Reminder

all salts are strong electrolytes fully dissociated in water

$\alpha = 1$

but

Just after (infinitesimal time) …!

very weak conj. acid

very weak conj. base

$NaCl + H_2O \longrightarrow Na^+_{aq} + Cl^-_{aq}$

$NaHCO_3 + H_2O \longrightarrow Na^+_{aq} + HCO_3^-{}_{aq}$

strong conj. base

$NH_4Cl + H_2O \longrightarrow NH_4^+{}_{aq} + Cl^-_{aq}$

strong conj. acid

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$Na^+HCO_3^-$ (sodium-bicarbonate !)

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^- \qquad \text{(eq. 1)}$$

$$HCO_3^- + H_3O^+ \rightleftarrows H_2CO_3 + H_2O \qquad \text{(eq. 2)}$$

these 2 equilibria coexist in the same solution

$$\cancel{H_2O} + H_2O + HCO_3^- + \cancel{H_3O^+} \rightleftarrows \cancel{H_3O^+} + OH^- + H_2CO_3 + \cancel{H_2O}$$

let's simplify (by cancelling species identical before and after reaction)

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

Net hydrolytic event

Hydrolysis

$$HCO_{3\ aq}^{-} + \overbrace{H_3O^{+} + OH^{-}}^{\mathit{H_2O\ auto\text{-}protolysis}} \rightleftharpoons H_2CO_3 + H_2O + OH^{-}$$

$$HCO_{3\ aq}^{-} + H_2O \rightleftharpoons H_2CO_3 + OH^{-}$$

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Salt hydrolysis

Salt formula	**Derived from**	**pH**
$CH_3COO^-Na^+$	*weak* acid – *strong* base *(basic salt)*	↑
$NH_4^+Cl^-$	*weak* base – *strong* acid *(acidic salt)*	↓
$CH_3COO^-NH_4^+$	*both* weak – acid and base *(pH depends…)*	↑↓
K^+Cl^-	*both* strong – acid and base *(no hydrolysis)*	**7.0**

The strong conjugated species react with H_2O (…the H^+ and OH^-)

$$HCO_{3\ aq}^{-} + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

$$HPO_{4\ aq}^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$$

$$NH_{4\ aq}^{+} + H_2O \rightleftharpoons NH_4OH + H^+$$

and pH varies

Ex.s all salts of bio-cellular interest:
Salts deriving form organic acids (Krebs cycle), pyruvate lactate, succinate, oxalacetate…etc.

CH_3-CO-COOH
Pyruvic acid

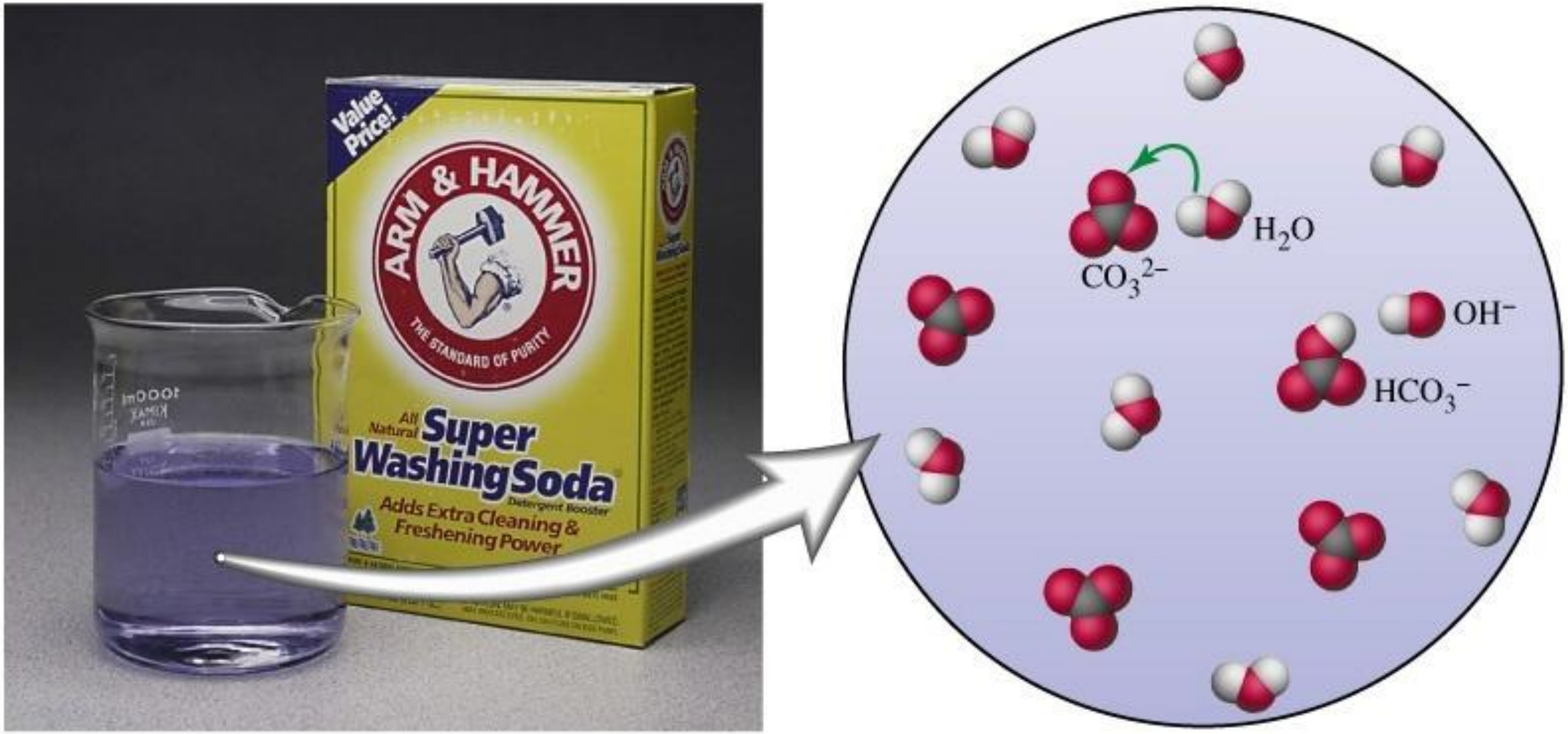
CH_3-HCOH-COOH
Lactic acid

CH_3-CO-COO^-Na^+
Pyruvate

CH_3-HCOH-COO^-Na^+
Lactate

$$CO_3{}^{2-}{}_{aq} + H_2O \rightleftharpoons HCO_3{}^- + OH^-$$

Carbonate *bicarbonate*



$$HCO_3{}^-{}_{aq} + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

bicarbonate *carbonic acid*

Hydrolysis reactions (net)

$$HCO_3^{-}{}_{aq} + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

$$HPO_4^{2-}{}_{aq} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$$

$$NH_4^{+}{}_{aq} + H_2O \rightleftharpoons NH_4OH + H^+$$

Basic (Alkaline) hydrolysis, *evaluating pH*

Salt in solution (*added or therein generated*) !

