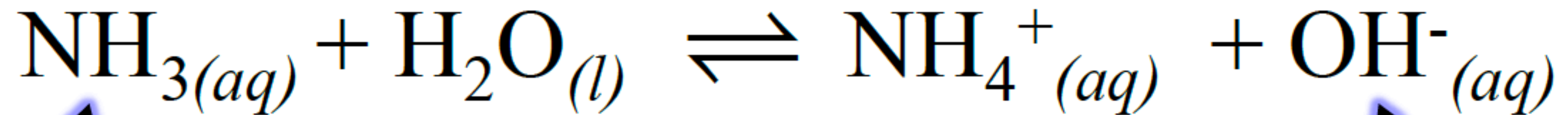
Step 2: Find pH



I			
C			
E			

Weak Bases

- Weak bases react with water to produce hydroxide ions, OH⁻.



Weak Base

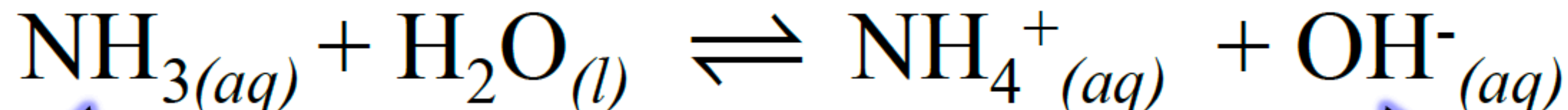
Hydroxide Ion

The equilibrium for weak base reactions normally lies to the left.

Example: Calculating pH for Weak Base Solutions

- Find the pH of a 3.5 M solution of NH_3 .

$$\text{pK}_b = 4.74$$



Step 1: Find K_b

Step 3: Find pOH using $[\text{OH}^-]$

Step 2: Find $[\text{OH}^-]$ using an ICE chart

Step 4: Find pH

Polyprotic Acids

- Polyprotic acids can donate more than one H⁺ in a solution.

e.g. H₂SO₄ and H₂CO₃

Sulfuric acid

Carbonic Acid



- Always use K_{a1} to calculate [H⁺] and pH.
 - Most of the H⁺ ions come from the first ionization.
 - The H⁺ ions from the first ionization drive the equilibrium(s) for the other ionizations to the left.

8.4 Acid-Base Reactions & Buffers

- Strong Acid-Strong Base
- Weak Acid-Strong Base
- Strong Acid-Weak Base
- Weak Acid-Weak Base

Acid-Base Reactions

- Reactions between acids and bases are called *neutralization reactions*.
- If a strong acid or base is involved, $K_{\text{eq}} > 1$, the reaction goes to completion and a one way arrow is used.
- In a weak acid-weak base reaction, $K_{\text{eq}} < 1$, a state of equilibrium is established and two way arrows are used.

Strong Acid - Strong Base Reactions

- Strong acids and strong bases experience 100% ionization.
- H^+ and OH^- ions combine to form H_2O .
 - These reactions go to completion.
 - $[\text{H}^+][\text{OH}^-] = K_w = 1 \times 10^{-14}$ at 25°C .
- The other parts of these acids and bases act as spectator ions.
- The pH can be determined from the excess reactant.

Example: Strong Acid - Strong Base Reactions

- 250.0 mL of 0.35 M HCl is mixed with 150.0 mL of 0.50 M NaOH. Write the net ionic equation for the reaction and find the pH of the final solution. Assume that the volumes are additive.

Step 1. Find the excess reactant.

$$0.2500 \text{ L} \times \frac{0.35 \text{ mol H}^+}{1.0 \text{ L}} = 0.088 \text{ mol H}^+$$

$$0.1500 \text{ L} \times \frac{0.50 \text{ mol OH}^-}{1.0 \text{ L}} = 0.075 \text{ mol OH}^-$$

Step 2. Find $[\text{H}^+]$

$$\frac{0.088 \text{ mol H}^+ - 0.075 \text{ mol OH}^-}{0.2500 \text{ L} + 0.1500 \text{ L}} = 0.033M \text{ H}^+$$

Weak Acid - Strong Base Reactions

- Strong bases completely dissociate.
- Each OH^- ion rips an H^+ ion off of a weak acid molecule.
- This produces water and the conjugate base of the weak acid.
- Equal volumes of 1.0 M HNO_2 and 1.0 M KOH are mixed. Write the net ionic equation for the reaction and identify the aqueous species that have the highest concentrations at equilibrium.

Example: Weak Acid - Strong Base Reactions

- 55 mL of 2.5 M NaOH is added to 55 mL of 2.0 M HF. Assuming the volumes are additive, find the pH of the final solution at 25°C.

Step 1: Find the limiting reactant

Step 3: Find pOH of the final solution

Step 2: Find [OH⁻] in the final solution

Step 4: Find pH of the final solution

Henderson - Hasselbalch Equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad \text{pH} = \text{p}K_a + \log \frac{[\text{Base}]}{[\text{Acid}]}$$

$$\text{p}K_a = -\log_{10} K_a$$

$[\text{A}^-]$ = molarity of conjugate base

$[\text{HA}]$ = molarity of weak acid (initial molarity)

$\log \frac{[\text{Base}]}{[\text{Acid}]}$

- Must be a conjugate acid-base pair
- A weak base and its conjugate acid

K_a and pK_a - Remember!

$$pK_a = -\log K_a$$

and

$$K_a = 10^{-pK_a}$$

Example: Weak Acid - Strong Base

- 20.0 mL of 1.5 M KOH is added to 50.0 mL of 3.0 M CH₃COOH. pK_a = 4.8 at 25°C for CH₃COOH. Find the pH of the final solution.

