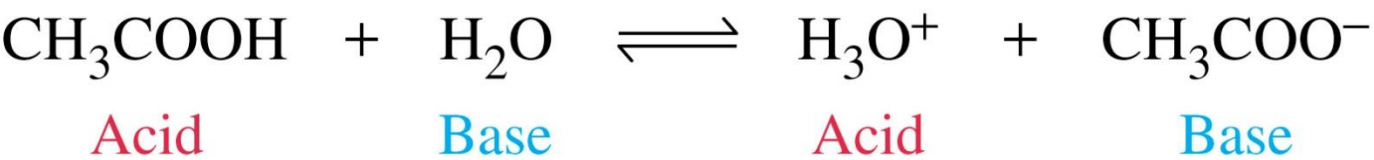# Chapter 17
Aqueous Equilibrium

The Common Ion Effect

- Consider a solution of acetic acid.

- If we add acetate ion as a second solute (i.e., sodium acetate), the pH of the solution will *increase*:

When a salt supplies CH_3COO^-, equilibrium shifts to the *left*.

$$CH_3COOH \ + \ H_2O \ \rightleftharpoons \ H_3O^+ \ + \ CH_3COO^-$$

Acid   Base   Acid   Base

The ***common ion effect*** is the suppression of the ionization of a weak acid or a weak base by the presence of a common ion from a strong electrolyte.

Buffer Solutions

- A ***buffer solution*** is a solution that changes pH *only slightly* when small amounts of a strong acid or a strong base are added.

- A buffer contains significant concentrations of both
  - a weak acid and its conjugate base, or
  - a weak base and its conjugate acid.

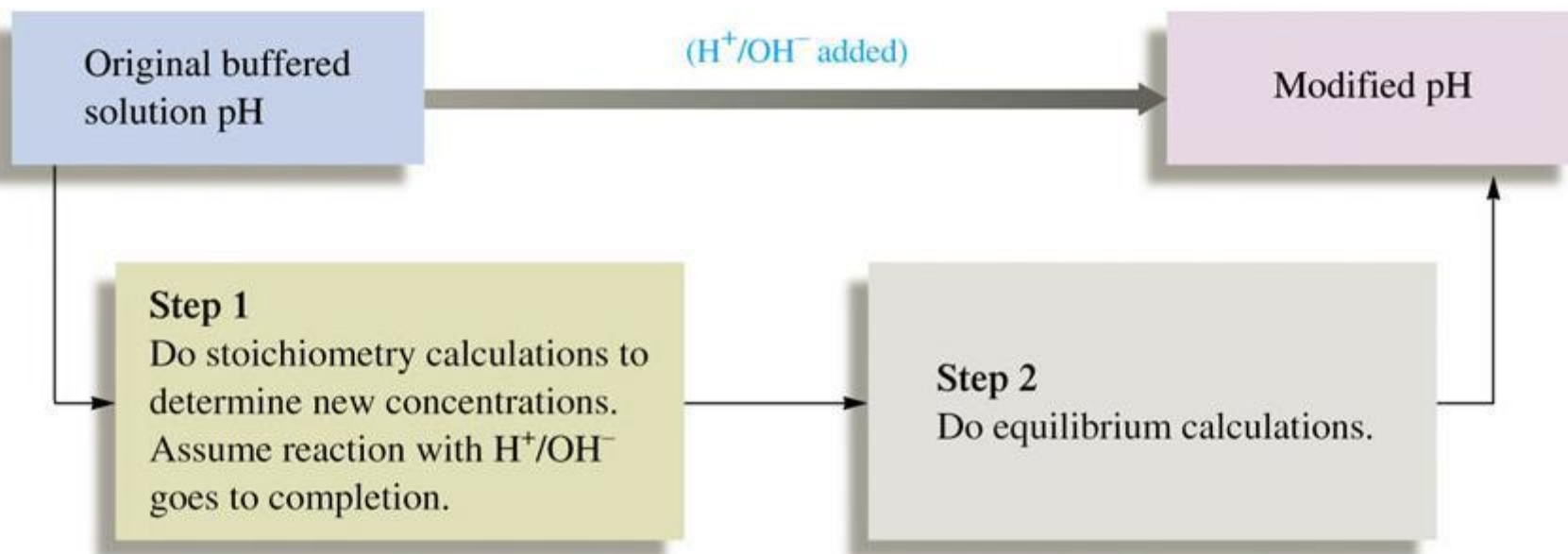## Table 15.1 Relative Strengths of Some Brønsted–Lowry Acids and Their Conjugate Bases

Acid	Conjugate Base
HI (hydroiodic acid)	I^- (iodide ion)
HBr (hydrobromic acid)	Br^- (bromide ion)
HCl (hydrochloric acid)	Cl^- (chloride ion)
H_2SO_4 (sulfuric acid)	HSO_4^- (hydrogen sulfate ion)
HNO_3 (nitric acid)	NO_3^- (nitrate ion)
H_3O^+ (hydronium ion)	H_2O (water)
HSO_4^- (hydrogen sulfate ion)	SO_4^{2-} (sulfate ion)
HNO_2 (nitrous acid)	NO_2^- (nitrite ion)
HF (hydrofluoric acid)	F^- (fluoride ion)
CH_3COOH (acetic acid)	CH_3COO^- (acetate ion)
H_2CO_3 (carbonic acid)	HCO_3^- (hydrogen carbonate ion)
NH_4^+ (ammonium ion)	NH_3 (ammonia)
HCO_3^- (hydrogen carbonate ion)	CO_3^{2-} (carbonate ion)
H_2O (water)	OH^- (hydroxide ion)
CH_3OH (methanol)	CH_3O^- (methoxide ion)

Increasing acid strength

Increasing base strength

17 - Aqueous Equilibrium

4

Original buffered solution pH

(H$^+$/OH$^-$ added)

Modified pH

Step 1
Do stoichiometry calculations to determine new concentrations. Assume reaction with H$^+$/OH$^-$ goes to completion.

Step 2
Do equilibrium calculations.

Water

1.00 L water + 0.010 mol OH^-

1.00 L water

1.00 L water + 0.010 mol H_3O^+

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

Buffer solution

1.00 L buffer + 0.010 mol OH^-

1.00 L buffer

1.00 L buffer + 0.010 mol H_3O^+

Copyright © 2005 Pearson Prentice Hall, Inc.

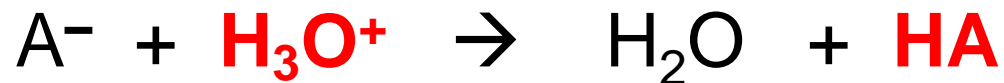**In contrast, the same amounts of OH⁻ and H_3O^+ added to a buffer solution barely change the pH.**
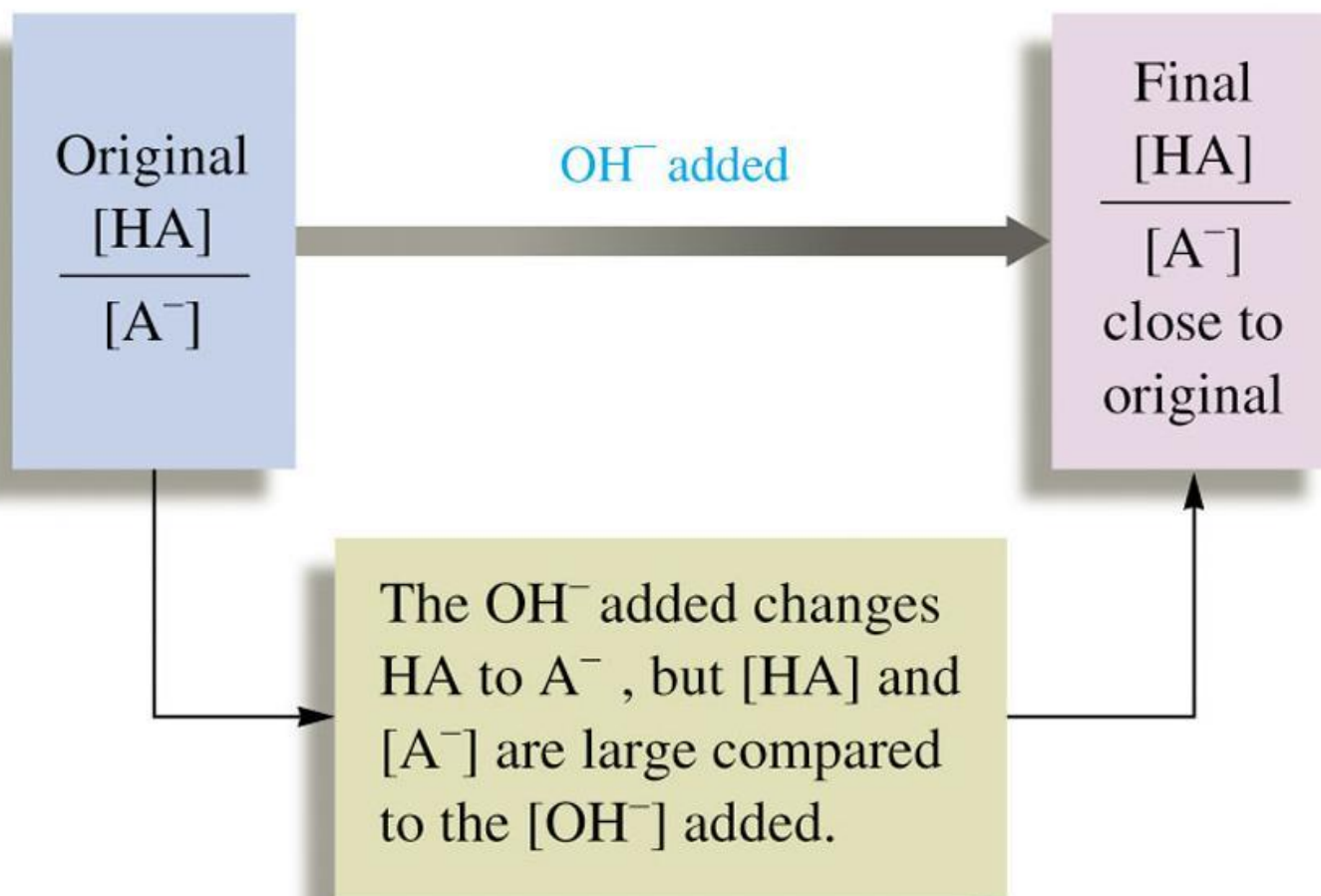
17 - Aqueous Equilibrium

6

Buffer Solutions

- The acid component of the buffer neutralizes small added amounts of OH$^-$, forming the *weaker* conjugate base which does not affect pH much:

$$HA \ + \ OH^- \ \rightarrow \ H_2O \ + \ A^-$$

- The base component neutralizes small added amounts of H$_3$O$^+$, forming the *weaker* conjugate acid which does not affect pH much.

$$A^- \ + \ H_3O^+ \ \rightarrow \ H_2O \ + \ HA$$

Original $\dfrac{[HA]}{[A^-]}$

OH⁻ added

Final $\dfrac{[HA]}{[A^-]}$ close to original

The OH⁻ added changes HA to A⁻ , but [HA] and [A⁻] are large compared to the [OH⁻] added.

8

An Equation for Buffer Solutions

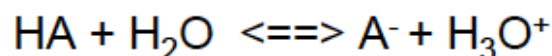$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \Rightarrow \quad [H^+] = K_a \frac{[HA]}{[A^-]}$$

- The ***Henderson–Hasselbalch equation***:

$$pH = pK_a + \log \frac{[conjugate\ base]}{[weak\ acid]}$$

- To use this equation without considering any change in the initial concentrations (the 5% rule), both concentrations should exceed K_a by a factor of 100 or more.

The pH value of a Buffer

For a buffered solution made from weak acid and its salt.

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$K_a = [A^-][H_3O^+] / [HA]$

$[H_3O^+] = K_a \times ([HA]/[A^-])$ (The [HA] and [A$^-$] are known.)

$pH = -\log(K_a) - \log([HA]/[A^-])$

    $= pK_a + \log([A^-]/[HA])$

==> for the same conjugate acid-base pair, the pH of its buffer solution is dependent on the ratio of ($[A^-]/[HA]$).

$HC_2H_3O_2$	$NaC_2H_3O_2$	$[A^-]/[HA]$	pH
5.0 M	3.0 M	0.6	4.52
0.05 M	0.03 M	0.6	4.52

Calculating Buffer pH

What is the pH of a 1.0 L buffer containing 0.50 M acetic acid and 0.50 M sodium acetate, and what is the pH of the solution after adding 0.01 Mole of NaOH(s)?

$K_a = 1.8 \times 10^{-5}$

$$K_a = [C_2H_3O_2^-][H_3O^+]/[HC_2H_3O_2]$$
$$= (0.5 + x)(x)/(0.5 - x)$$
$$\approx x$$
$$= 1.8 \times 10^{-5} \, M$$

$[H_3O^+] = 1.8 \times 10^{-5} \, M$

$\Rightarrow pH = 4.74$

Calculating Buffer pH

What is the pH of a 1.0 L buffer containing 0.50 M acetic acid and 0.50 M sodium acetate, and what is the pH of the solution after adding 0.01 Mole of NaOH(s)?

$K_a = 1.8 \times 10^{-5}$

$[C_2H_3O_2^-] = [(0.5 \times 1.0) + 0.01]/1.0 = 0.51$

$[HC_2H_3O_2] = [(0.5 \times 1.0) - 0.01]/1.0 = 0.49$

$K_a = [C_2H_3O_2^-][H_3O^+]/[HC_2H_3O_2]$

$= (0.51 + x)(x)/(0.49 - x)$

$\approx [0.51(x)] / 0.49$

$= 1.8 \times 10^{-5} \text{ M}$

The pH of 0.01 M NaOH(aq)

$[H_3O^+] = K_w / [OH^-] = 1.0 \times 10^{-12}$

pH = 12

$[H_3O^+] = 1.7 \times 10^{-5} \text{ M}$

=> pH = 4.76

Buffer Capacity and Buffer Range

- There is a limit to the ability of a buffer solution to neutralize added acid or base.