$$HCOO^-Na^+ \; + \; H_2O \longrightarrow HCOO^-_{aq} \; + \; Na^+_{aq}$$

$$HCOO^- \; + \; H_2O \rightleftarrows HCOOH \; + \; OH^-$$

Basic hydrolysis!

$$K_{eq} = \frac{[HCOOH]\,[OH^-]}{[HCOO^-]\,[H_2O]}$$

$$K_{eq} = \frac{[HCOOH]\,[OH^-]}{[HCOO^-]\,[H_2O]} \rightarrow K_{eq} \times [H_2O] = K_i = \frac{[HCOOH]\,[OH^-]}{[HCOO^-]}$$

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Alkaline hydrolysis, *evaluating pH*

$$K_{eq} = \frac{[HCOOH]\,[OH^-]}{[HCOO^-]\,[H_2O]} \rightarrow K_{eq} \times [H_2O] = K_i = \frac{[HCOOH]\,[OH^-]}{[HCOO^-]}$$

$$Ki = \frac{[OH^-]^2}{[HCOO^-]}$$

$$[HCOO^-] \approx Cs$$

$$[OH^-] = \sqrt{Ki \times Cs}$$

$$pOH = \log 1/[OH^-] \rightarrow pH = 14 - pOH$$

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Acidic hydrolysis, *evaluating pH*

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Salt in solution (*added or therein generated*) !

$$NH_4Cl + H_2O \longrightarrow NH_4^+ + Cl^-$$

$$pH = \log 1/[H^+]$$

$$NH_4^+ + H_2O \rightleftarrows NH_4OH + H^+$$

Hydrolysis !

$$Ki = \frac{[NH_4OH]\ [H^+]}{[NH_4^+]} \rightarrow \qquad [H^+]^2 = Ki \times [NH_4^+]$$

$$\boxed{[H^+] = \sqrt{Ki \times Cs}}$$

$$K_{eq} = \frac{[NH_4OH]\ [H^+]}{[NH_4^+]\ [H_2O]} \rightarrow K_{eq} \times [H_2O] = K_i = \frac{[NH_4OH]\ [H^+]}{[NH_4^+]}$$

Ki , Kw and Ka or Kb

Alkalyne hydrolysis

$HCOO^- + H_2O \rightleftarrows HCOOH + OH^-$

$$OH^- = \frac{Kw}{H+}$$

$$K_i = \frac{[HCOOH]\ \ [OH^-]}{[HCOO^-]} = \frac{[HCOOH]\ \ K_W}{[HCOO^-]\ \ [H^+]} = \frac{K_W}{K_a}$$

$AH \rightleftarrows A^- + H^+$

Acidic hydrolysis

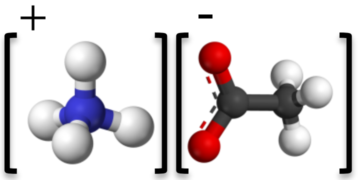
$NH_4^+ + H_2O \rightleftarrows NH_4OH + H^+$

$$H^+ = \frac{Kw}{OH^-}$$

$$Ki = \frac{[NH_4OH]\ \ [H^+]}{[NH_4^+]} = \frac{[NH_4OH]\ \ K_W}{[NH_4^+]\ [OH^-]} = \frac{K_W}{K_b}$$

$BOH \rightleftarrows B^+ + OH^-$

Ammonium acetate



$$CH_3COO^-NH_4^+ \xrightarrow{H_2O} CH_3COO^- \;+\; NH_4^+$$

both are conjugated **strong** species

The two equilibria coexist

$$A^- + H_2O \rightleftarrows AH + OH^-$$

$$B^+ + H_2O \rightleftarrows BOH + H^+$$

$$Ki = \frac{Kw}{Ka + Kb}$$

pH will vary consistently with the values of Ka and Kb.

e.g. if Ka < Kb then the cojugated base of the acid, A^-,
is (relatively) stronger than the cojugated acid, B^+, of the base, and…

$$[OH^-] > [H^+]$$

Therefore pH…??