Step 1: Find the limiting reactant

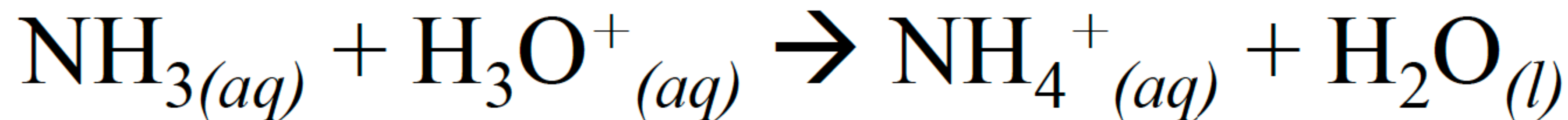
Step 3: Find pH of the final solution

Step 2: Find [CH₃COO⁻] and [CH₃COOH] in the final solution

KOH is the limiting reactant. When the weak acid is the excess reactant, a buffered solution is created and the pH is calculated using the Henderson-Hasselbalch equation.

Strong Acid - Weak Base Reactions

- Weak Bases will accept protons from a strong acid.
- Weak Bases may be nitrogen containing compounds such as NH_3 or the conjugate base of weak acids.
- **Example:** Equal volumes of 2.0 M NH_3 and 2.0 M HI are mixed. Write the net ionic equation for the reaction and identify the aqueous species that have the highest concentrations at equilibrium.



I^- and NH_4^+ will have the highest concentrations at equilibrium.

Example: Strong Acid - Weak Base Reactions

- 125 mL of 2.5 M HCl is added to 115 mL of 2.2 M NH₃. Find the pH of the final solution at 25°C.

Step 1: Find the limiting reactant

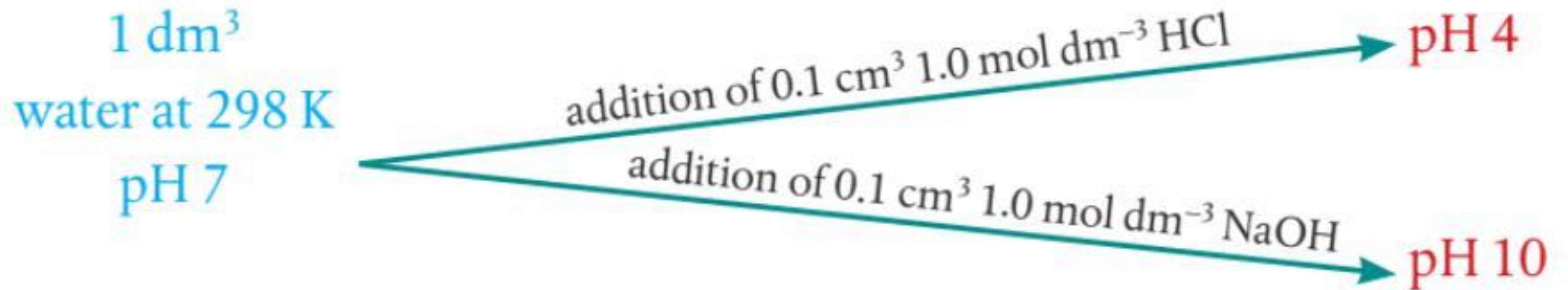
Step 3: Find pH of the final solution

Step 2: Find [H₃O⁺] in the final solution.

NH₃ is the limiting reactant. When the strong acid is the excess reactant, the pH can be found from the moles of excess H₃O⁺ and the total volume of the final solution.

Buffer Solutions

- Something that acts to reduce the impact of one thing on another (a shock absorber of sorts)
- A *buffer solution* is resistant to changes in pH with the addition of **small amounts** of acid or base.



How Buffers Work

- 2 main types:
 - *acidic* - maintain the pH at a value less than 7
 - *basic* - maintain the pH at a value more than 7
- Mixture of 2 solutions
 - each contain a conjugate acid-base pair

Acidic Buffers

- Made by mixing a weak acid with a solution of its salt of a strong alkali
 - i.e. $\text{CH}_3\text{COOH}_{(\text{aq})}$ with NaCH_3COO
 - weak acid salt of weak acid with strong alkali
- Two equilibria exist in this buffer
 - $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$
 - $\text{NaCH}_3\text{COO} \rightleftharpoons \text{Na}^+ + \text{CH}_3\text{COO}^-$

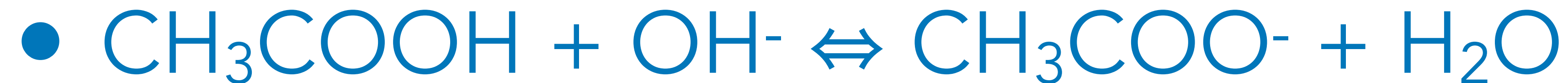
Has high concentrations of both acid and base - ready to react with either H^+ or OH^-