- **_Buffer capacity_** is defined as the moles of an acid or base necessary to change the pH of a solution by 1 divided by the volume of buffer in liters.

- This **buffer capacity** is reached *before* either buffer component has been consumed.

- In general, the more concentrated the buffer components in a solution, the more added acid or base the solution can neutralize.

Buffer Capacity and Buffer Range

- As a rule, a buffer is most effective if the concentrations of the buffer acid and its conjugate base are **equal** or nearly so.

- Therefore, a buffer is most effective when the desired pH of the buffer is very near pK_a of the weak acid of the buffer.

The *Henderson–Hasselbalch equation*:

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

For a good buffer, the ratio should have a value between 0.1 and 10.

$$pH \leftarrow pK_a \pm 1$$

Buffer Capacity and Buffer Range

Acetate   Acetic acid

TABLE 8.1 Change in $[C_2H_3O_2^-]/[HC_2H_3O_2]$ for Two Solutions When 0.01 mol of H^+ Is Added to 1.0 L of Each Solution

Solution	$\left(\dfrac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)_{orig}$	$\left(\dfrac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)_{new}$	Change	Percent Change
A	$\dfrac{1.00\ M}{1.00\ M} = 1.00$	$\dfrac{0.99\ M}{1.01\ M} = 0.98$	$1.00 \rightarrow 0.98$	2.00%
B	$\dfrac{1.00\ M}{0.01\ M} = 100$	$\dfrac{0.99\ M}{0.02\ M} = 49.5$	$100 \rightarrow 49.5$	50.5%
C	$\dfrac{0.02\ M}{0.01\ M} = 2$	$\dfrac{0.01\ M}{0.02\ M} = 0.5$	$2 \rightarrow 0.5$	75%

Both the amount of the acidic and basic components of the buffer system should be considerably more than that of the added H^+ or OH^-.
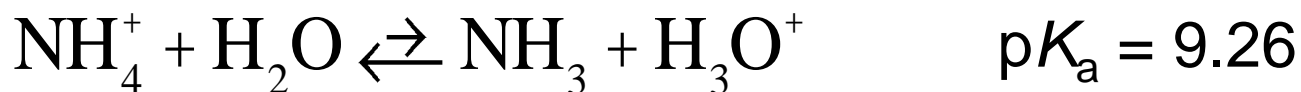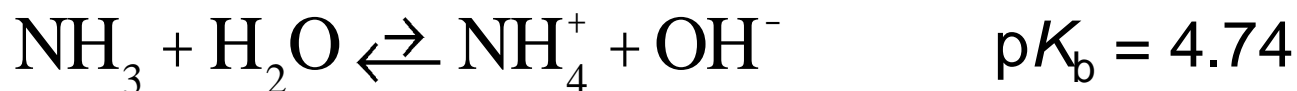
For a good buffer, the ratio should have a value between 0.1 and 10.

15

Learning Check

A buffer solution is 0.240 M NH_3 and 0.200 M NH_4Cl. (a) What is the pH of this buffer? (b) If 0.0050 mol NaOH is added to 0.500 L of this solution, what will be the pH? [$K_b = 1.8 \times 10^{-5}$]

(a)

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad pK_b = 4.74$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad pK_a = 9.26$$

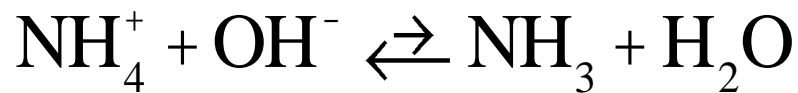$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$

$$pH = 9.26 + \log \frac{0.240}{0.200} = 9.34$$

Learning Check

A buffer solution is 0.240 M NH_3 and 0.200 M NH_4Cl. (a) What is the pH of this buffer? (b) If 0.0050 mol NaOH is added to 0.500 L of this solution, what will be the pH?

[$K_b = 1.8 \times 10^{-5}$]

(b)

$$NH_4^+ + OH^- \rightleftarrows NH_3 + H_2O$$

$[NH_4^+] = (0.200 \times 0.500 - 0.0050) / 0.500 = 0.19$ M

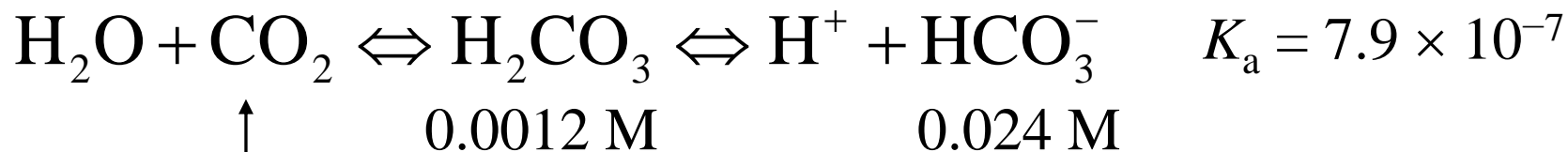$[NH_3] = (0.240 \times 0.500 + 0.0050) / 0.500 = 0.250$ M

$$pH = 9.26 + \log \frac{0.250}{0.19} = 9.38$$

Buffers in Vivo

Human blood, pH of 7.35 to 7.45
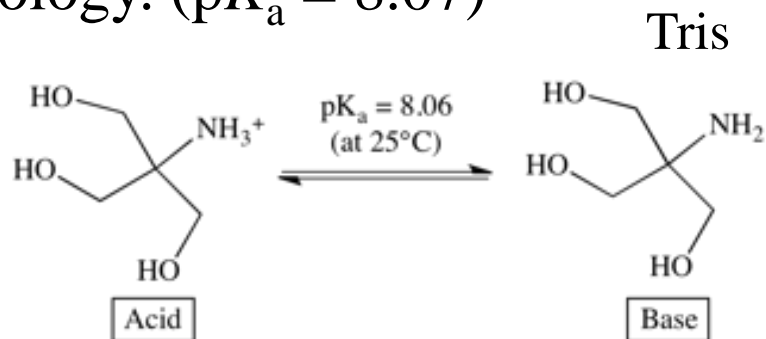
Kidney

Buffer system used to control blood pH

$$H_2O + CO_2 \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \qquad K_a = 7.9 \times 10^{-7}$$

0.0012 M   0.024 M

Lung

$$pH = pK_a + \log\left(20\right) = 7.40$$

Our buffering system has a high capacity to neutralize additional acid
- large amount of CO_2 are produced by metabolism, which increases $[H^+]$

Buffers in Vitro

Tris.HCl buffer is extensively used in biochemistry and molecular biology. ($pK_a = 8.07$)

Tris

For a solution of 10 mL of 0.1 M Tris, how much HCl (1.0 M) are needed to prepare a buffer at pH 7.70?

$$7.70 = 8.07 + \log \frac{(0.10 \times 10.0 - x \times 1.0)/(10.0 + x)}{x \times 1.0/(10.0 + x)}$$

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

$$x = 0.70 \text{ mL}$$

Buffers in Vitro

Good's buffers are twenty buffering agents for biochemical and biological research selected and described by Norman Good and colleagues during 1966−1980s

Buffer	pK_a at 20°C	Solubility in water at 0°C
TES	7.5	2.6 M
HEPES	7.55	2.25 M
DIPSO	7.6	0.24 M
Acetamidoglycine	7.7	Very large
TAPSO	7.7	1.0 M
POPSO	7.85	-
HEPPSO	7.9	2.2 M
HEPPS	8.1	Large
Tricine	8.15	0.8 M
Glycinamide	8.2	6.4 M (As HCl)
Bicine	8.35	1.1 M
TAPS	8.55	Large

Zwitterionic buffer

HEPES

http://www.reachdevices.com/Protein/BiologicalBuffers.html
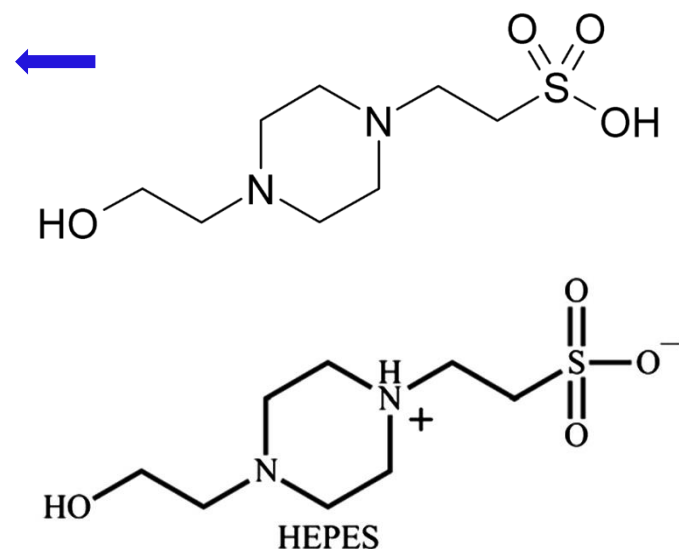
Learning Check

1. Write down the reaction relevant to the buffering capacity of HEPES.
2. HEPES is commercially available as a sodium salt. After solubilizing some sodium HEPES in water, should you add acid or base to prepare a buffer at 7.40?

$$^{+}\text{HEPES}^{-} + \text{H}_2\text{O} \rightleftarrows \text{HEPES}^{-} + \text{H}_3\text{O}^{+} \qquad \text{p}K_\text{a} = 7.55$$

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

Titration Curve
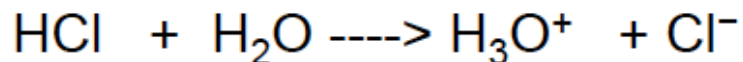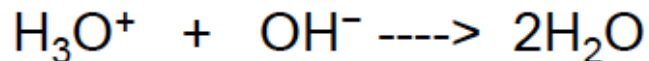
Strong acid with strong base

22
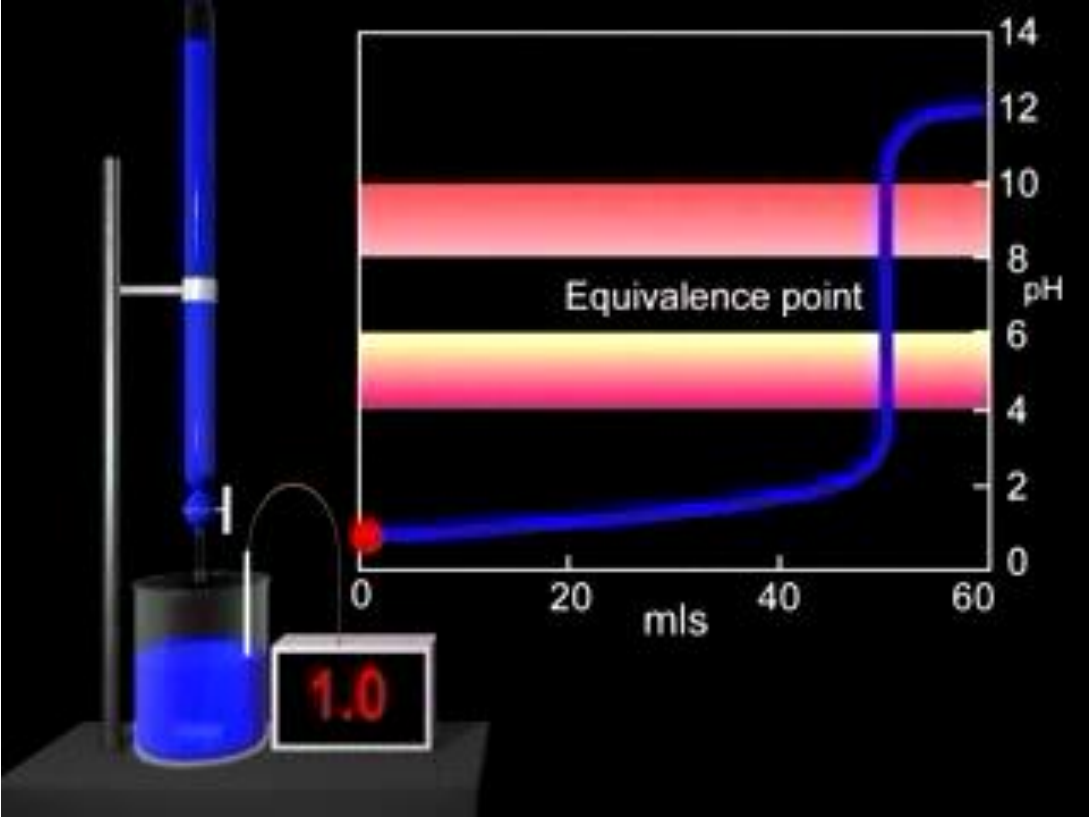
Neutralization Reactions

Neutralization is the reaction of
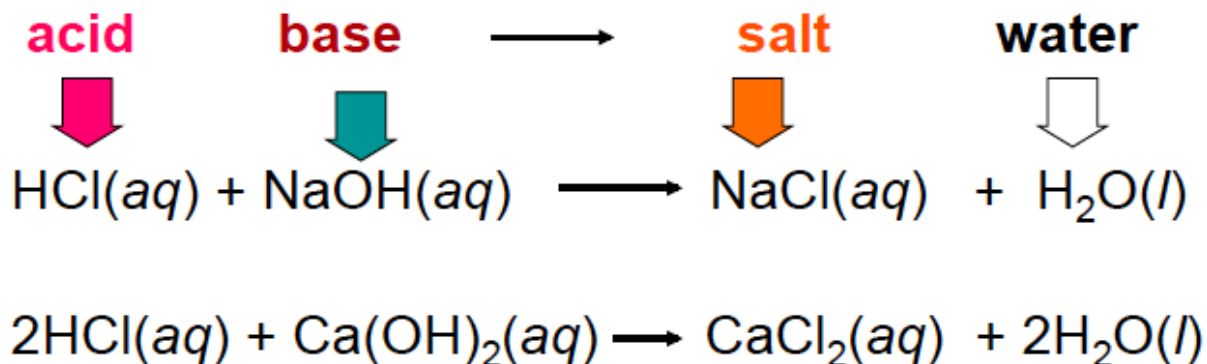
- An acid such as HCl and a base such as NaOH.

$$HCl \ + \ H_2O \ ----> H_3O^+ \ + \ Cl^-$$
$$NaOH \ ----> Na^+ \ + \ OH^-$$

- The H_3O^+ from the acid and the OH^- from the base to form water.

$$H_3O^+ \ + \ OH^- \ ----> \ 2H_2O$$

Neutralization Equations

- In the equation for neutralization, an acid and a base produce a salt and water.

acid   base   ⟶   salt   water

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

$$2HCl(aq) + Ca(OH)_2(aq) \longrightarrow CaCl_2(aq) + 2H_2O(l)$$

Acid-Base Titration

Titration

- Is a laboratory procedure used to determine the molarity of an acid.