Acid/base reaction:
Simple stoichiometry (1:1)
stabile product

$$H^+ \quad + \quad :OH^- \rightleftharpoons H_2O$$

acid base product

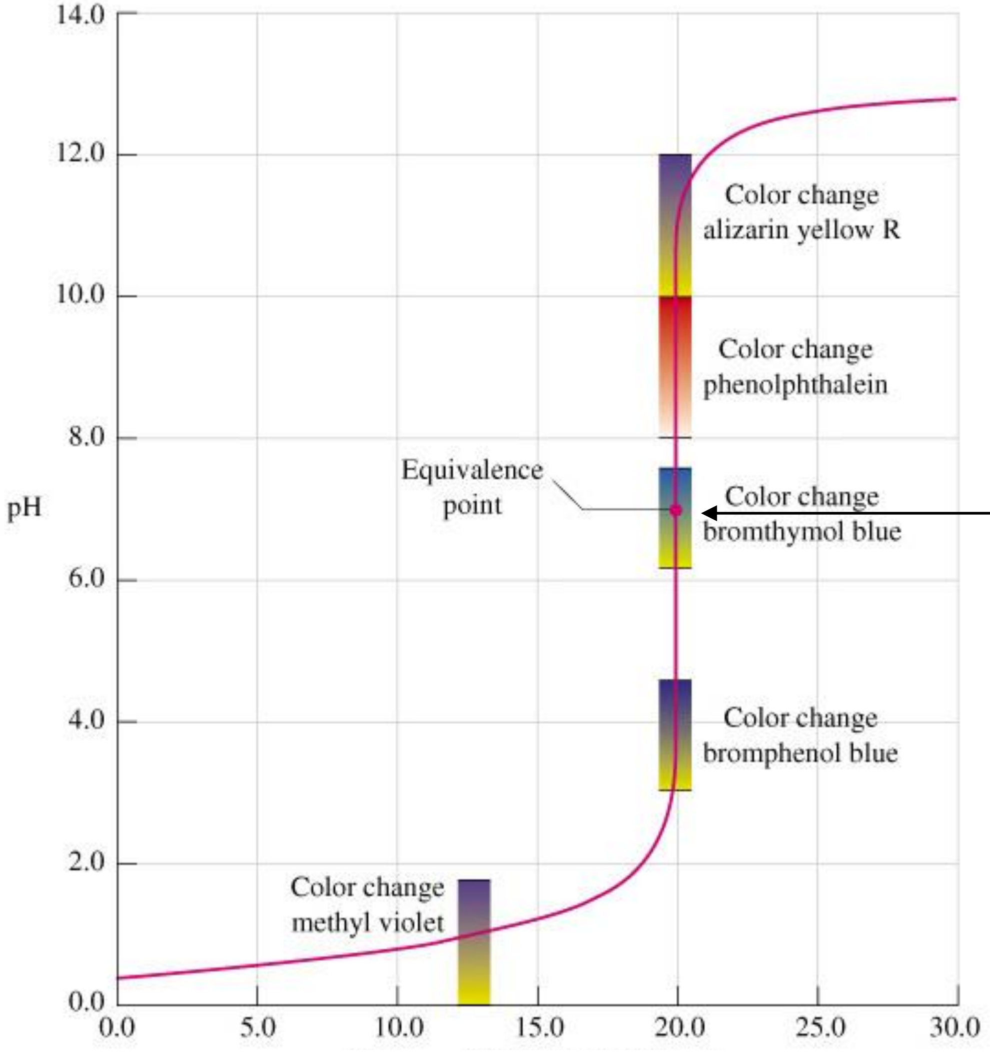
$\Delta G << 0 \;=\; 15$ Kcal/mol

	pH
$HCl + NaOH \longrightarrow H_2O + Na^+Cl^-$	7,0
$HCOOH + NaOH \longrightarrow H_2O + HCOO^-Na^+$	> 7,0
$NH_3.H_2O + HCl \longrightarrow H_2O + NH_4^+Cl^-$	< 7,0

ACID-BASE titration

Strong acid & strong base

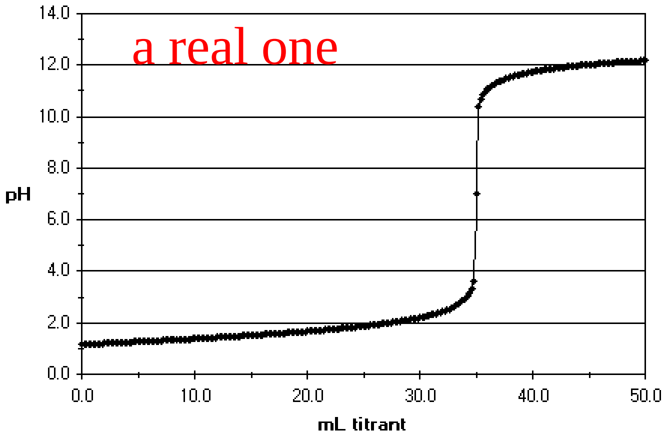
$$HCl + NaOH \longrightarrow H_2O + NaCl$$



Volume of 0.5 M NaOH, ml

Equivalence

pH = 7.0



a real one

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Weak acid & strong base

Let's work out pH under these conditions:

1) In the absence of base
2) 50% neutralization
3) 100% neutralization

1

Let's have 0.1 M CH_3COOH *in 1 liter* H_2O

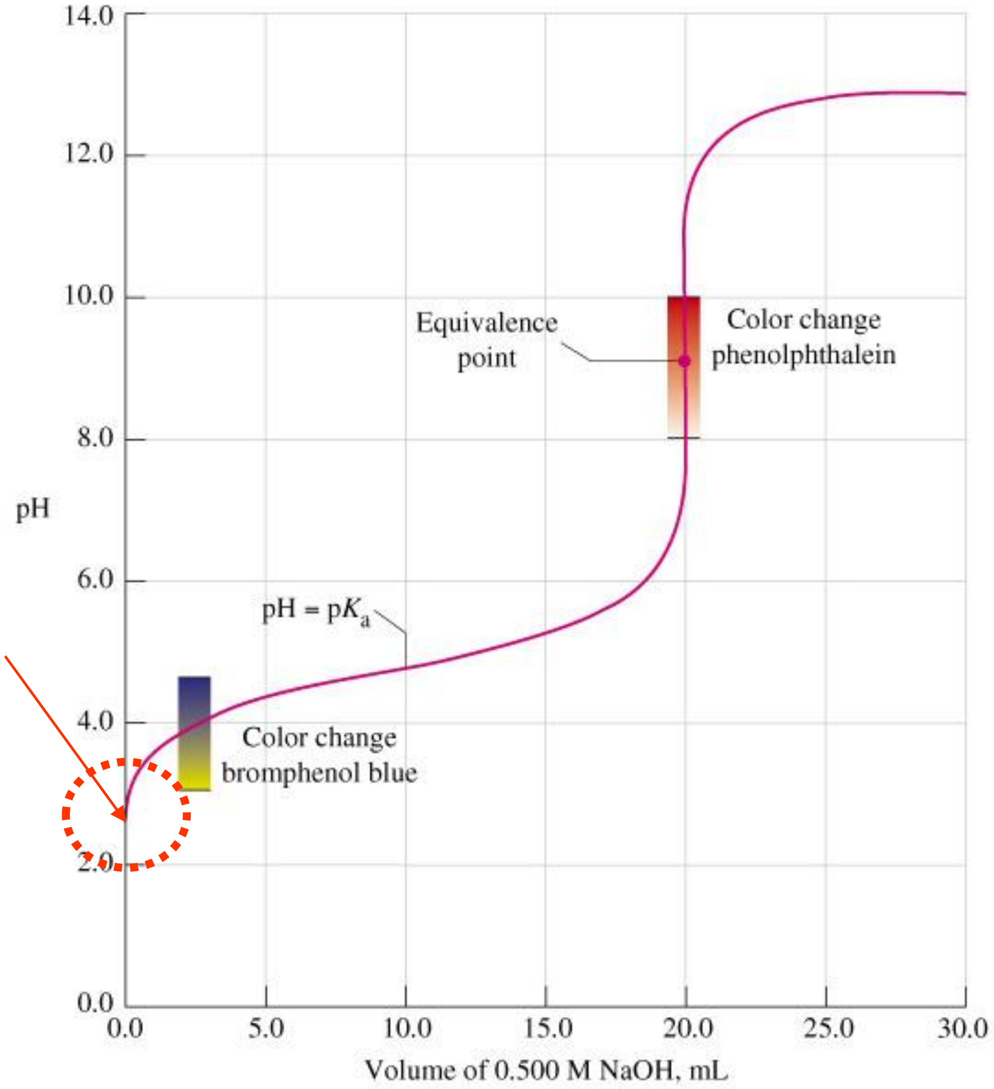
$$\boxed{[H^+] = \sqrt{Ka \times Ca}}$$

$$[H^+] = \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.34 \times 10^{-3}\ M$$

$$\boxed{pH = \log 745 = 2.87}$$

Weak Acid neutralised with strong Base

$CH_3COOH + NaOH \longrightarrow H_2O + CH_3COONa$



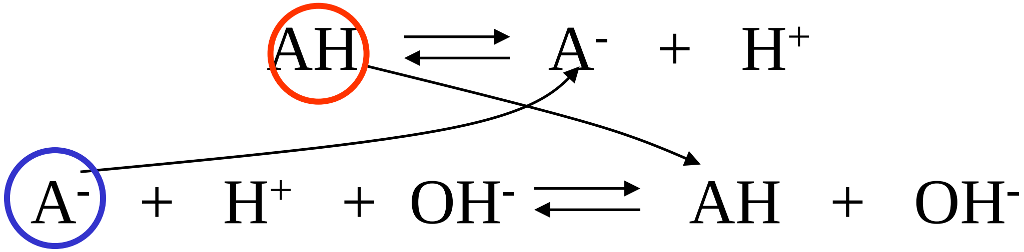
2

50 % neutralised

AH	$+ \; NaOH$	$\longrightarrow \; A^-Na^+$	$+ \; H_2O$	
0.1	*0.05*	*0*	*0*	(initial)
0.05	0.0	0.05	0.05	(after reaction)

We have (same solution) **AH** (acido) and **A**$^-$ (conjugated base) from salt, both reactive!

the 2 equilibria (dissociation & hydrolysis) coexist with *common species*



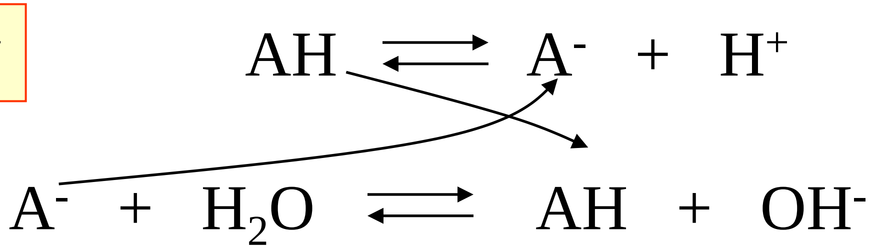
$$AH \rightleftharpoons A^- + H^+$$

$$A^- + H^+ + OH^- \rightleftharpoons AH + OH^-$$

AH is a H$^+$ donor A- is a H$^+$ acceptor ……!

In the same solution
AH & A$^-$ reciprocally ihibit the parallel reaction,
so called “*common species*” effect (Le Chatelier), so that
AH ≈ Ca ed A$^-$ ≈ Cs.

Let’s find H^+



$$\mathrm{AH} \rightleftharpoons \mathrm{A}^- + \mathrm{H}^+$$

$$\mathrm{A}^- + \mathrm{H_2O} \rightleftharpoons \mathrm{AH} + \mathrm{OH}^-$$

$$\mathrm{Ka} = \frac{[\mathrm{A}^-]\ [\mathrm{H}^+]}{[\mathrm{AH}]} \rightarrow [\mathrm{H}^+] = \mathrm{Ka}\ \frac{[\mathrm{AH}]}{[\mathrm{A}^-]}$$

$$\mathrm{Log}\ 1/[\mathrm{H}+] = \log 1/\mathrm{Ka} + \log [\mathrm{A}-]/[\mathrm{AH}]$$