Response to Added Acids & Bases

- Adding acid -



- Adding base



Basic Buffers

- Made by mixing a weak base with a solution of its salt of a strong acid
- i.e. NH_3 with NH_4Cl
 - $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
 - $\text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^-$

Has high concentrations of both acid and base - ready to react with either H^+ or OH^-

Response to Added Acids & Bases

- Addition of acid
 - H^+ combines with the base NH_3 to form NH_4^+
- Addition of base
 - OH^- combines with the acid NH_4^+ to form NH_3 and water, removing most of OH^-

How to Make a Buffer Solution

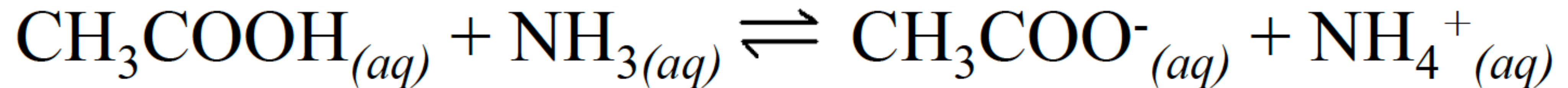
- Start with a weak acid whose pK_a is very close to the desired pH of the buffer (or weak base whose pK_b is close to the desired pOH).
- Then, react this acid or base with enough strong alkali or strong acid so that one half of it is converted into salt.

	CH_3COOH	NaOH	CH_3COONa	H_2O
I	2	1	0	0
C	-1	-1	1	1
E	1	0	1	1

End up with
equal amounts
of weak acid
and salt

Weak Acid - Weak Base Reactions

- Generally do not go to completion.
- Acids and bases are mostly undissociated.
- We write these as proton transfer reactions.
- Equal volume of 0.2 M aqueous ammonia and 0.2 M acetic acid are mixed.



A two way arrow is used, as a state of equilibrium is established.

8.5 Acid-Base Titrations

- Endpoint
- Equivalence Point
- Half-Equivalence Point

Acid-Base Titrations



Acid-base titrations are often used to determine the concentration of an acid or a base in a solution.

- A strong acid of known concentration (titrant) is added to a base of unknown concentration (analyte), which is mixed with an indicator; or,
- A strong base of known concentration (titrant) is added to an acid of unknown concentration (analyte), which is mixed with an indicator.
- The indicator changes color to signal the arrival of the **Endpoint** .

Acid-Base Titrations



Endpoint

- When the correct indicator is chosen, the endpoint is very close to the *Equivalence Point*.
- *Equivalence Point*
- At the equivalence point, the number of moles of titrant added is equal to the number of moles of analyte that were originally present.