- Uses a base such as NaOH to neutralize a measured volume of an acid.
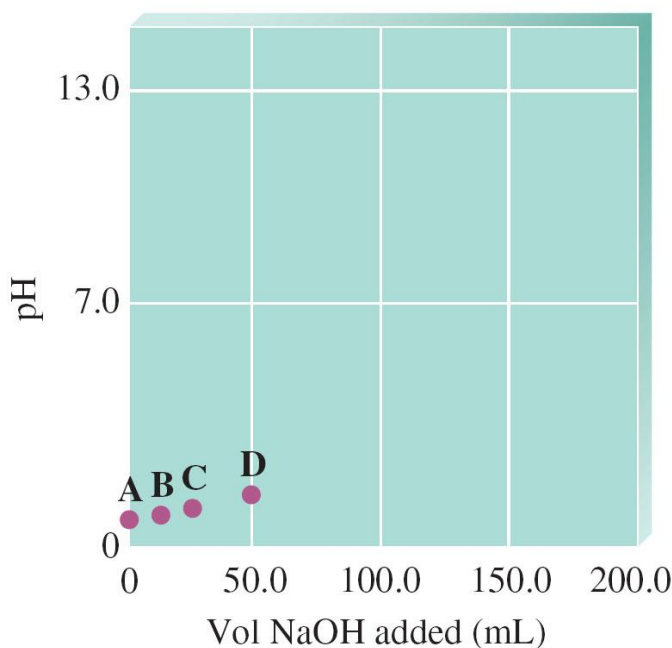
Base (NaOH)

Acid solution

Indicator

An indicator

- Is added to the acid in the flask.

- Causes the acid solution to change color when the acid is neutralized.

19

17 - Aqueous Equilibrium

The pH Curve of Titration

For *strong* acid-base

- Titration of 50.0 mL of 0.200 M HNO_3 with 0.100 M NaOH.

A. 0 mL of NaOH: $[H^+]$ = 0.200 M => pH = 0.699

B. 10.0 mL :
$[H^+]$ = [(50.0 × 0.200) − (10.0 × 0.100)] / (50.0 + 10.0)
= 0.15 M   => pH = 0.82

C. 20.0 mL :
$[H^+]$ = [(50.0 × 0.200) − (20.0 × 0.100)] / (50.0 + 20.0)
= 0.11 M   => pH = 0.94

D. 50.0 mL :
$[H^+]$ = [(50.0 × 0.200) − (50.0 × 0.100)] / (50.0 + 50.0)
= 0.050 M => pH = 1.30

27

The pH Curve of Titration

- Titration of 50.0 mL of 0.200 M HNO_3 with 0.100 M NaOH.
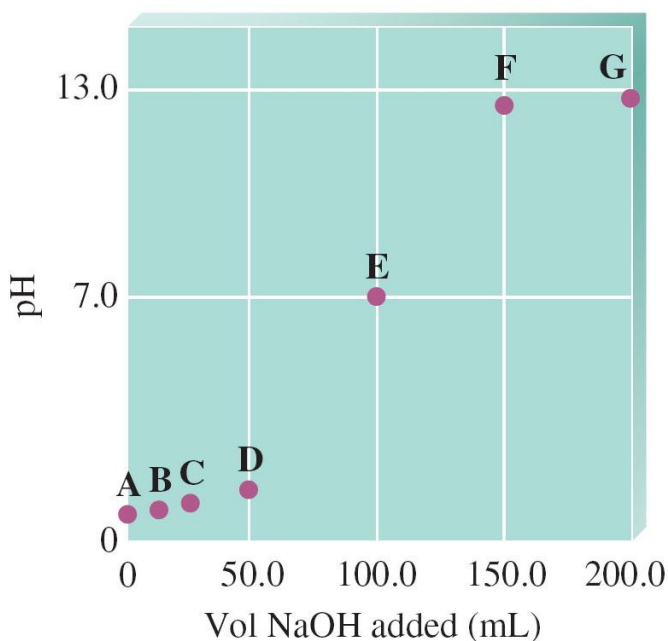
E. 100 mL :
$50.0 \times 0.200 = 100.0 \times 0.100$
mole of acid = mole of base (equivalence point)
$[H^+] = 1.0 \times 10^{-7}$ => pH = 7.00

F. 150 mL :
$[OH^-] = [(150.0 \times 0.100) - (50.0 \times 0.200)] / (150.0 + 50.0)$
$= 0.025$ M
$[H^+] = 1.0 \times 10^{-14} / 0.025 = 4.0 \times 10^{-13}$ M
=> pH = 12.40

G. 200 mL :
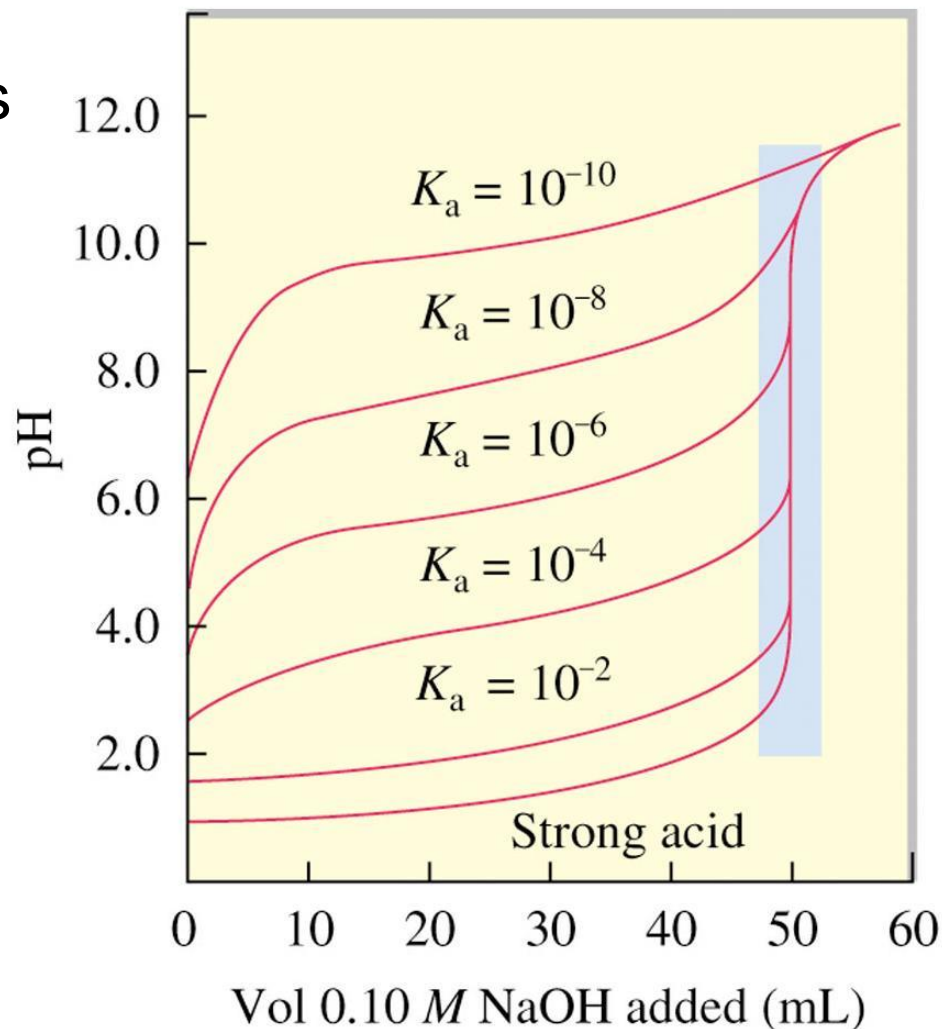$[OH^-] = [(200.0 \times 0.100) - (50.0 \times 0.200)] / (200.0 + 50.0)$
$= 0.04$ M
$[H^+] = 1.0 \times 10^{-14} / 0.04 = 2.5 \times 10^{-13}$M
=> pH = 12.60

Titration Curve

Strong base with weak acids

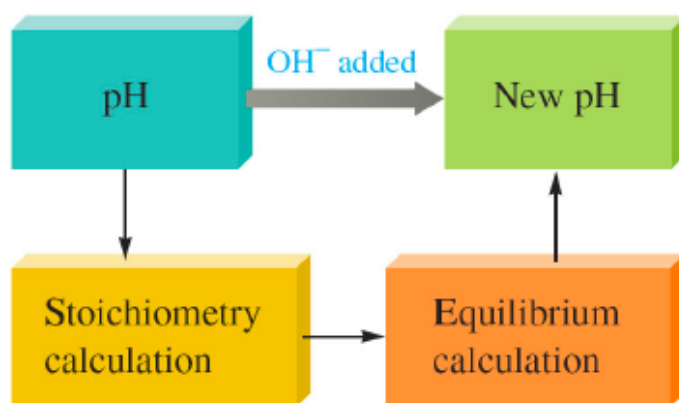The change in pH is less drastic as the acid becomes weaker.

$K_a = 10^{-10}$
$K_a = 10^{-8}$
$K_a = 10^{-6}$
$K_a = 10^{-4}$
$K_a = 10^{-2}$
Strong acid

pH

12.0
10.0
8.0
6.0
4.0
2.0

0   10   20   30   40   50   60

Vol 0.10 M NaOH added (mL)

The pH Curve of Titration

For *weak* acid with strong base

- Must deal with the weak acid dissociation equilibrium.
- The acid reacts essentially to completion with OH^-.

(1) Stoichiometry calculation: use the amount of OH$^-$ to calculate the amount of *conjugate base* of the weak acid.

(2) Equilibrium calculation: use the amount of acid left, amount of conjugate base, and K_a to determine the [H$^+$] and pH.

The pH Curve of Titration

For *weak* acid   CH$_3$COOH, acetic acid

- Titration of 50.0 mL of 0.100 M HC$_2$H$_3$O$_2$ (K_a = 1.8 $\times$ 10^{-5}) with 0.100 M NaOH.

0 mL of NaOH:
K_a = 1.8 $\times$ 10^{-5} = x^2 / 0.100 x = 1.3 $\times$ 10^{-3}
[H$^+$] = 1.3 $\times$ 10^{-3} M => pH = 2.89

10.0 mL :
[HC$_2$H$_3$O$_2$] = [(50.0 $\times$ 0.100) $-$ (10.0 $\times$ 0.100)] / (50.0 + 10.0) = (4.00/60.0)
[C$_2$H$_3$O$_2$$^-$] = (10.0 $\times$ 0.100) / (50.0 + 10.0) = (1.00/60.0)
[H$^+$] = K_a $\times$ [HC$_2$H$_3$O$_2$] / [C$_2$H$_3$O$_2$$^-$] = 7.2 $\times$ 10^{-5} => pH = 4.14

25.0 mL :
[HC$_2$H$_3$O$_2$] = [(50.0 $\times$ 0.100) $-$ (25.0 $\times$ 0.100)] / (50.0 + 25.0) = (2.5/75)
[C$_2$H$_3$O$_2$$^-$] = (25.0 $\times$ 0.100) / (50.0 + 25.0) = (2.5/75)
[H$^+$] = K_a $\times$ [HC$_2$H$_3$O$_2$] / [C$_2$H$_3$O$_2$$^-$] = 1.8 $\times$ 10^{-5} => pH = 4.74

The pH Curve of Titration
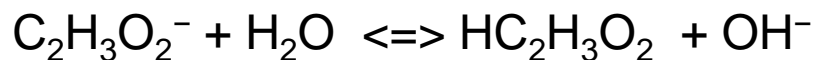
For *weak* acid

- Titration of 50.0 mL of 0.100 M $HC_2H_3O_2$ ($K_a = 1.8 \times 10^{-5}$) with 0.100 M NaOH.

  50.0 mL : equivalence point
   amount of acid = amount of base
  Major components in solution are Na^+, H_2O, and $C_2H_3O_2^-$

  $$C_2H_3O_2^- + H_2O \iff HC_2H_3O_2 + OH^-$$

  $K_b = [HC_2H_3O_2][OH^-] / [C_2H_3O_2^-] = K_w / K_a = 5.6 \times 10^{-10}$
  $5.6 \times 10^{-10} = x^2 / [(50.0 \times 0.100) / (50.0 + 50.0)]$
  $x = [OH^-] = 5.3 \times 10^{-6}$
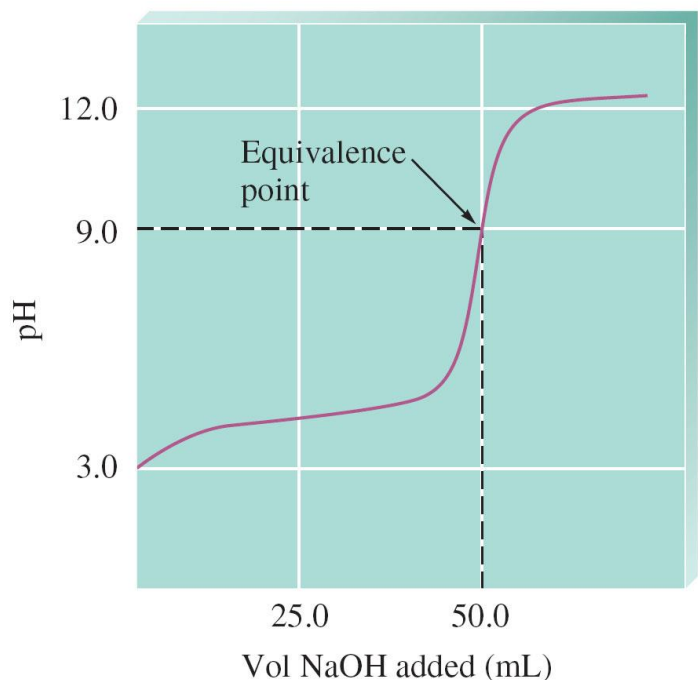 $[H^+] = K_w / [OH^-] = 1.9 \times 10^{-9}$ M => pH = 8.72

  The pH at the equivalence point of a titration of a weak acid with a strong base is always greater than 7.