$$\mathrm{pH} = \mathrm{pKa} + \log \frac{\mathrm{Cs}}{\mathrm{Ca}}$$

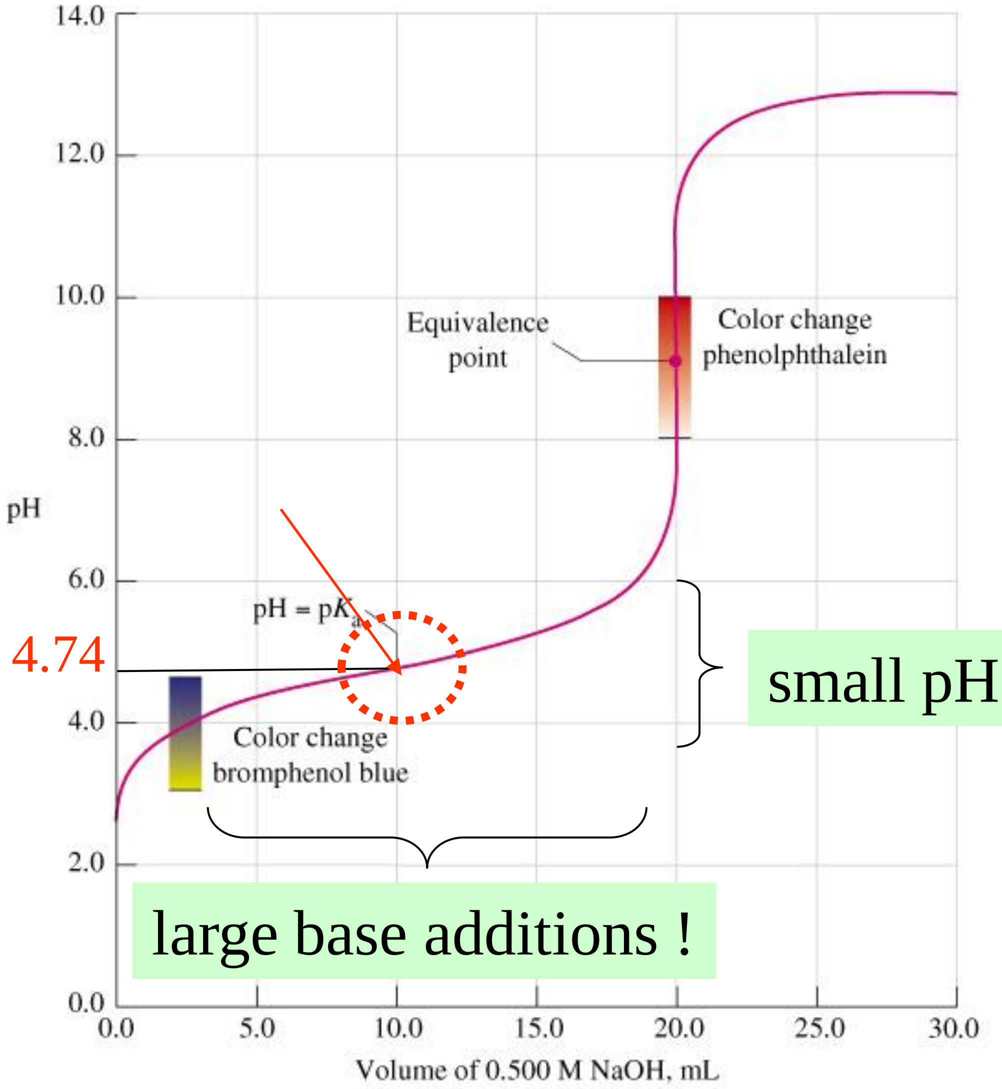
Eq. *Henderson Hasselbalch* !!

Example

$$\mathrm{pH} = \mathrm{pKa} + \log \frac{0.05}{0.05} \rightarrow \mathrm{pH} = \mathrm{pKa} = 4.74$$

50 %

$$CH_3COOH + NaOH \longrightarrow H_2O + CH_3COONa$$



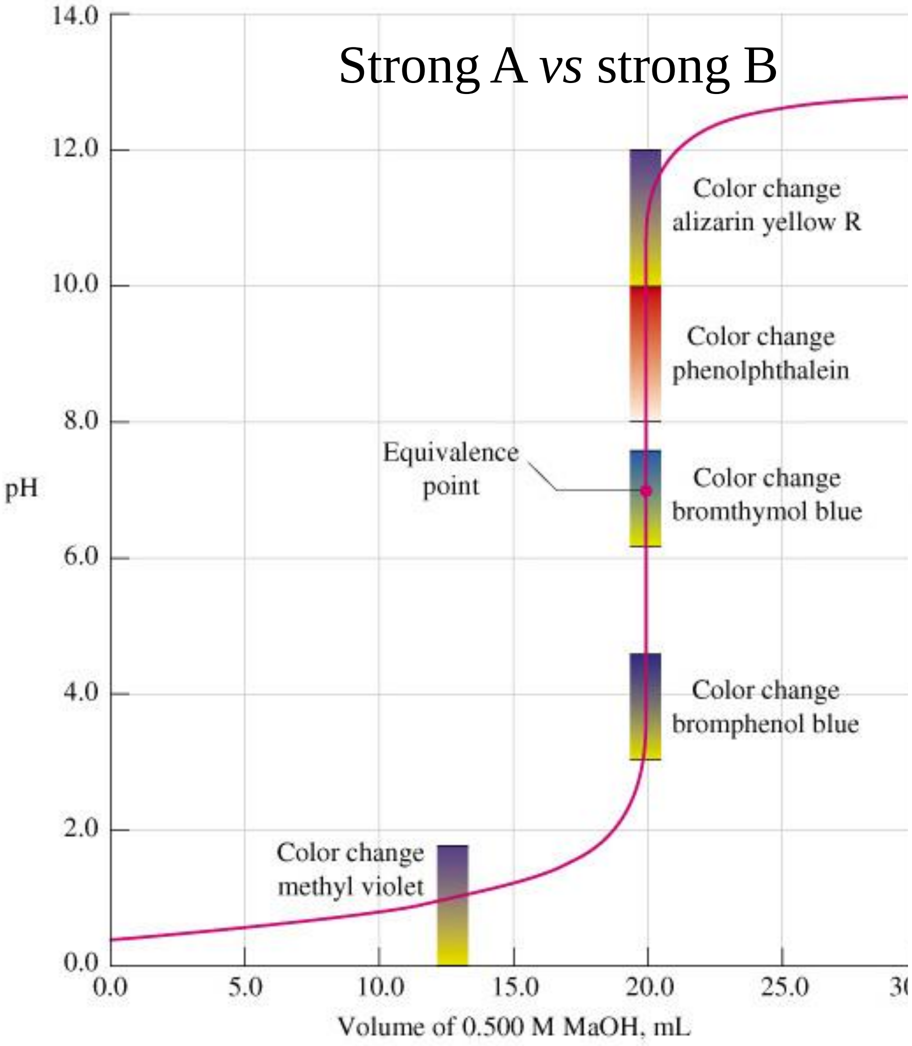
small pH variations!