$$M_a V_a = M_b V_b$$

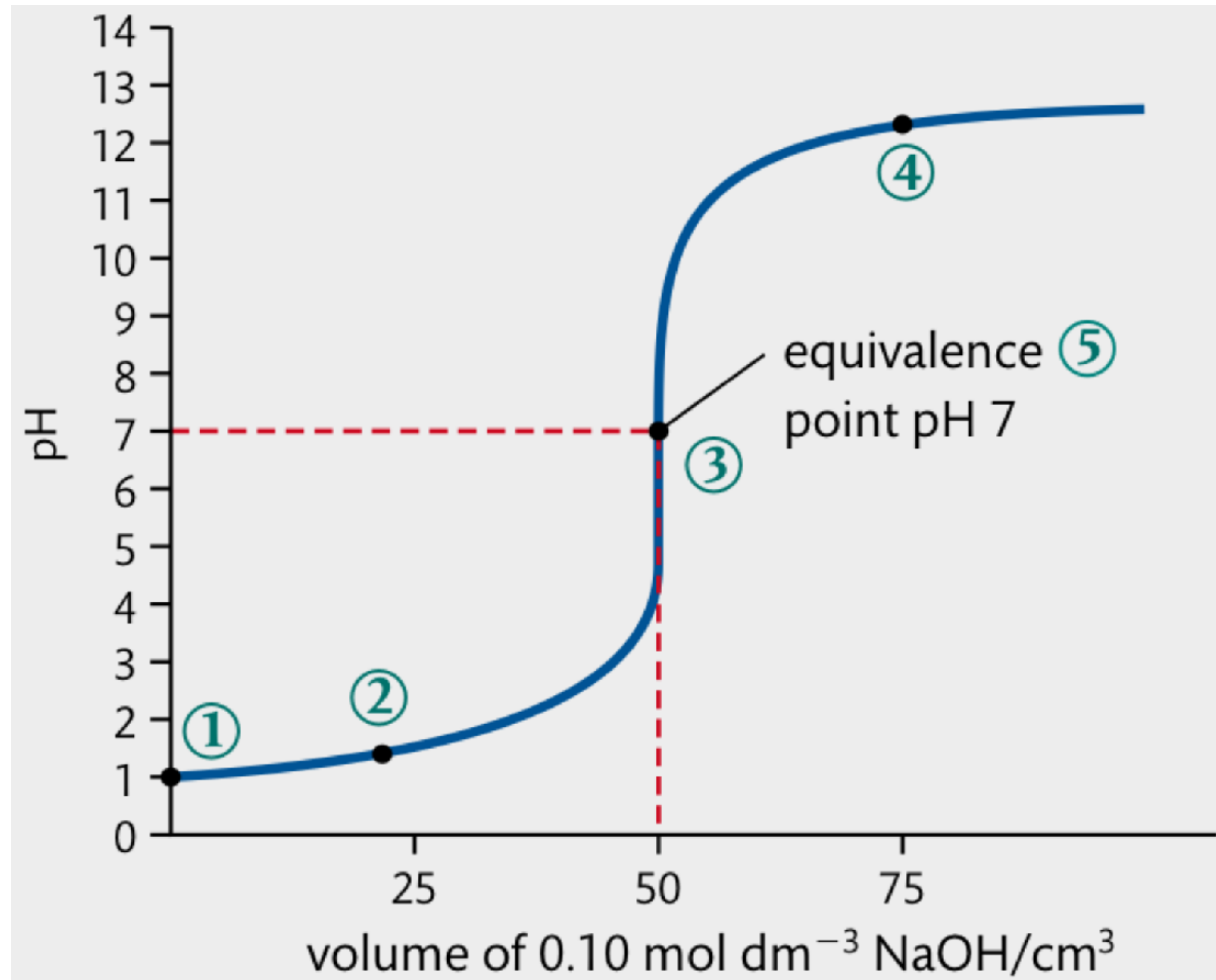
Three Types of Acid-Base Titrations



1. Strong acid - strong base
2. Weak acid - strong base
3. Weak base - strong acid

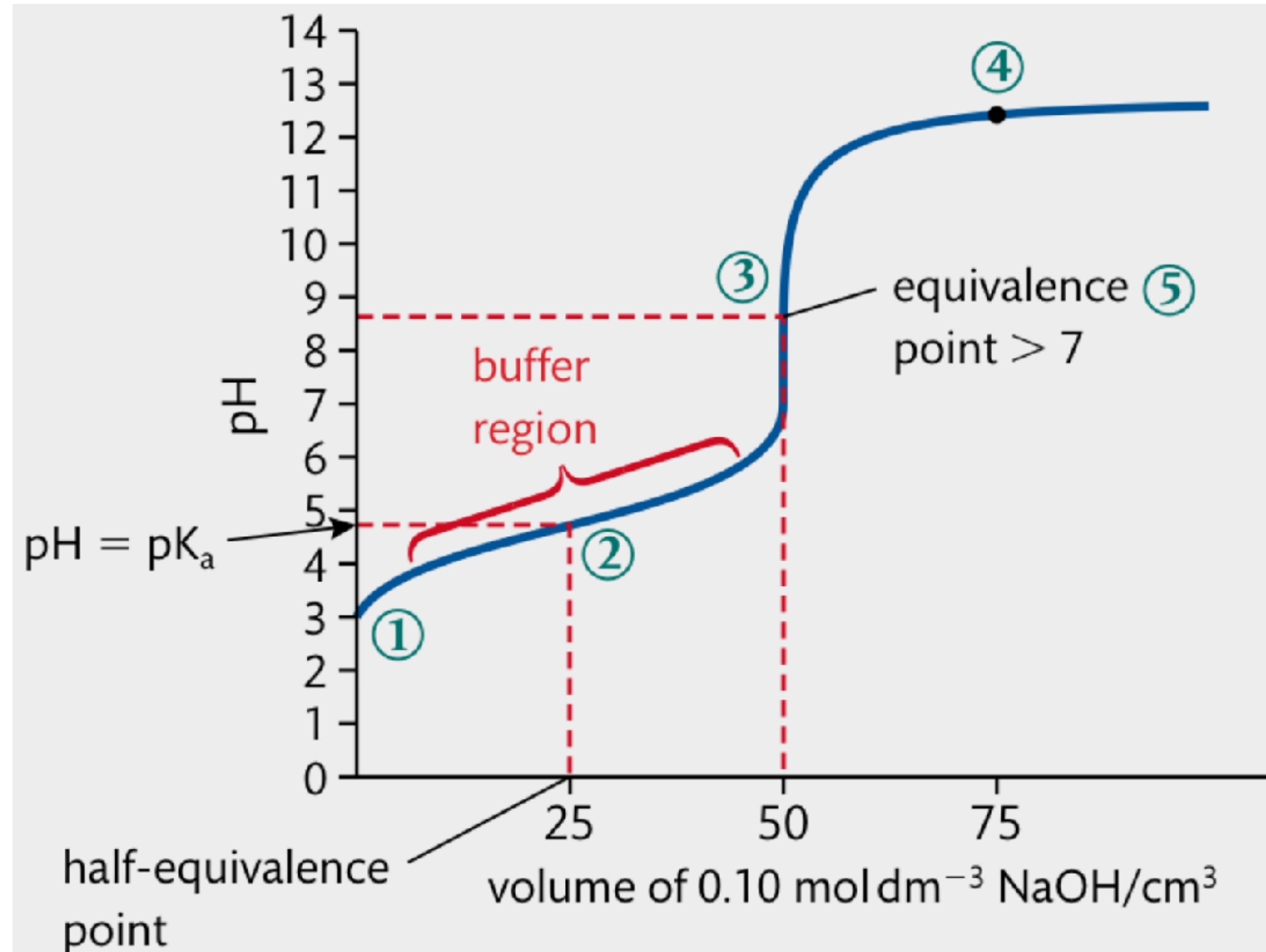
Strong Acid & Strong Base

- (1) Initial pH = 1
- (2) pH changes only gradually until equivalence.
- (3) Very sharp jump in pH at equivalence: from 3 to 11
- (4) After equivalence, the curve flattens out at a high value.
- (5) The pH at equivalence is 7