The pH Curve of Titration

For *weak* acid

- Titration of 50.0 mL of 0.100 M $HC_2H_3O_2$ ($K_a = 1.8 \times 10^{-5}$) with 0.100 M NaOH.

60.0 mL :
Major components in solution are Na^+, H_2O, $C_2H_3O_2^-$, and OH^-

OH^- is a much stronger base than $C_2H_3O_2^-$

$[OH^-]$
$= [(60.0 \times 0.100) - (50.0 \times 0.100)] / (60.0 + 50.0)$
$= 9.1 \times 10^{-3}$

$[H^+] = K_w / [OH^-] = 1.1 \times 10^{-12}$ M
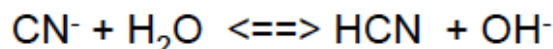=> pH = 11.96

The pH value at equivalence point

The pH at equivalence point of

- Titration of 50.0 mL of 0.100 M HCN (K_a = 6.2 x 10^{-10}) with 0.100 M NaOH.

50 mL : equivalence point
 amount of acid = amount of base
Major component is solution is Na^+, H_2O, and CN^-

$$CN^- + H_2O \iff HCN + OH^-$$
$$K_b = [HCN][OH^-]/[CN^-] = K_w / K_a = 1.6 \times 10^{-5}$$
$$1.6 \times 10^{-5} = x^2 / [(50.0 \times 0.100)/(50 + 50)]$$
$$x = [OH^-] = 8.9 \times 10^{-4}$$
$$[H^+] = K_w / [OH^-] = 1.1 \times 10^{-11} \text{ M} \implies pH = 10.96$$

The HCN is a weaker acid than $HC_2H_3O_2$, therefore the pH at the equivalence point of a titration is greater.

The pH Curve of Titration

Titration of acid with strong base

- The equivalence point is determined by the amount of acid.

- The pH value at the equivalence point is affected by the acid strength.
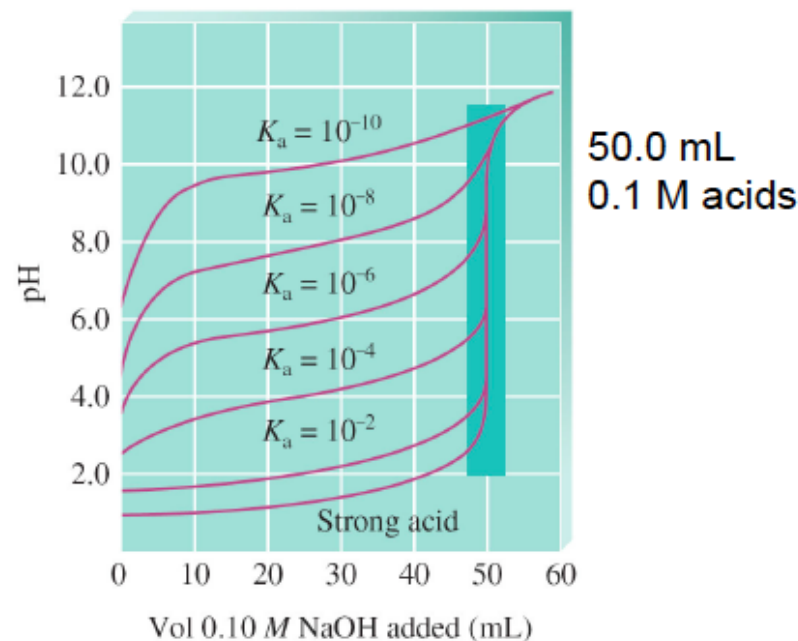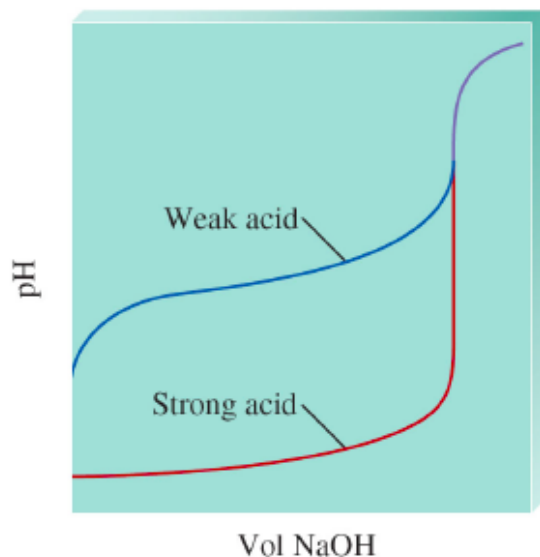
Weak acid

Strong acid

Vol NaOH

$K_a = 10^{-10}$

$K_a = 10^{-8}$

$K_a = 10^{-6}$

$K_a = 10^{-4}$

$K_a = 10^{-2}$

Strong acid

50.0 mL
0.1 M acids

Vol 0.10 M NaOH added (mL)

17 - Aqueous Equilibrium

Buffering Region

$$\text{pH} = \text{p}K_a$$

$$[\text{HA}] \approx \left[\text{A}^-\right]$$

Weak acid

Strong acid

pH

Vol NaOH

Buffering?

Strong Acid−Strong Base

Big change in [H$^+$]

pH

[H$^+$]
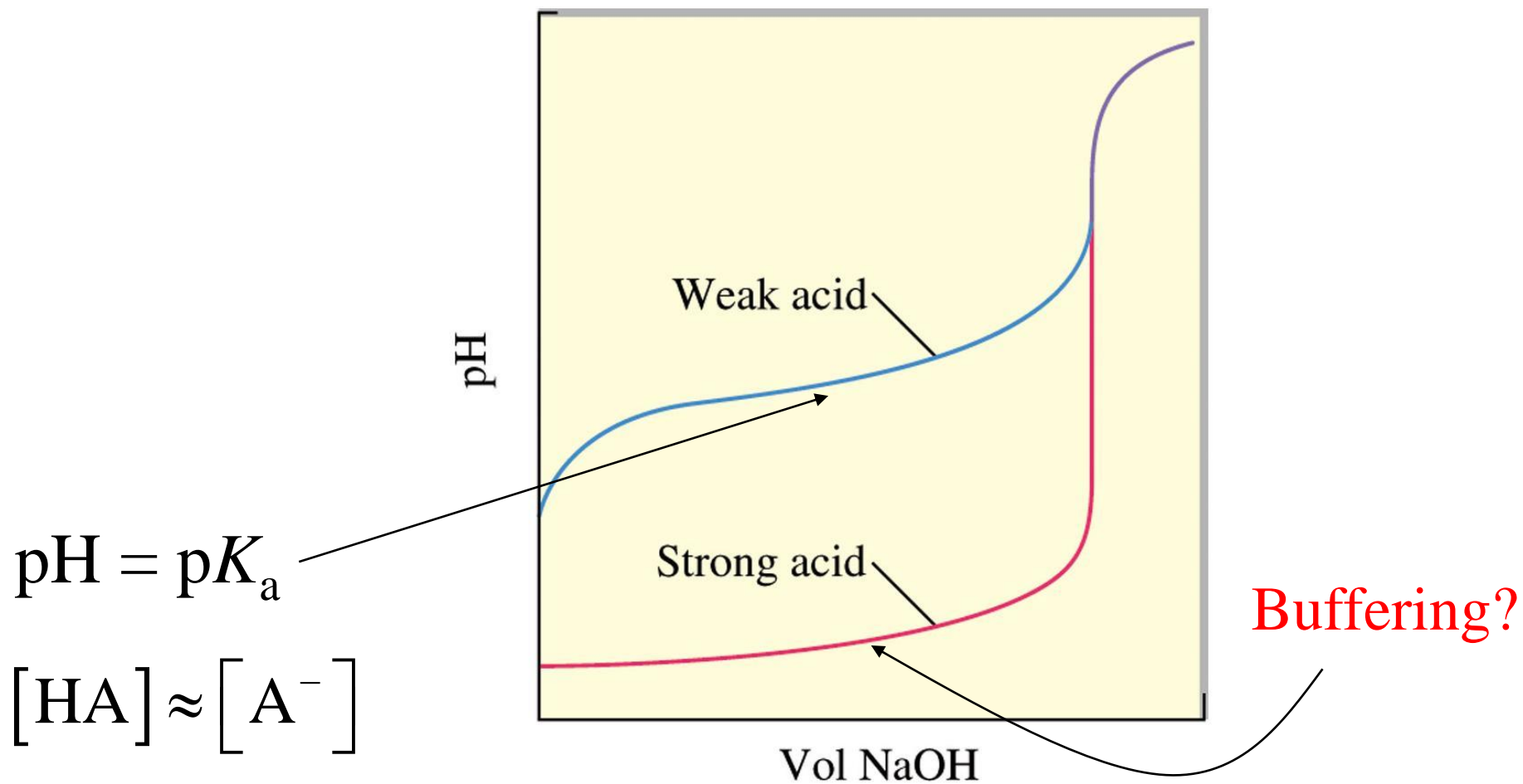
NaOH added (mole)
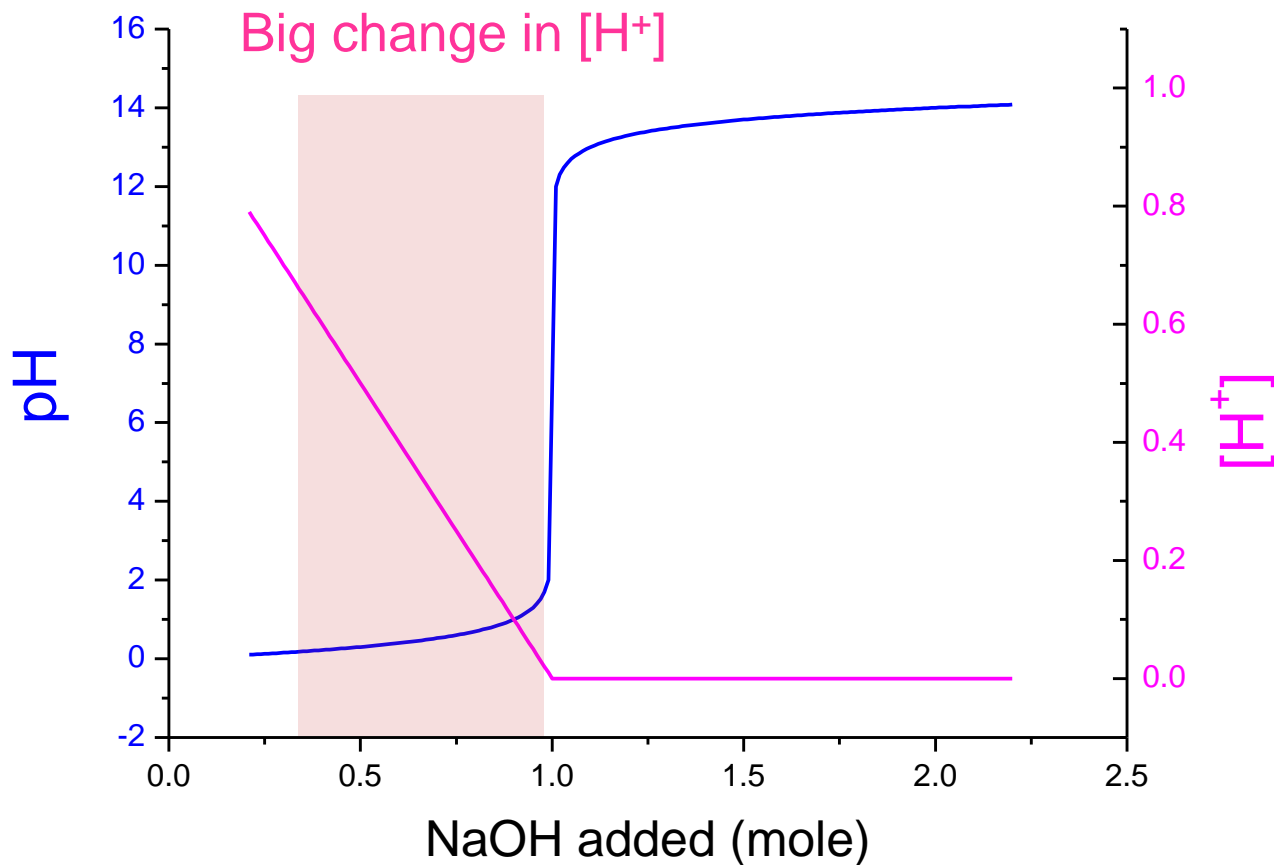
Initial state

HCl = 1.0 mole

Vol = 1.0 dm^3

Final state

NaOH = 1.2 mole

NaCl = 1.0 mole

Vol = 1.0 dm^3

Learning Check

This titration curve involves 1.0 M solutions of an acid and a base. Identify the type of titration it represents.