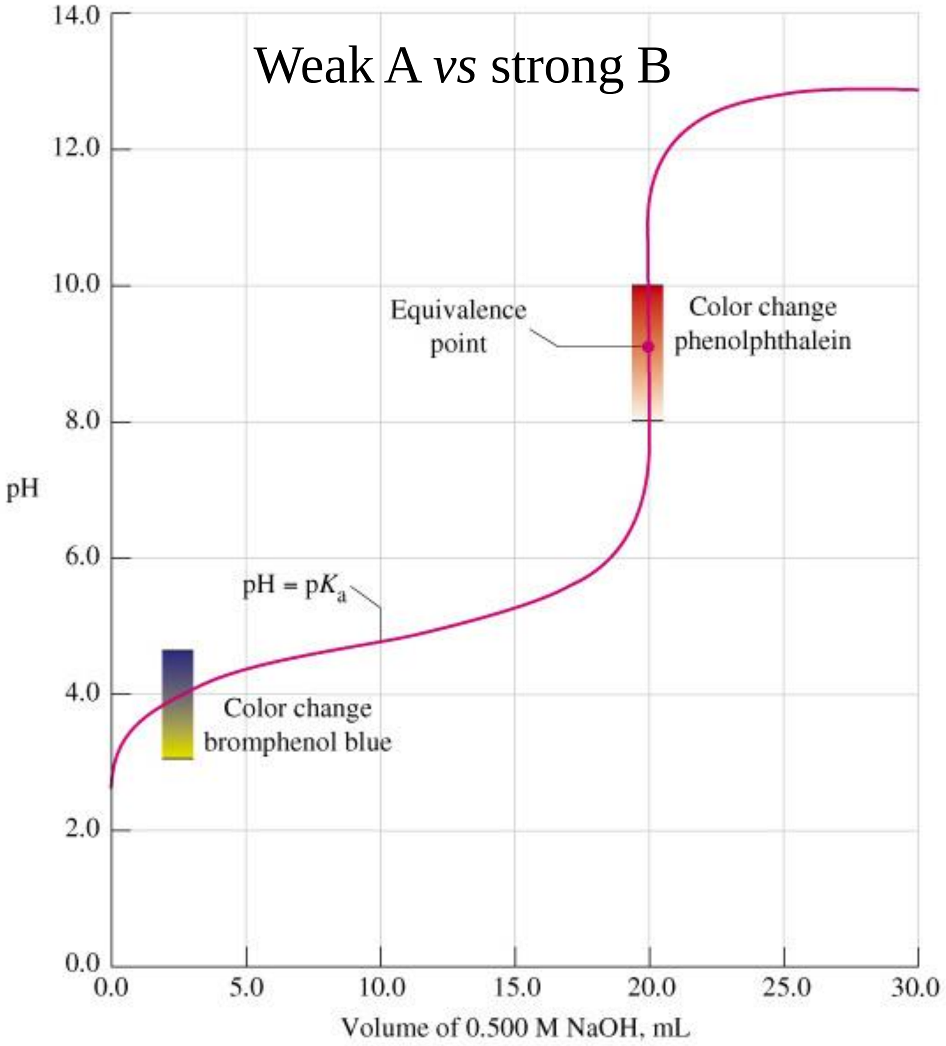
large base additions !

Buffering effect - buffer power…!

Better observed by adding H^+ or OH^- in the pH region close to the pKa (weak acid) or pKb (weak base)

To be compared !


Strong A *vs* strong B


Weak A *vs* strong B

3

100 %

AH +	NaOH $\longrightarrow$	A^-Na^+ +	H_2O	
0.1	0.1	0	0	(*initial*)
0.0	0.0	0.1	0.1	(*after neutralization*)

generated A^- 0.1 M (conjugated bases)
alkaline hydrolysys

$$[OH^-] = \sqrt{Ki \times Cs}$$

$$[OH^-] = \sqrt{Kw/Ka \times 0.1}$$

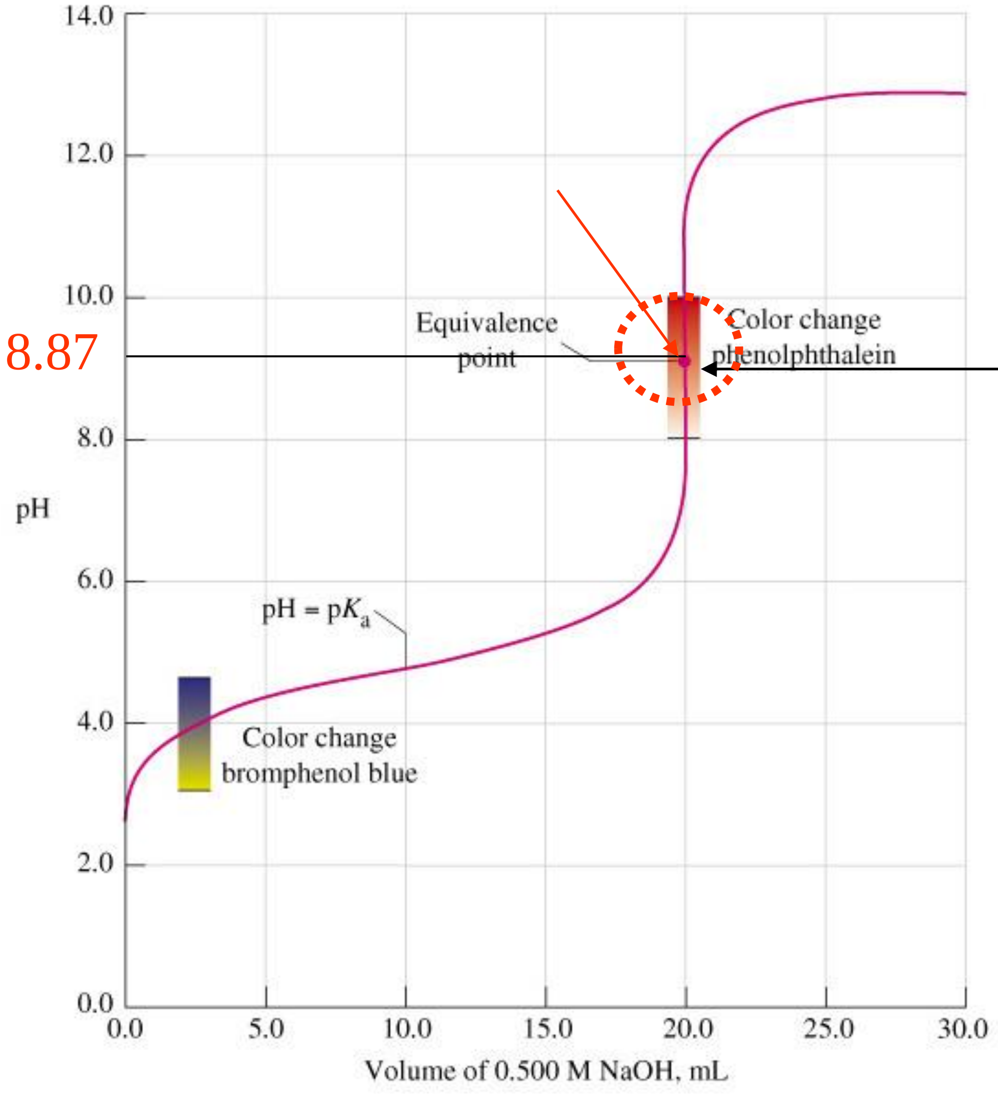
$$[OH^-] = \sqrt{1 \times 10^{-14} / 1.8 \times 10^{-5} \times 0.1}$$