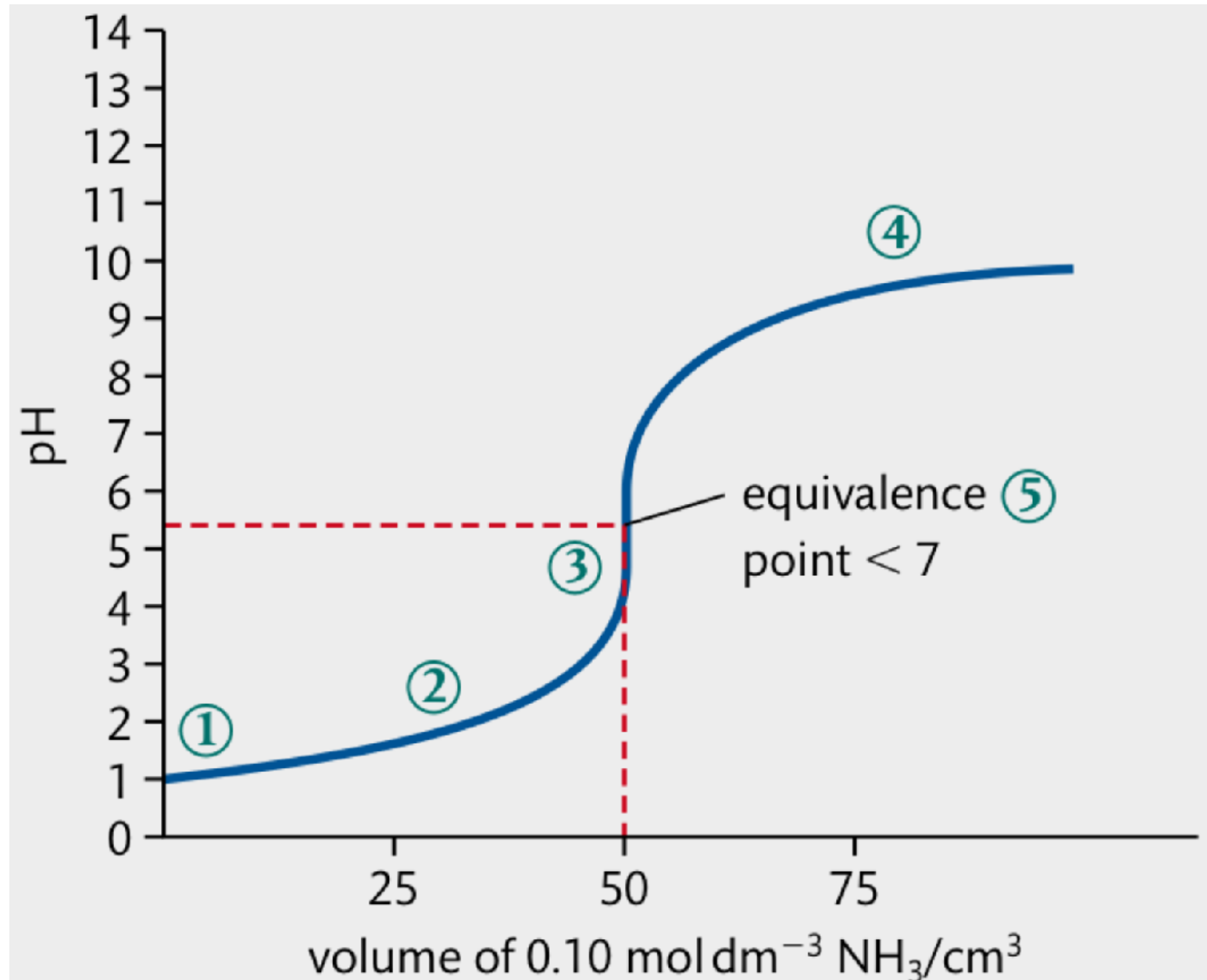
Weak Acid & Strong Base

- (1) Initial pH fairly high
- (2) pH stays relatively constant until equivalence - labeled as **buffer region**
- (3) Jump in pH at equivalence from about pH 7-11, which is not as much of a jump as for a SA-SB titration
- (4) After equivalence, the curve flattens out at a high value (SB)
- (5) **pH at equivalence is > 7**



Strong Acid & Weak Base

- (1) Initial pH = 1 (SA)
- (2) pH stays relatively constant through the buffer region to equivalence.
- (3) Jump in pH at equivalence from about 3.0-7.0
- (4) After equivalence, the curve flattens out at a fairly low pH (WB)
- (5) pH at equivalence < 7



Example: Strong Acid - Strong Base Titration

30 mL of 0.50 M HCl was titrated with 0.50 M NaOH. Assume that volumes are additive and the final temperature of all solutions is 25°C.