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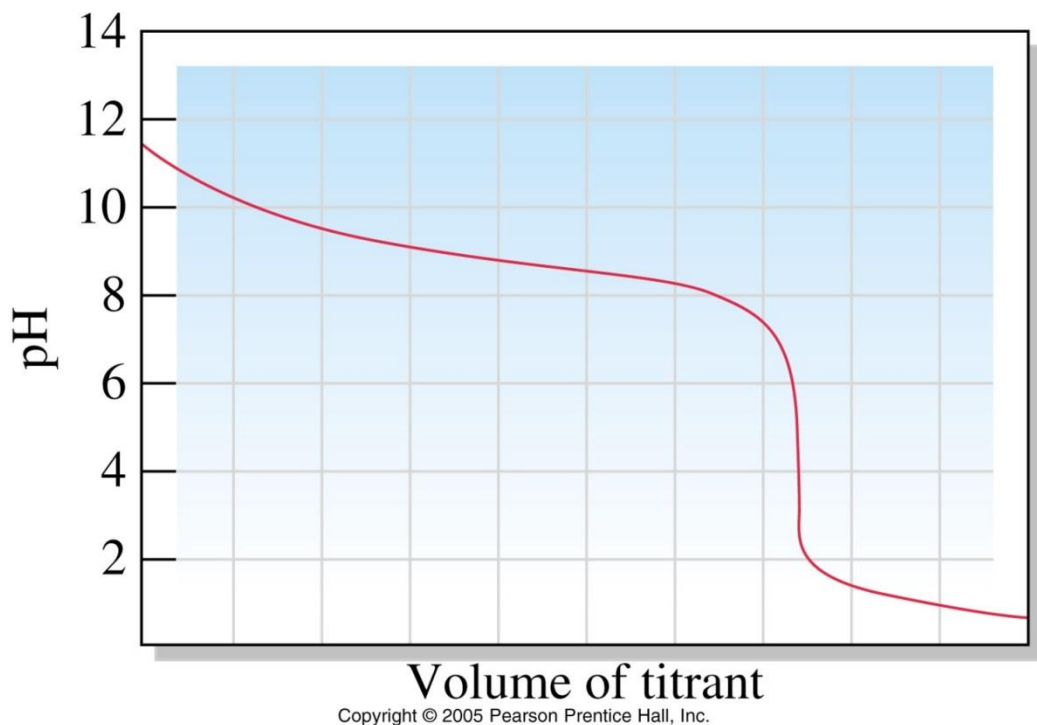
1. Strong acid added to weak base because the equivalent point is smaller than 7
2. Buffering region occurs at around pH 9

Neutralization Reactions

- At the ***equivalence point*** in an acid–base titration, the acid and base have been brought together in precise stoichiometric proportions.

- The ***endpoint*** is the point in the titration at which the indicator changes color.

- Ideally, the indicator is selected so that the endpoint and the equivalence point are very close together.

Acid–Base Indicators

- An acid–base ***indicator*** is a weak acid or base.

- The acid form (HA) of the indicator has one color, the conjugate base (A^-) has a different color. One of the "colors" may be colorless.

- In an acidic solution, [H_3O^+] is high. Because H_3O^+ is a common ion, it suppresses the ionization of the indicator acid, and we see the color of HA.

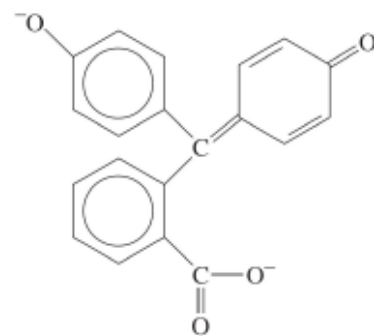- In a basic solution, [OH^-] is high, and it reacts with HA, forming the color of A^-.

End Point of Titration

At the end point,

- The indicator has a permanent color.

- The useful pH range of an indicator is given by $pK_a \pm 1$

- Phenolphthalein (酚酞)
  $K_a = 1.0 \times 10^{-8}$
  $pK_a = -\log K_a = 8$
  useful pH range $7 \sim 9$
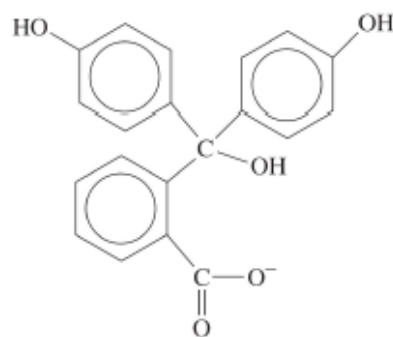
Colorless acid form, HIn

Pink base form, In⁻

Indicator

An acid-base indicator

- Marks the end point by changing color. (one tenth of initial form)
- The end point is not necessarily equals to the equivalence point.
- Choose your indicator carefully.
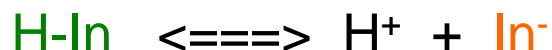
$$H\text{-}In \iff H^+ + In^-$$

$$K_a = \frac{[H^+][In^-]}{[H\text{-}In]} \qquad [H^+] = K_a \times \frac{[H\text{-}In]}{[In^-]} \qquad pH = pK_a + \log \frac{[In^-]}{[H\text{-}In]}$$

Low pH to high pH (mostly H-In)

$$pH = pK_a + \log \frac{[In^-]}{[H\text{-}In]}$$

$$pH = pK_a + \log (1/10)$$

$$= pK_a - 1$$

High pH to low pH (mostly In⁻)

$$pH = pK_a + \log \frac{[In^-]}{[H\text{-}In]}$$

$$pH = pK_a + \log (10/1)$$

$$= pK_a + 1$$

Different indicators have different values of K_a, so they exhibit color changes at different values of pH …
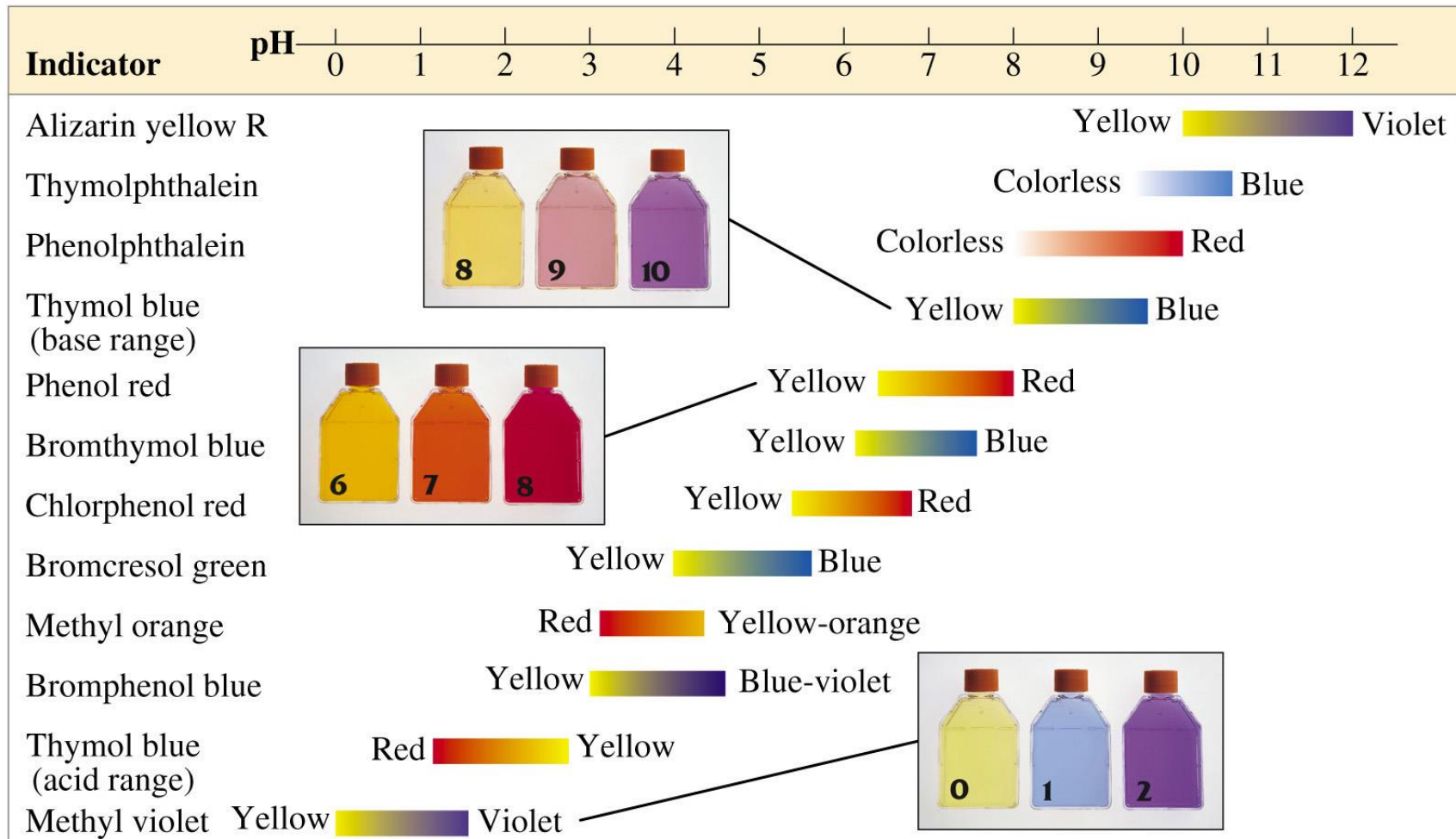
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Strong Acid–Strong Base

Bromphenol blue, bromthymol blue, and phenolphthalein all change color at very nearly 20.0 mL

Weak Acid−Strong Base
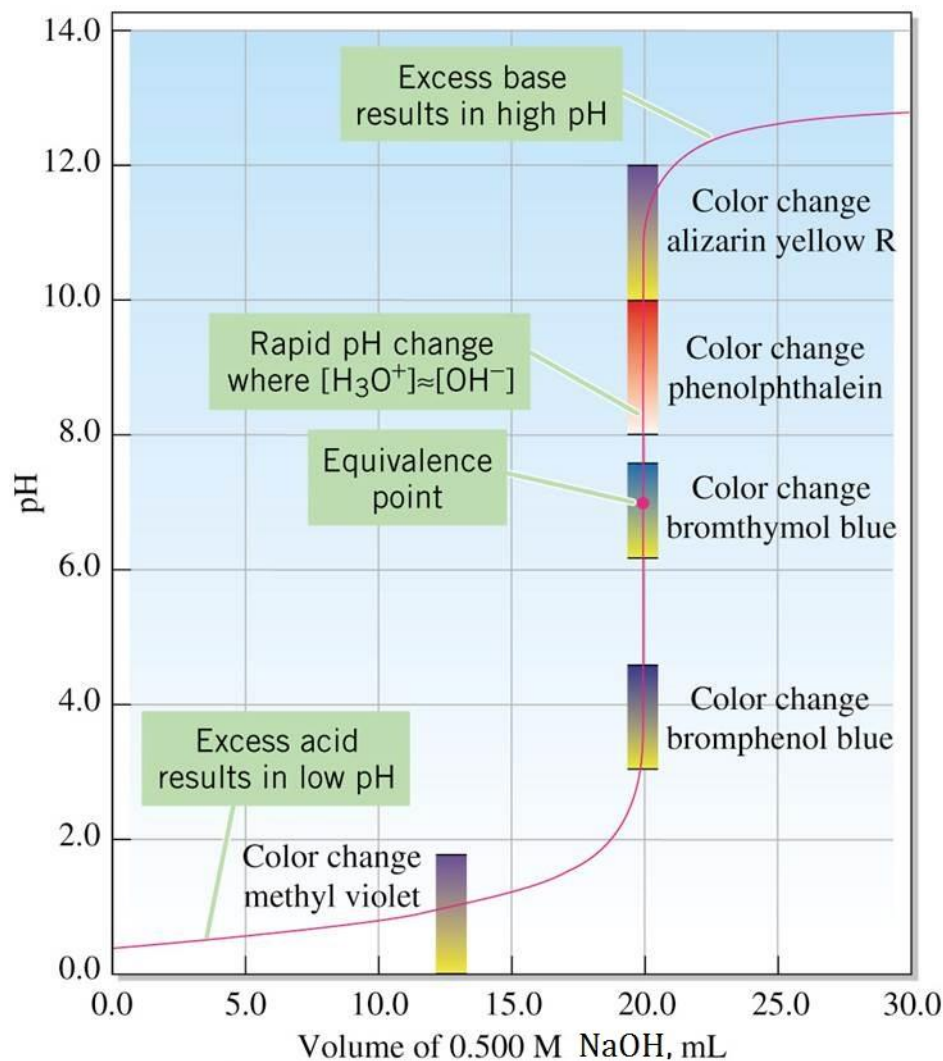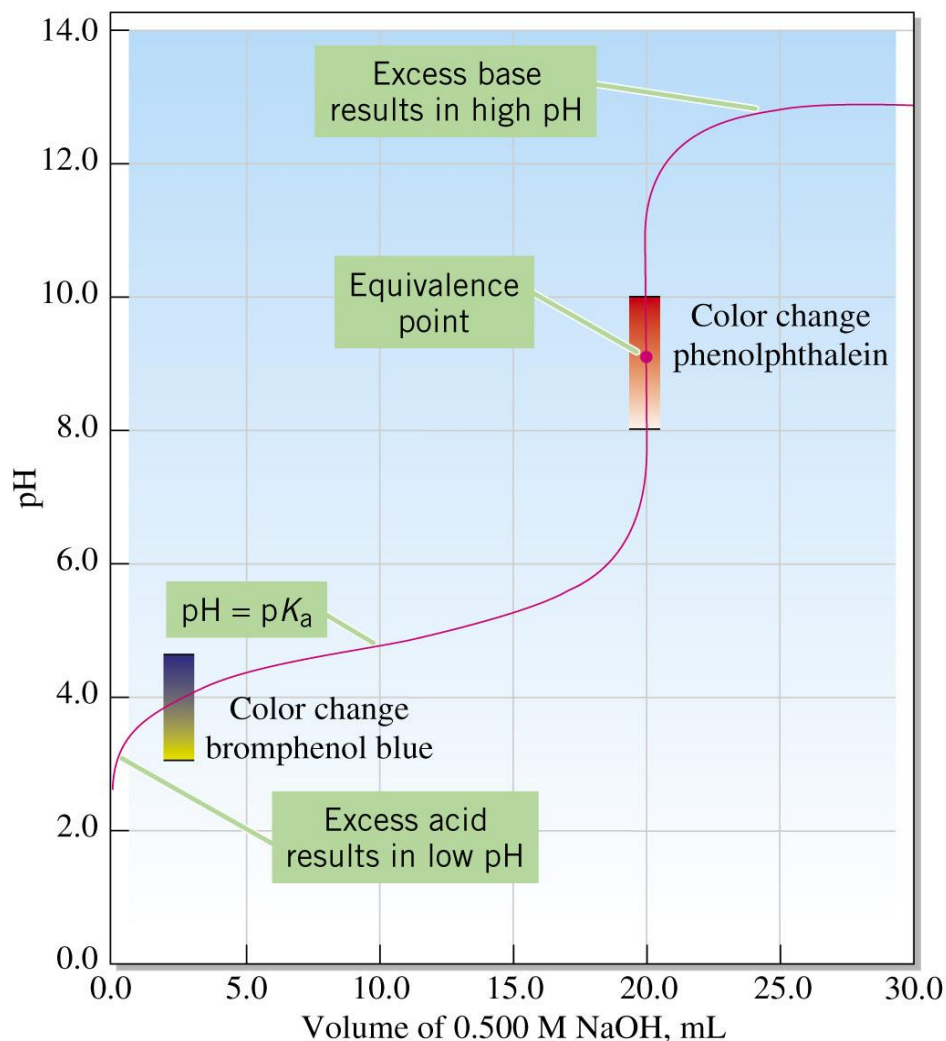
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Bromphenol blue was ok for the strong acid/strong base titration, but it changes color far too early to be useful here.