$$[OH^-] = \sqrt{5.55 \times 10^{-11}} = 7.45 \times 10^{-6}$$

pOH = 5.13 → pH = 14 – 5.13 = 8.87

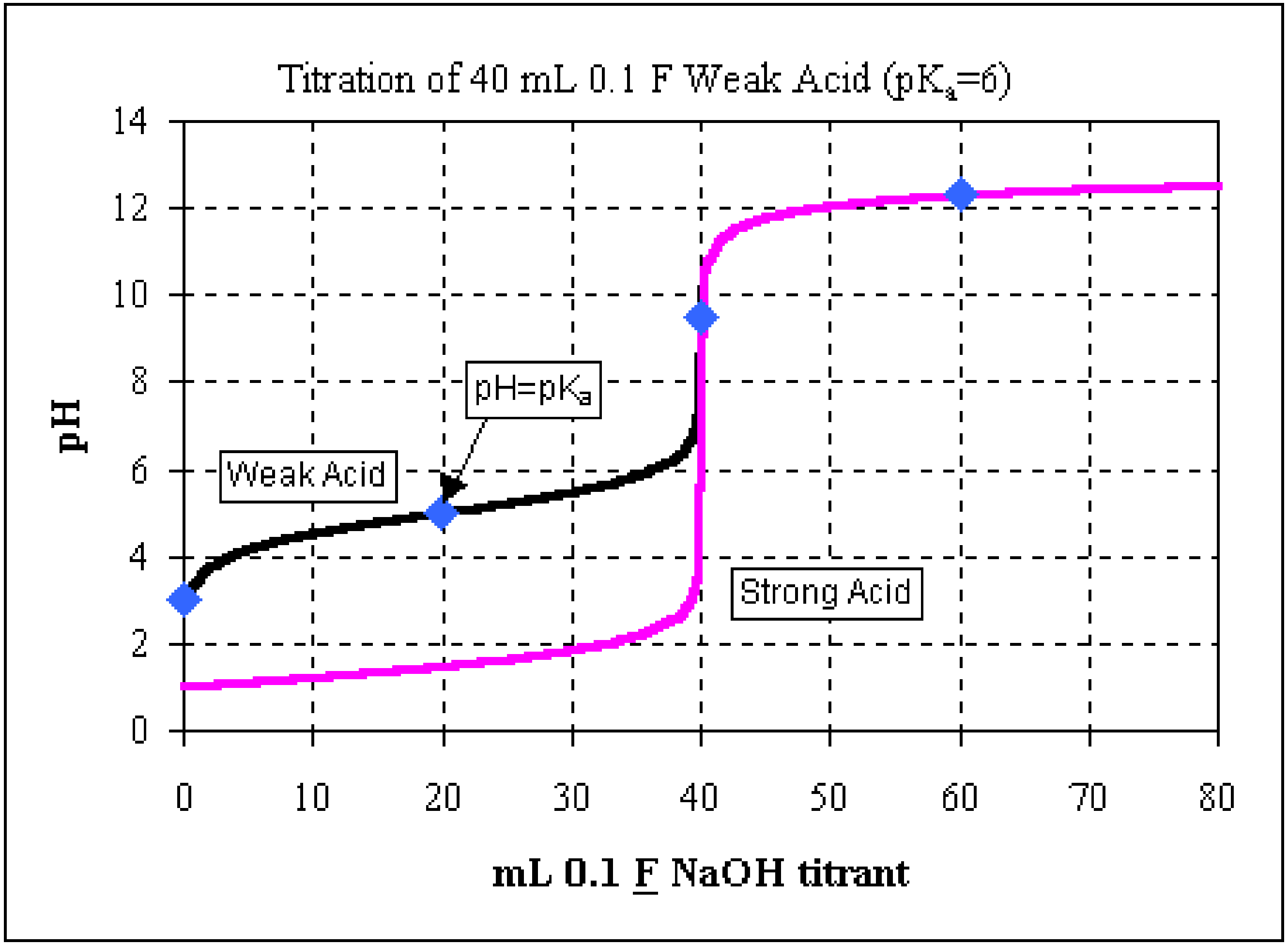
100 %

$$CH_3COOH + NaOH \longrightarrow H_2O + CH_3COONa$$

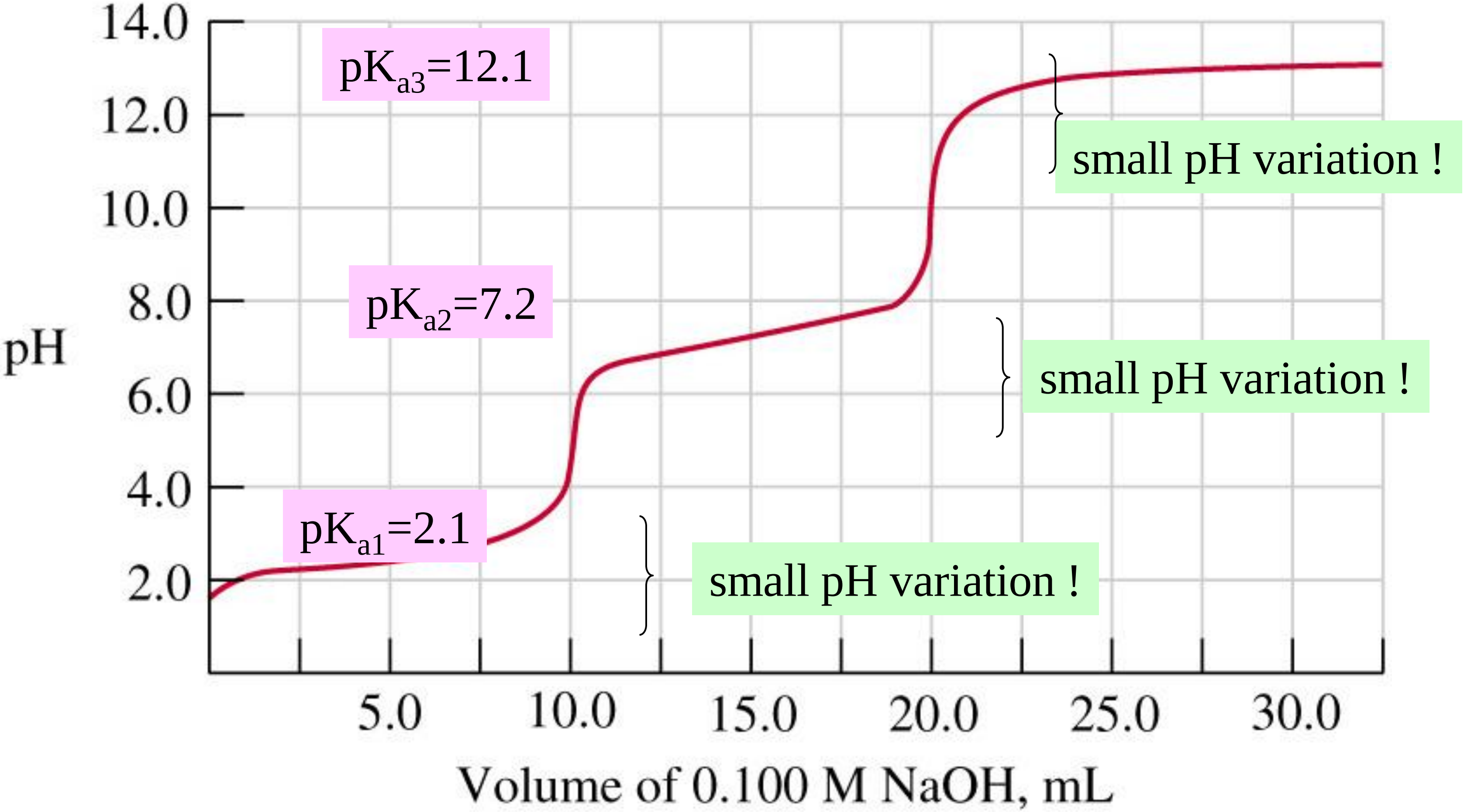


Equivalence point:
(fully) neutralised weak acid
with strong base…

Comparing strong and weak acids



Polyprotic acid H_3PO_4



$pK_{a3}=12.1$

$pK_{a2}=7.2$

$pK_{a1}=2.1$

small pH variation !