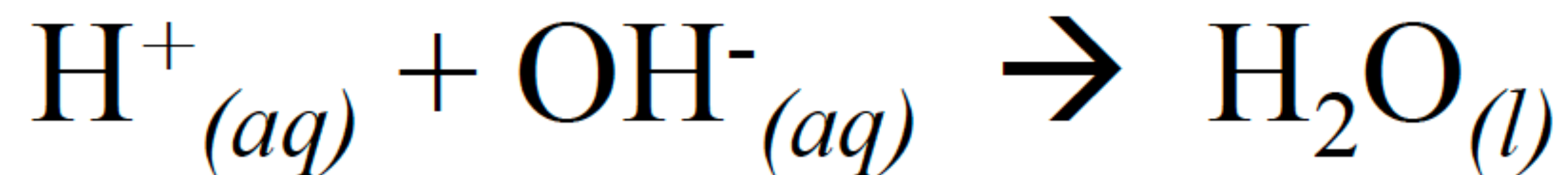
a) Find the initial pH of 0.5 M HCl

c) Find pH after 30 mL of NaOH was added.

b) Find pH after 15 mL of NaOH was added.

d) Find the pH after 45 mL of NaOH was added.

The net ionic equation



Example: Weak Acid - Strong Base Titration

30 mL of 0.50 M CH_3COOH was titrated with 0.50 M NaOH.

a) Determine the volume of 0.50 M NaOH that must be delivered to reach the half equivalence point.

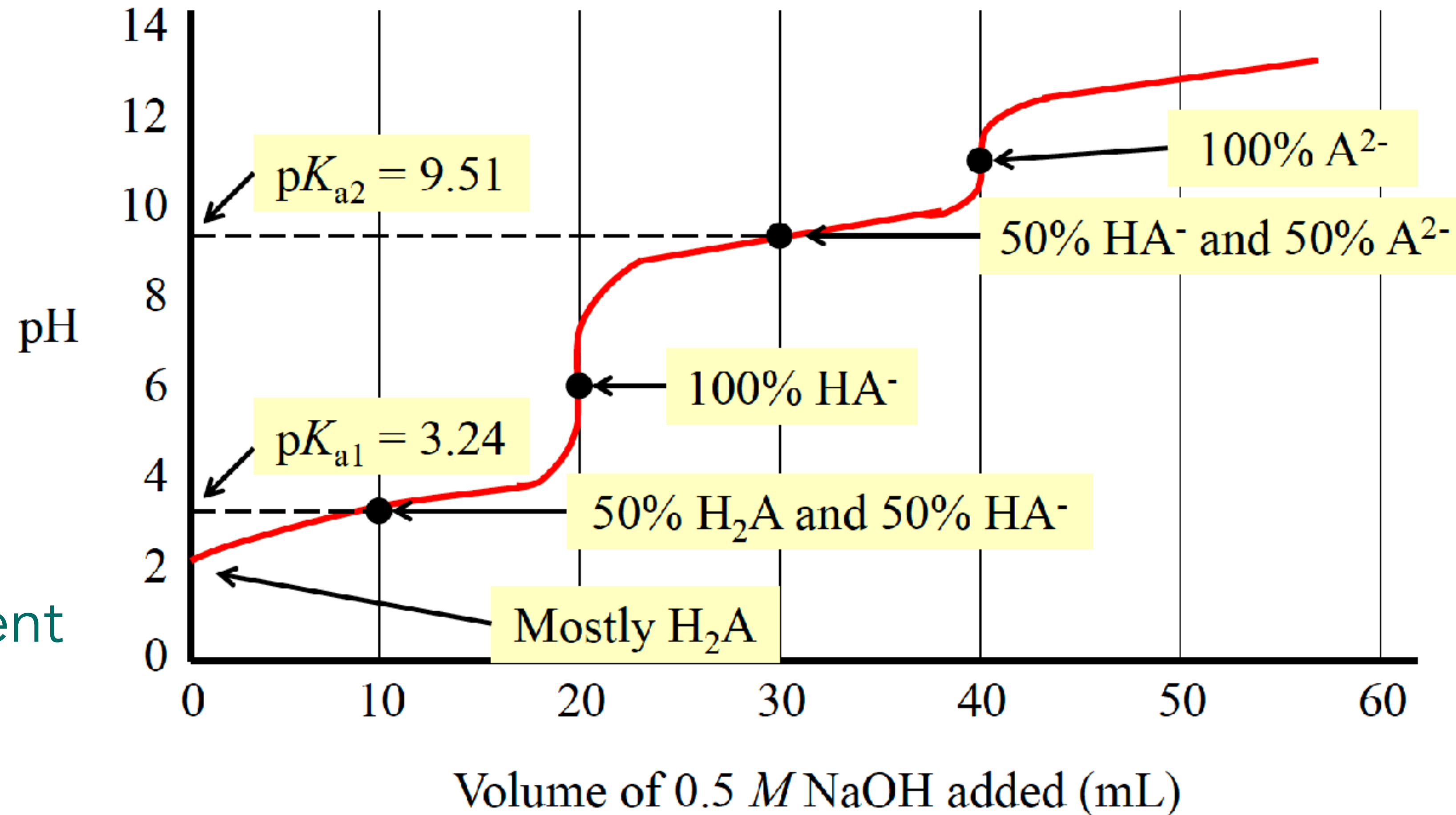
b) The pH at the half equivalence point is measured to be 4.74. Find pK_a for CH_3COOH .

c) Identify the main species that are present in the solution being titrated at the half equivalence point.