Titration of Polyprotic Acids

$$H_3A\,(aq) \rightleftharpoons H^+(aq) + H_2A^-(aq)$$

$$H_2A^-\,(aq) \rightleftharpoons H^+(aq) + HA^{2-}(aq)$$

$$HA^{2-}\,(aq) \rightleftharpoons H^+(aq) + A^{3-}(aq)$$

What are the pH values at the equivalence points?

The appropriate equilibrium expression must be first chosen by knowing what major species are present!

Titration of Polyprotic Acids

Before the first equivalence point:

$$H_3A \, (aq) + H_2O \, (l) \Leftrightarrow H_3{}^+O \, (aq) \; + \; H_2A^- (aq) \qquad K_{a1} = \frac{[H^+][H_2A^-]}{[H_3A]}$$
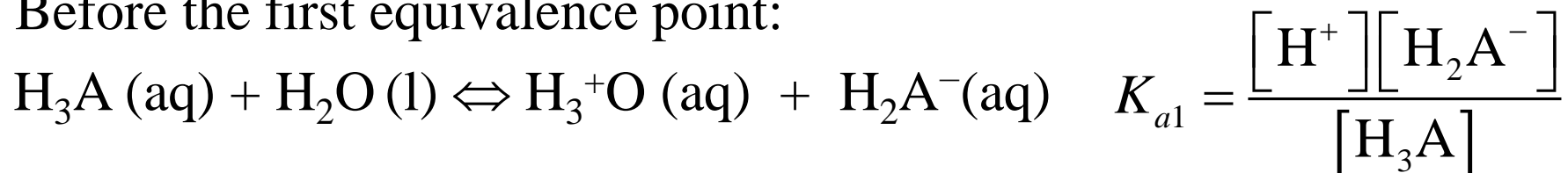
At the first equivalence point, which of the following equation best describes the reaction of H_2A^-?

$$H_2A^- \, (aq) \; \Leftrightarrow \; H^+ \, (aq) \; + \; HA^{2-} \, (aq) \qquad K_{a2} = 6.2 \times 10^{-8}$$

$$H_2A^- \, (aq) + H_3{}^+O \, (aq) \; \Leftrightarrow \; H_3A \, (aq) + H_2O \, (l) \qquad K_1 = 133$$

$$H_2A^- \, (aq) + H_2O \, (aq) \; \Leftrightarrow \; H_3A \, (aq) + OH^- \, (aq) \qquad K_2 = 1.3 \times 10^{-12}$$

$$H_2A^- \, (aq) + H_2A^- \, (aq) \; \Leftrightarrow \; H_3A \, (aq) + HA^{2-} \, (aq) \qquad K_3 = 8.2 \times 10^{-6}$$
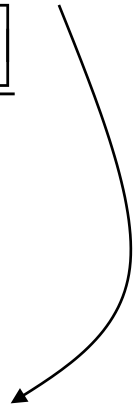
Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}

Titration of Polyprotic Acids

At the first equivalence point:

$$H_2A^- \text{ (aq)} + H_2A^- \text{ (aq)} \rightleftharpoons H_3A \text{ (aq)} + HA^{2-} \text{ (aq)}$$
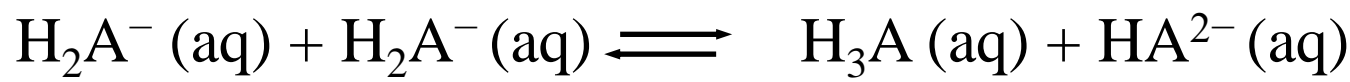
$$K_{eq} = \frac{[H_3A][HA^{2-}]}{[H_2A^-]^2} = \frac{[H_3A]}{[H_2A^-][H^+]} \times \frac{[H^+][HA^{2-}]}{[H_2A^-]}$$

$$= \frac{1}{K_{a1}} \times K_{a2}$$

Since we also have $\quad [H_3A] = [HA^{2-}]$

$$\Longrightarrow \quad \frac{[H_3A]^2}{[H_2A^-]^2} = \frac{K_{a2}}{K_{a1}} \qquad \Longrightarrow \quad \frac{[H_3A]}{[H_2A^-]} = \sqrt{\frac{K_{a2}}{K_{a1}}}$$

Titration of Polyprotic Acids

$$\frac{[H_3A]}{[H_2A^-]} = \sqrt{\frac{K_{a2}}{K_{a1}}}$$

Rewrite the left hand side by

$$K_{a1} = \frac{[H_2A^-][H^+]}{[H_3A]}$$
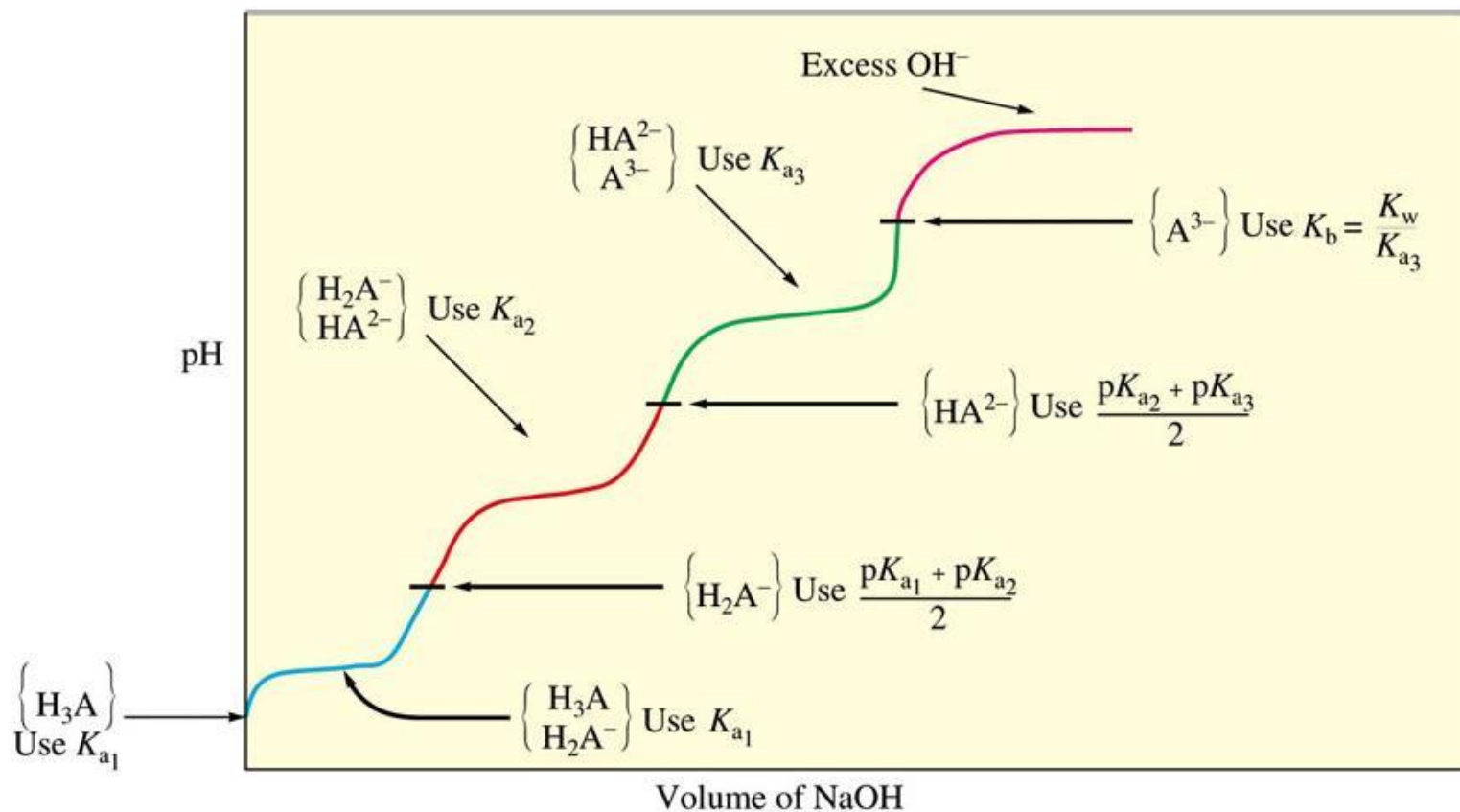
$$[H^+] = \sqrt{K_{a1}K_{a2}}$$

$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$

pH at the first equivalence point!

- Applicable to solution containing H_2A^- and H_2O mainly
- Independent of the concentration of H_2A^-

Titration of H$_3$A Acid

Excess OH$^-$

$\left\{\begin{matrix} HA^{2-} \\ A^{3-} \end{matrix}\right\}$ Use K_{a_3}

$\left\{A^{3-}\right\}$ Use $K_b = \dfrac{K_w}{K_{a_3}}$

$\left\{\begin{matrix} H_2A^- \\ HA^{2-} \end{matrix}\right\}$ Use K_{a_2}

$\left\{HA^{2-}\right\}$ Use $\dfrac{pK_{a_2} + pK_{a_3}}{2}$

pH

$\left\{H_2A^-\right\}$ Use $\dfrac{pK_{a_1} + pK_{a_2}}{2}$

$\left\{H_3A\right\}$
Use K_{a_1}

$\left\{\begin{matrix} H_3A \\ H_2A^- \end{matrix}\right\}$ Use K_{a_1}

Volume of NaOH

50

17 - Aqueous Equilibrium

Titration of Alanine

$$K_{a2} = \frac{\left[\text{Ala}^-\right]\left[\text{H}_3\text{O}^+\right]}{\left[^+\text{Ala}^-\right]}$$

$$K_{a1} = \frac{\left[^+\text{Ala}^-\right]\left[\text{H}_3\text{O}^+\right]}{\left[^+\text{Ala}\right]}$$

Isoelectric Point

$$K_{a1} = \frac{[\mathbf{Z}][H^+]}{[\mathbf{P}]} \qquad K_{a2} = \frac{[\mathbf{N}][H^+]}{[\mathbf{Z}]}$$
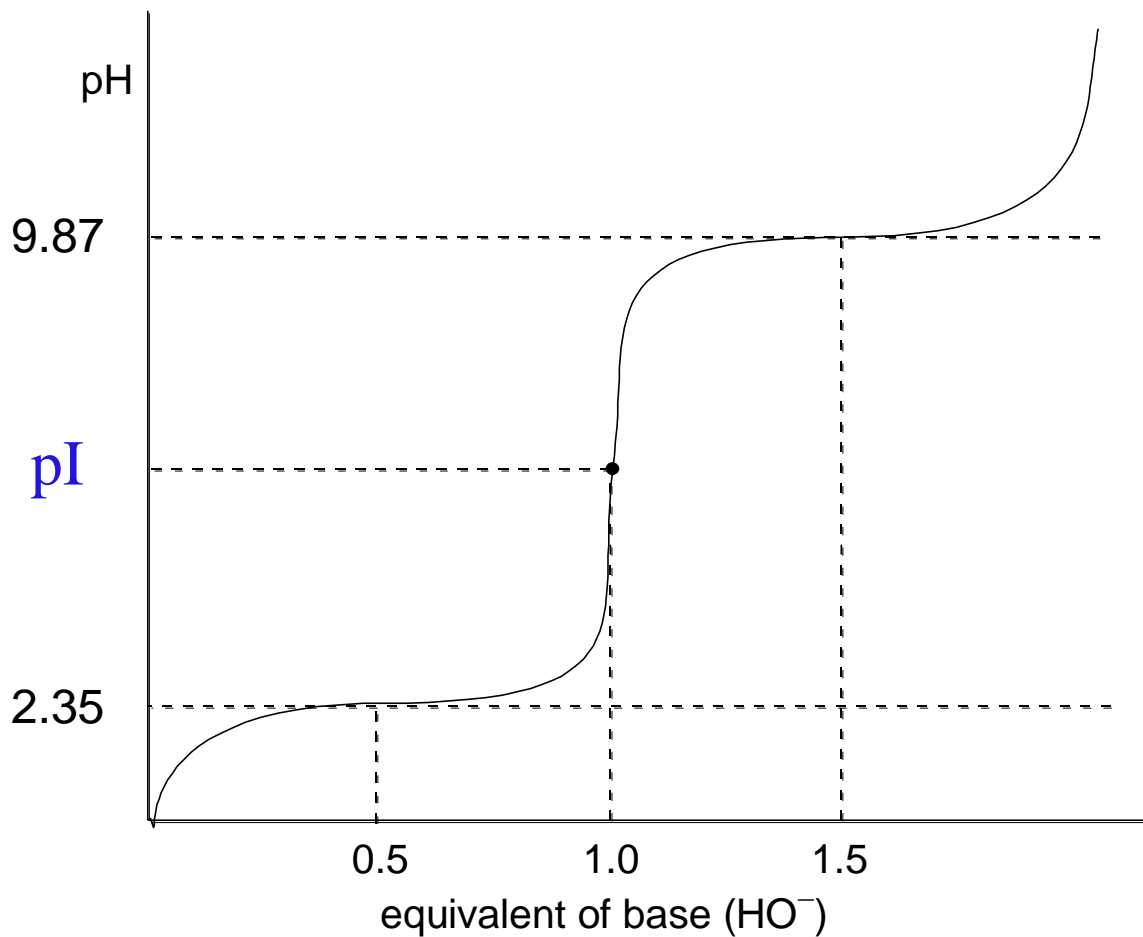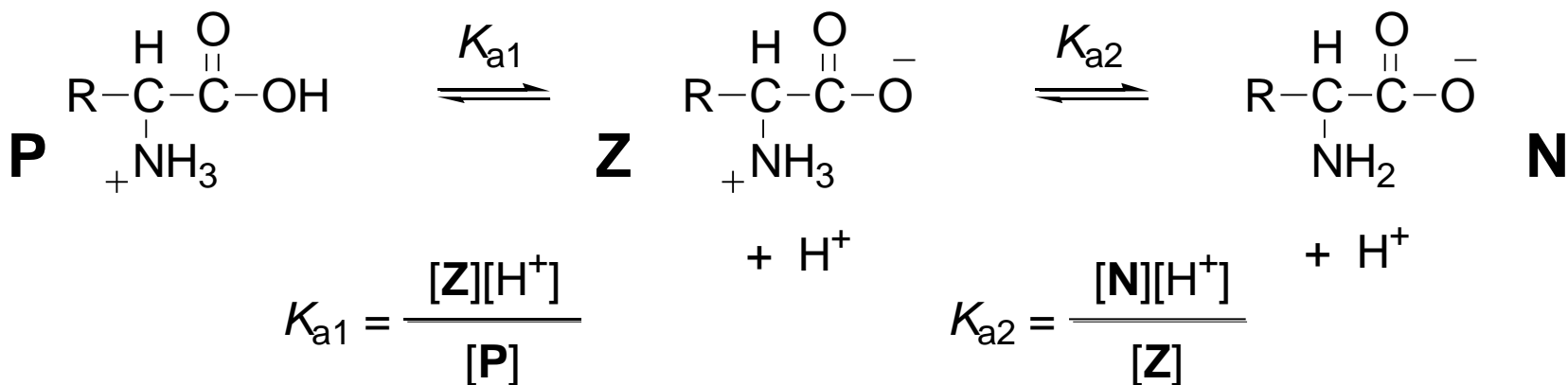
pI: Isoelectric point

$$pK_{a1} = -\log[H^+] - \log\frac{[\mathbf{Z}]}{[\mathbf{P}]} \qquad pK_{a2} = -\log[H^+] - \log\frac{[\mathbf{N}]}{[\mathbf{Z}]}$$

$$pK_{a1} + pK_{a2} = 2pH - \log\frac{[\mathbf{N}]}{[\mathbf{P}]}$$

Isoelectric Point

$$pK_{a1} + pK_{a2} = 2pH - \log\frac{[\mathbf{N}]}{[\mathbf{P}]}$$

$$pH = (pK_{a1} + pK_{a2})/2 \equiv pI$$
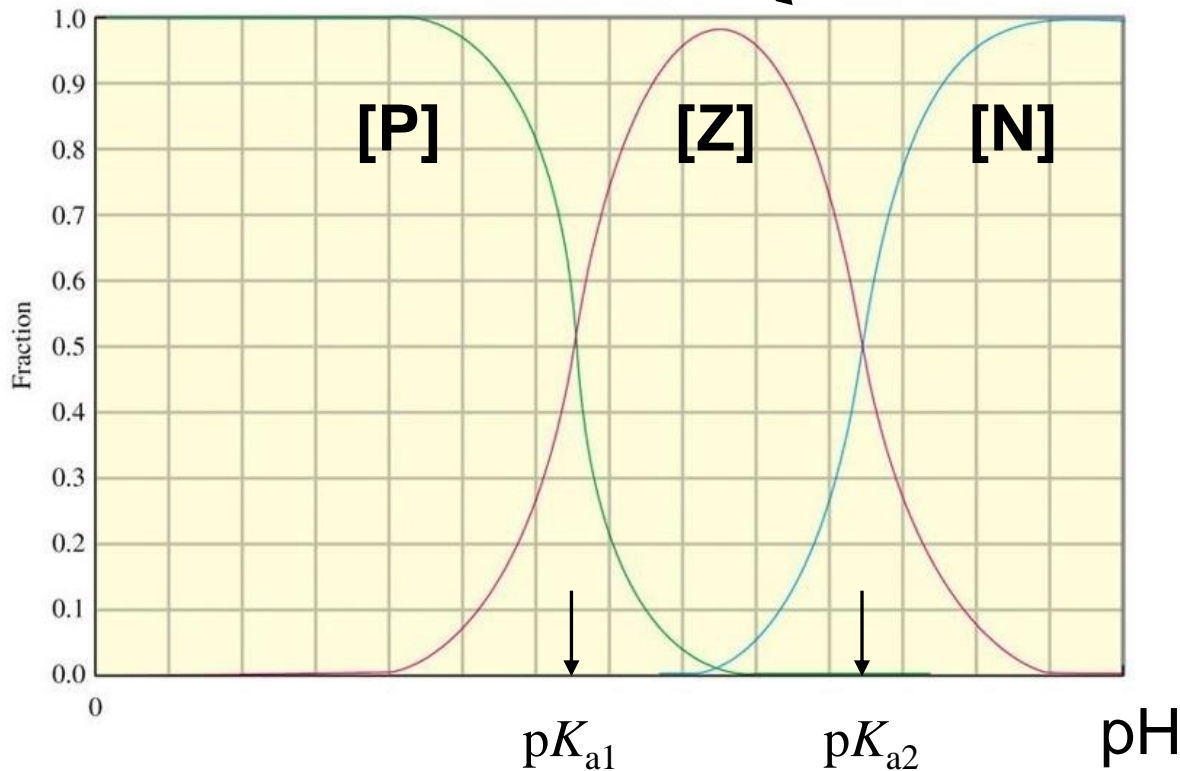
$[\mathbf{N}] = [\mathbf{P}]$

The zwitterionic form (dipolar ion) has the highest concentration

Solubility and Solubility Product

- **Relative Solubilities**
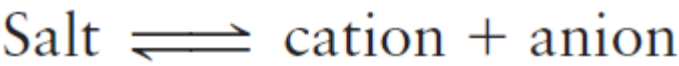
$$Salt \rightleftharpoons cation + anion$$

$$K_{sp} = [cation][anion]$$

$$[Cation] = x \text{ (mol/L)}$$

$$[Anion] = x$$

$$K_{sp} = [cation][anion] = x^2$$

$$x = \sqrt{K_{sp}} = solubility$$

$AgI(s)$ $K_{sp} = 1.5 \times 10^{-16}$

$CuI(s)$ $K_{sp} = 5.0 \times 10^{-12}$

$CaSO_4(s)$ $K_{sp} = 6.1 \times 10^{-5}$

Solubility:

$$CaSO_4 > CuI > AgI$$
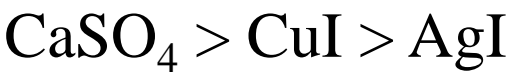
Largest K_{sp} Smallest K_{sp}

Solubility and Solubility Product

Solubilities of Cus, Ag_2S, and Bi_2S_3

Salt	K_{sp}
CuS	8.5×10^{-45}
Ag_2S	1.6×10^{-49}
Bi_2S_3	1.1×10^{-73}

$$Bi_2S_3(s) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$$
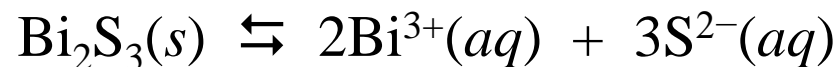
$$1.1 \times 10^{-73} = [Bi^{3+}]^2 [S^{2-}]^3$$
$$= (2x)^2 (3x)^3$$
$$\Rightarrow \quad x = 1.0 \times 10^{-15}$$

Solubility:

$$Bi_2S_3 > Ag_2S > CuS$$

Solubility products sometimes cannot directly
tell you the relative solubility of two compounds

Solubility and Solubility Product

- **Common Ion Effect**

  The solubility of silver chromate in 0.100 M silver nitrate solution:

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = 9.0 \times 10^{-12}$$

$$x \text{ mol/L } Ag_2CrO_4(s) \longrightarrow 2x \text{ mol/L } Ag^+(aq) + x \text{ mol/L } CrO_4^{2-}(aq)$$
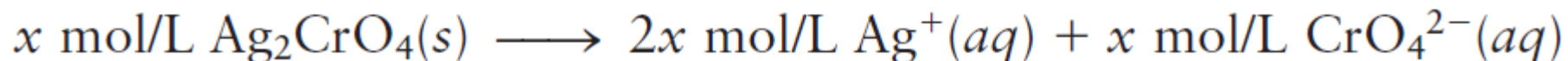
$$[Ag^+] = [Ag^+]_0 + \text{change} = 0.100 + 2x$$

$$[CrO_4^{2-}] = [CrO_4^{2-}]_0 + \text{change} = 0 + x = x$$

$$9.0 \times 10^{-12} = [Ag^+]^2[CrO_4^{2-}] = (0.100 + 2x)^2(x)$$

17 - Aqueous Equilibrium

Solubility and Solubility Product

$$9.0 \times 10^{-12} = (0.100 + 2x)^2(x) \approx (0.100)^2(x)$$

$$x \approx \frac{9.0 \times 10^{-12}}{(0.100)^2} = 9.0 \times 10^{-10} \text{ mol/L}$$

Solubility of Ag_2CrO_4 in 0.100 M $AgNO_3$ = x = 9.0×10^{-10} mol/L

$$[Ag^+] = 0.100 + 2x = 0.100 + 2(9.0 \times 10^{-10}) = 0.100 \ M$$

$$[CrO_4{}^{2-}] = x = 9.0 \times 10^{-10} \ M$$

$$(2x)^2(x) = K_{sp}$$

Solubility of Ag_2CrO_4 in pure water = 1.3×10^{-4} mol/L

Solubility of Ag_2CrO_4 in 0.100 M $AgNO_3$ = 9.0×10^{-10} mol/L

Solubility and Solubility Product

$$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad K_{sp} = 4.47 \times 10^{-9}$$

➡️ $[Ca^{2+}] = 6.69 \times 10^{-5}\ M$ ➡️ $x(CaCO_3) = 6.69\ mg/L$

Under ambient conditions:

$$P_{CO_2} = 35\ Pa$$

⬇️ Henry's law $\qquad P_{CO_2} = k_H [CO_2]$

$$[CO_2] = 12\ \mu M$$
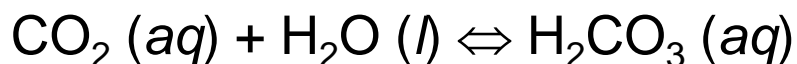
⬇️ $CO_2\ (aq) + H_2O\ (l) \Leftrightarrow H_2CO_3\ (aq) \qquad K_{eq} = 1.7 \times 10^{-3}$
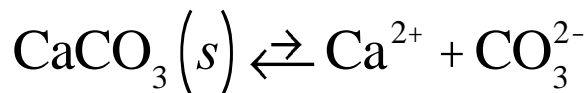
$$[H_2CO_3] = 2.0 \times 10^1\ nM$$

Solubility and Solubility Product

Solubility of $CaCO_3$ at pH 8.27 under ambient conditions:

$$\left[H_2CO_3 \right] = 2.0 \times 10^1 \text{ nM}$$

$$x(CaCO_3) = 6.69 \text{ mg/L}$$

$$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$$K_{sp} = 4.47 \times 10^{-9}$$

$$CO_3^{2-} + H_2O \Leftrightarrow HCO_3^- + OH^-$$

$$K_{b2} = 2.1 \times 10^{-4}$$

$$HCO_3^- + H_2O \Leftrightarrow H_2CO_3 + OH^-$$

$$K_{b1} = 2.3 \times 10^{-8}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$
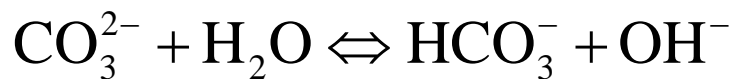
$$[H^+] + 2[Ca^{2+}] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

$$[Ca^{2+}] = 4.7 \times 10^{-4} \text{ M}; \quad x(CaCO_3) = 47 \text{ mg/L}$$

Equilibria Involving Complex Ions

$$Ag^+ + 2\ NH_3 \Leftrightarrow [Ag(NH_3)_2]^+ \qquad K_f = 1.7 \times 10^7$$

$$AgCl \Leftrightarrow Ag^+ + Cl^- \qquad K_{sp} = 1.6 \times 10^{-10}$$

$$AgCl + 2\ NH_3 \Leftrightarrow [Ag(NH_3)_2]^+ + Cl^- \qquad K = 2.8 \times 10^{-3}$$
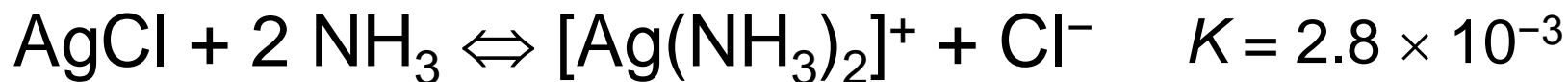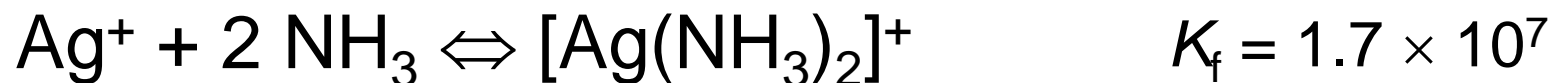
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Equilibria Involving Complex Ions