Titration Curves for Polyprotic Acids

The following can be determined:

- the number of acidic protons
- the pK_a value for each acidic proton of a weak polyprotic acid
- The major species present at any point along the curve.



8.7 pH and pK_a

8.8 Properties of Buffers

8.9 Henderson-Hasselbalch Equation

8.10 Buffer Capacity

- Buffered Solutions
- Acid-Base Indicators

The Common Ion Effect is Used to Create Buffer Solutions

Buffers resist changes in pH

- When small quantities of strong acids or strong bases are added to a buffered solution, the changes in pH are small.

Buffer

- A weak acid and its salt (extra conjugate base)
- or... a weak base with its salt (extra conjugate acid)

Buffer Capacity

Buffering Capacity

- The ability of a buffered solution to accept protons or hydroxide ions without significant change in pH
- Higher concentrations of HA and A⁻ in the solution result in greater buffering capacities.

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

$$\text{When } \frac{[\text{A}^-]}{[\text{HA}]} = 1, \log \frac{[\text{A}^-]}{[\text{HA}]} = 0 \text{ and } \text{pH} = \text{p}K_a$$

This is helpful when choosing a conjugate acid-base pair. If a buffer needs to have a certain pH, one would choose a weak acid with a pK_a value that is very close to the desired pH.

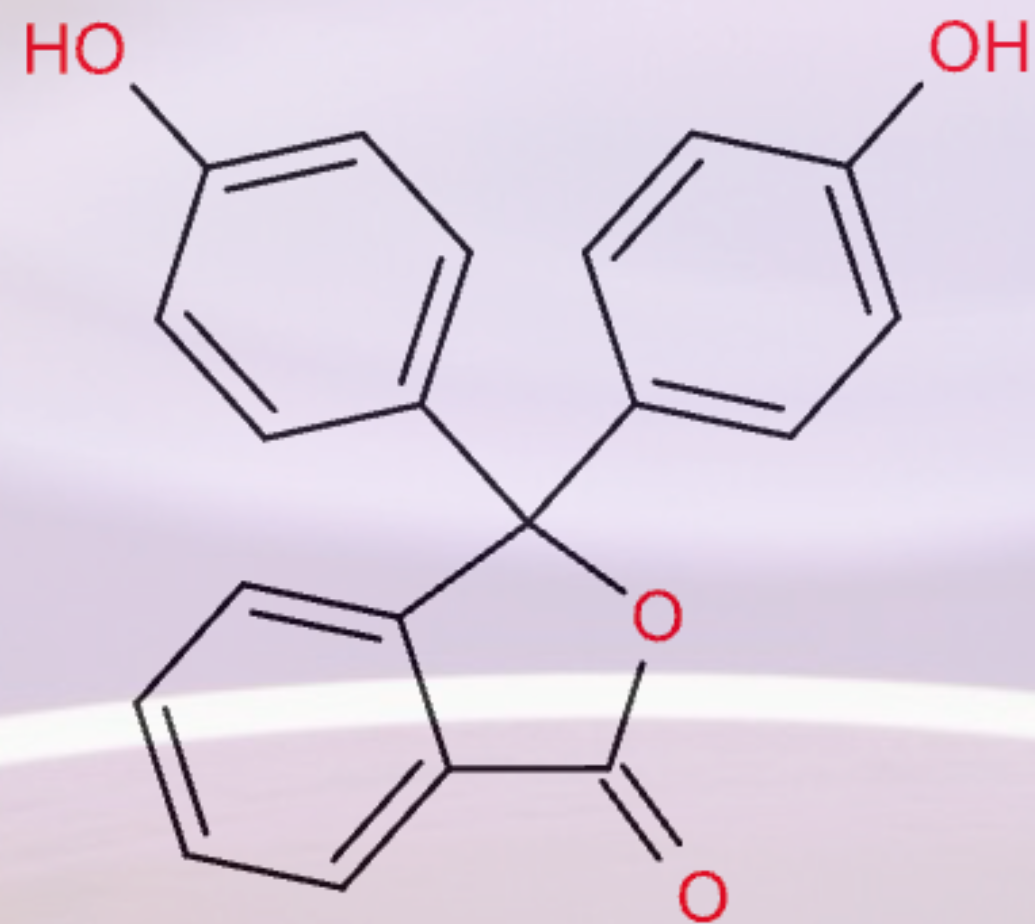
How Acid-Base Indicators Work

- In a titration, there is a large shift in pH as the equivalence point is passed.
- This large shift in pH causes the indicator's equilibrium to shift and its color to change.
- The color starts to change when $[HIn] \cong [In^-]$
- The color change experienced by different indicators occurs over different pH ranges.
- You must select an indicator that changes color at a pH that is as close to possible to the pH at the equivalence point.