The solubility of AgCl in 10.0 M NH_3 solution:

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq) + Cl^-(aq)$$
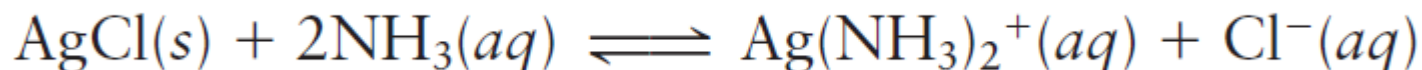
$$K = 2.8 \times 10^{-3} = \frac{[Ag(NH_3)_2{}^+][Cl^-]}{[NH_3]^2} = \frac{x^2}{(10.0 - 2x)^2}$$

$$\sqrt{2.8 \times 10^{-3}} = \frac{x}{10.0 - 2x}$$

$$x = 0.48 \text{ mol/L} = \text{solubility of AgCl}(s) \text{ in } 10.0 \text{ M } NH_3$$

The solubility of AgCl in 10.0 M NH_3 solution is much greater than in pure water, which is $\sqrt{K_{sp}} = 1.3 \times 10^{-5}$ mol/L

Activity (*a*)
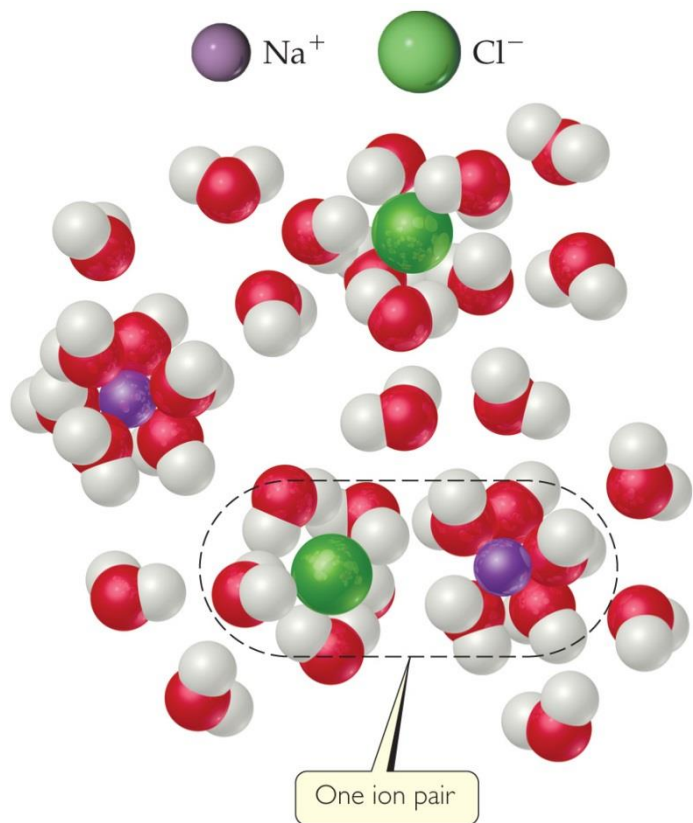
Concentration
- probability of finding the species

Such "probability" would reduce when there are
- solute−solute interactions
- interactions with other ions (Columbic interactions)

➡ Activity (effective concentration)
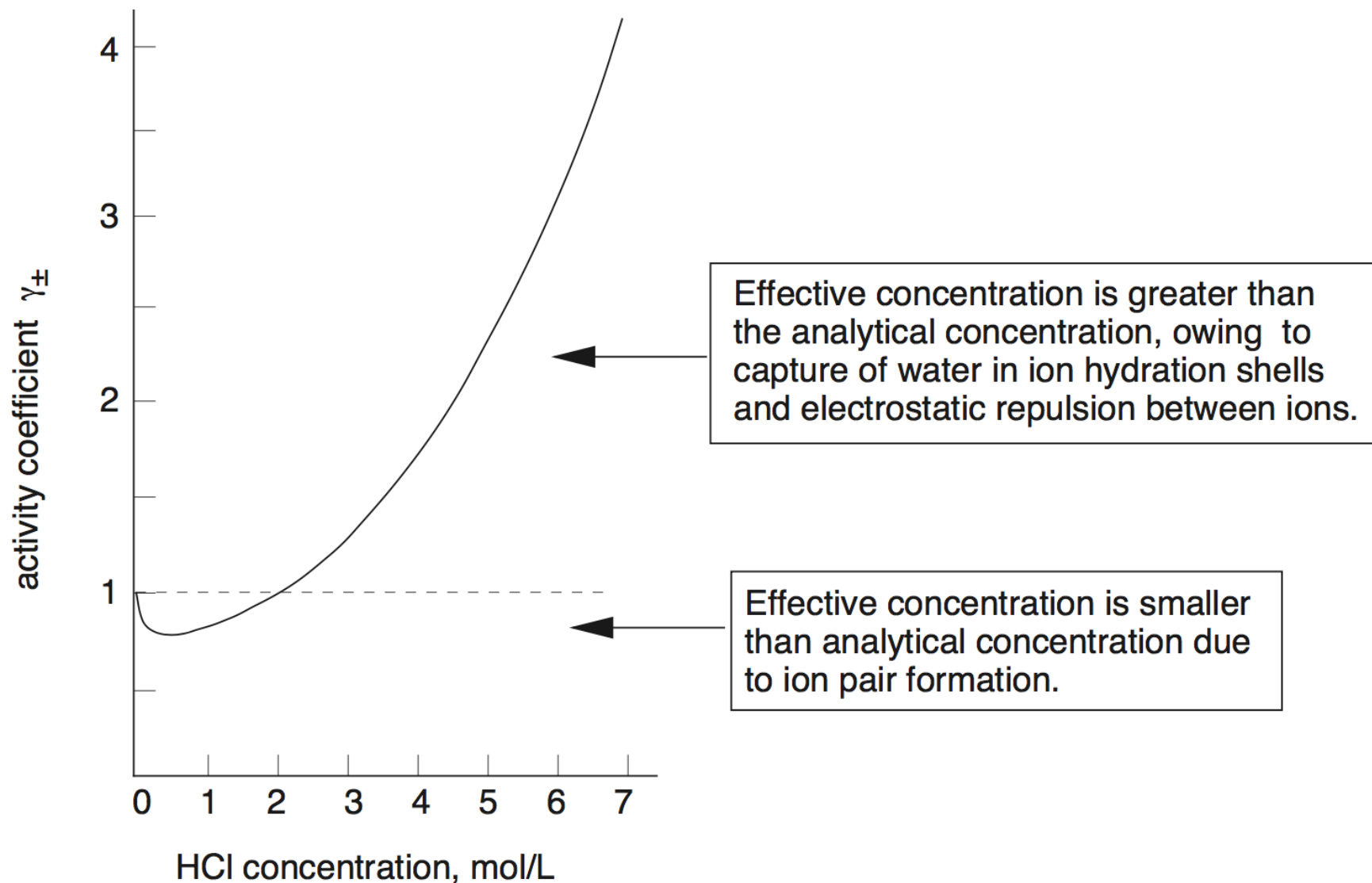
Figure 1: Mean ionic activity coefficient in HCl as a function of concentration

Concentration Dependence of K_C

$$A + B \Leftrightarrow C + D$$

At equilibrium

$$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$$

$$k_f a_A a_B = k_r a_C a_D$$

$$\frac{k_f}{k_r} = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C [C] \gamma_D [D]}{\gamma_A [A] \gamma_B [B]}$$

Concentration Dependence of K_C

$$A + B \Leftrightarrow C + D$$

At equilibrium

$$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$$

$$k_f a_A a_B = k_r a_C a_D$$

$$\frac{k_f \gamma_A \gamma_B}{k_r \gamma_C \gamma_D} = \frac{[C][D]}{[A][B]} = K_C$$

Concentration dependent

Concentration Dependence of K_a

$$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$$

Concentration	pKa
$\rightarrow$ 0 mM	4.756
1 mM	4.75
5 mM	4.73
10 mM	4.72
30 mM	4.70
100 mM	4.67

http://www.reachdevices.com/Protein/BiologicalBuffers.html

Ionization and Activities

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$$
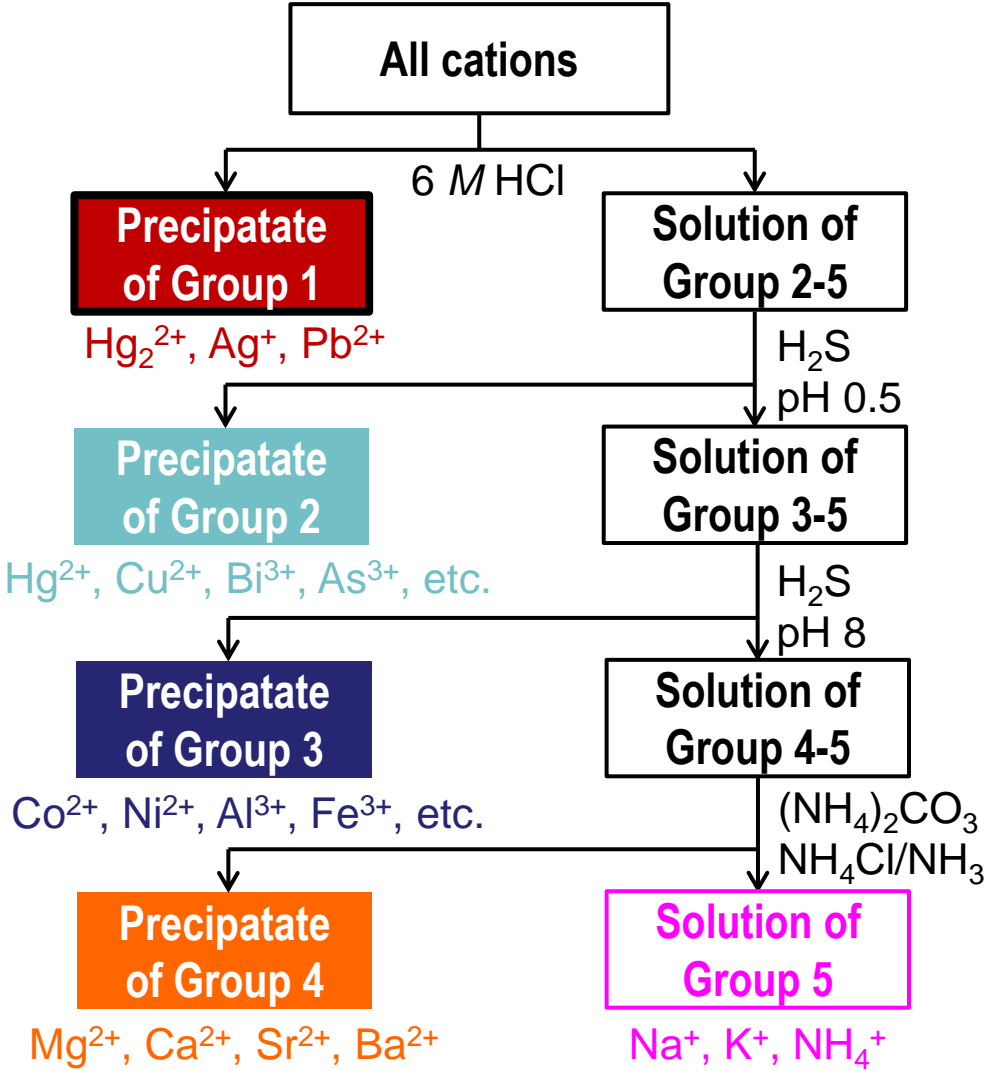
$$K_a = 4.3 \times 10^{-7} \text{ (in water)}$$
$$K_a = 7.9 \times 10^{-7} \text{ (in blood)}$$

Increased acidity of carbonic acid in blood occurs because of interionic attractions.

H^+ and HCO_3^- ions are surrounded by other ions of opposite charge in blood, which impede the collisions of H^+ and HCO_3^- ions.

Qualitative Analysis of Cations

I. **Separating cations into five groups based on their solubilities in the presence of various precipitating reagents.**

II. Selective and sequential dissolution of cations in the same group.

III. Verifying individual cations.

All cations

6 M HCl

Precipatate of Group 1
Hg_2^{2+}, Ag^+, Pb^{2+}

Solution of Group 2-5

H_2S pH 0.5

Precipatate of Group 2
Hg^{2+}, Cu^{2+}, Bi^{3+}, As^{3+}, etc.

Solution of Group 3-5

H_2S pH 8

Precipatate of Group 3
Co^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+}, etc.

Solution of Group 4-5

$(NH_4)_2CO_3$ NH_4Cl/NH_3

Precipatate of Group 4
Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}

Solution of Group 5
Na^+, K^+, NH_4^+

68

Qualitative Analysis of Cations

I. Separating cations into five groups based on their solubilities in the presence of various precipitating reagents.

II. Selective and sequential dissolution of cations in the same group.

III. Verifying individual cations.

$Hg_2Cl_2(s)$, $AgCl(s)$, $PbCl_2(s)$

Hot water

$Hg_2Cl_2(s)$, $AgCl(s)$

Solution with Pb^{2+}

NH_3

CH_3COOH
K_2CrO_4

$HgNH_2Cl(s)$, $Hg(l)$

$PbCrO_4(s)$

Solution with $[Ag(NH_3)_2]^+$

$AgCl(s)$