How Acid-Base Indicators Work

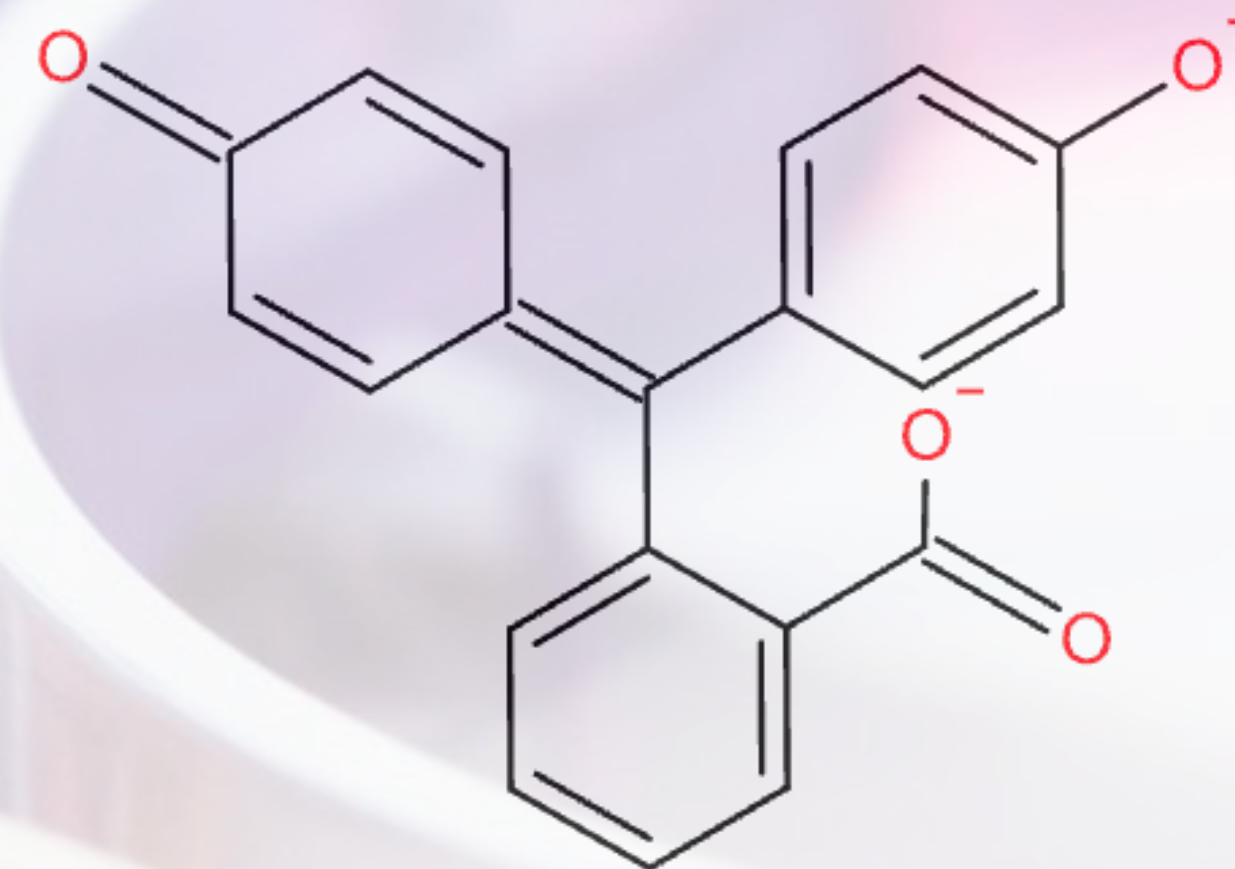


Colorless
pH < 8.3

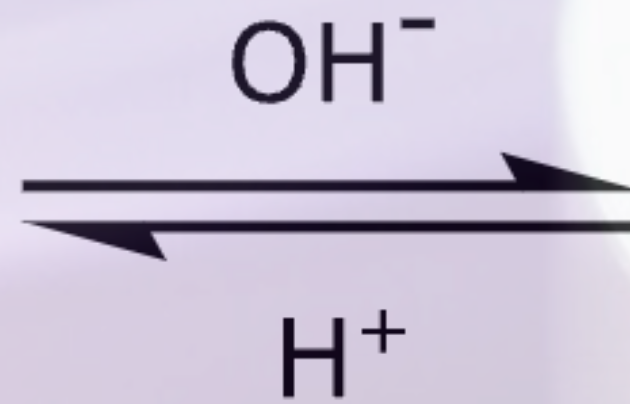


Benzoid form of
Phenolphthalein
(acidic conditions)

Pink colored
pH > 10.5



Quinonoid form of
Phenolphthalein
(basic conditions)



How Acid-Base Indicators Work



When $[\text{HIn}] = [\text{In}^-] \dots$

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$\text{pH} = \text{p}K_{\text{a}}$$

Choose the indicator that has:

$$\text{p}K_{\text{a}}(\text{indicator}) = \text{pH}(\text{equivalence point})$$

Choosing an Indicator

Indicator	pK_a
Methyl Orange	3.7
Methyl Red	5.1
Bromcresol Purple	6.3
Bromthymol Blue	7.0
Phenolphthalein	9.4
Alizarin Yellow	11.0

Example: Choosing an Indicator

Which indicator would you use when titrating HCl with NaOH? (Equivalence point occurs when pH = 7.0)

Indicator	pK_a
Methyl Orange	3.7
Methyl Red	5.1
Bromcresol Purple	6.3
Bromthymol Blue	7.0
Phenolphthalein	9.4
Alizarin Yellow	11.0