small pH variation !

small pH variation !

small pH variation *vs* large amounts of base

Buffer effect…!

H+ or *OH*- additions in the region of pH close to the 3 pKa values (H_3PO_4) induce small pH changes

…..

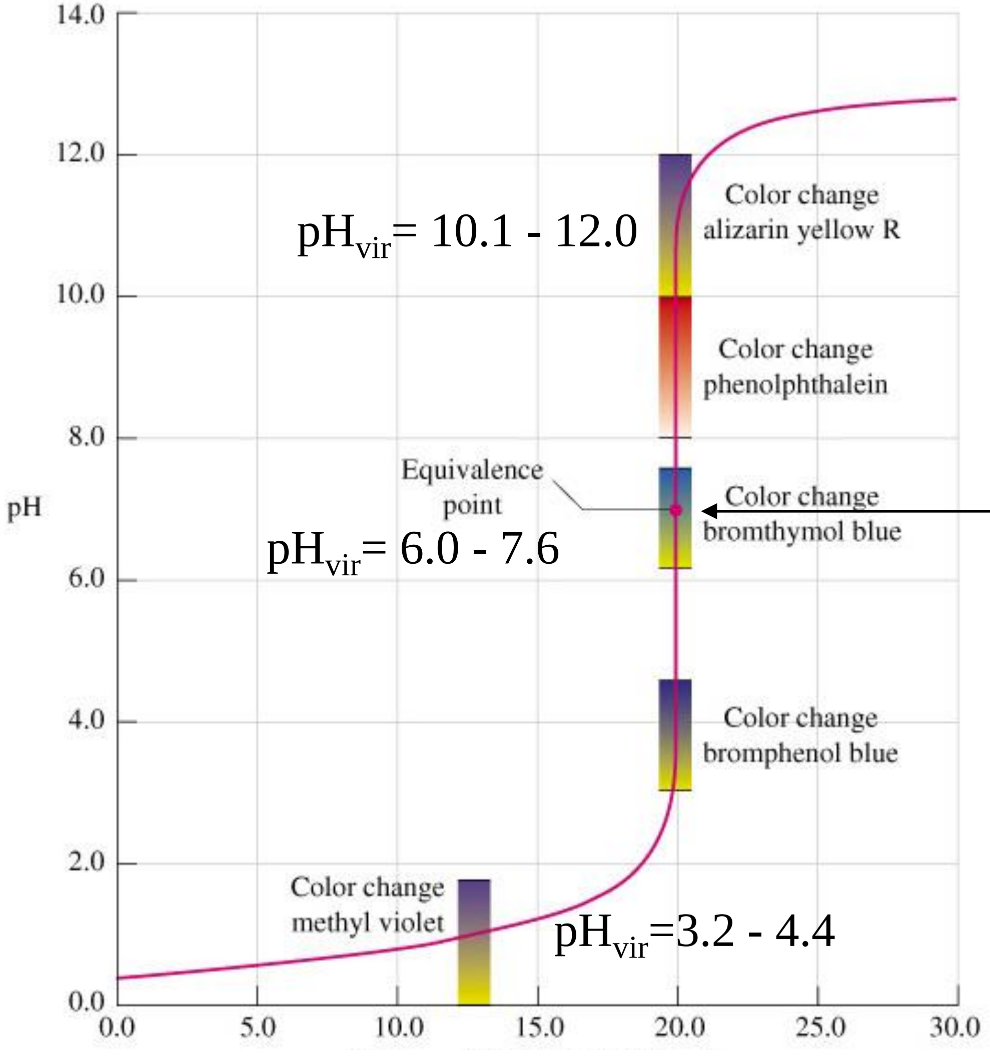
The pH value can be

- *worked out*
- *measured*

ACID – BASE titration

Strong acid + strong base

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



pH_{vir}= 10.1 - 12.0

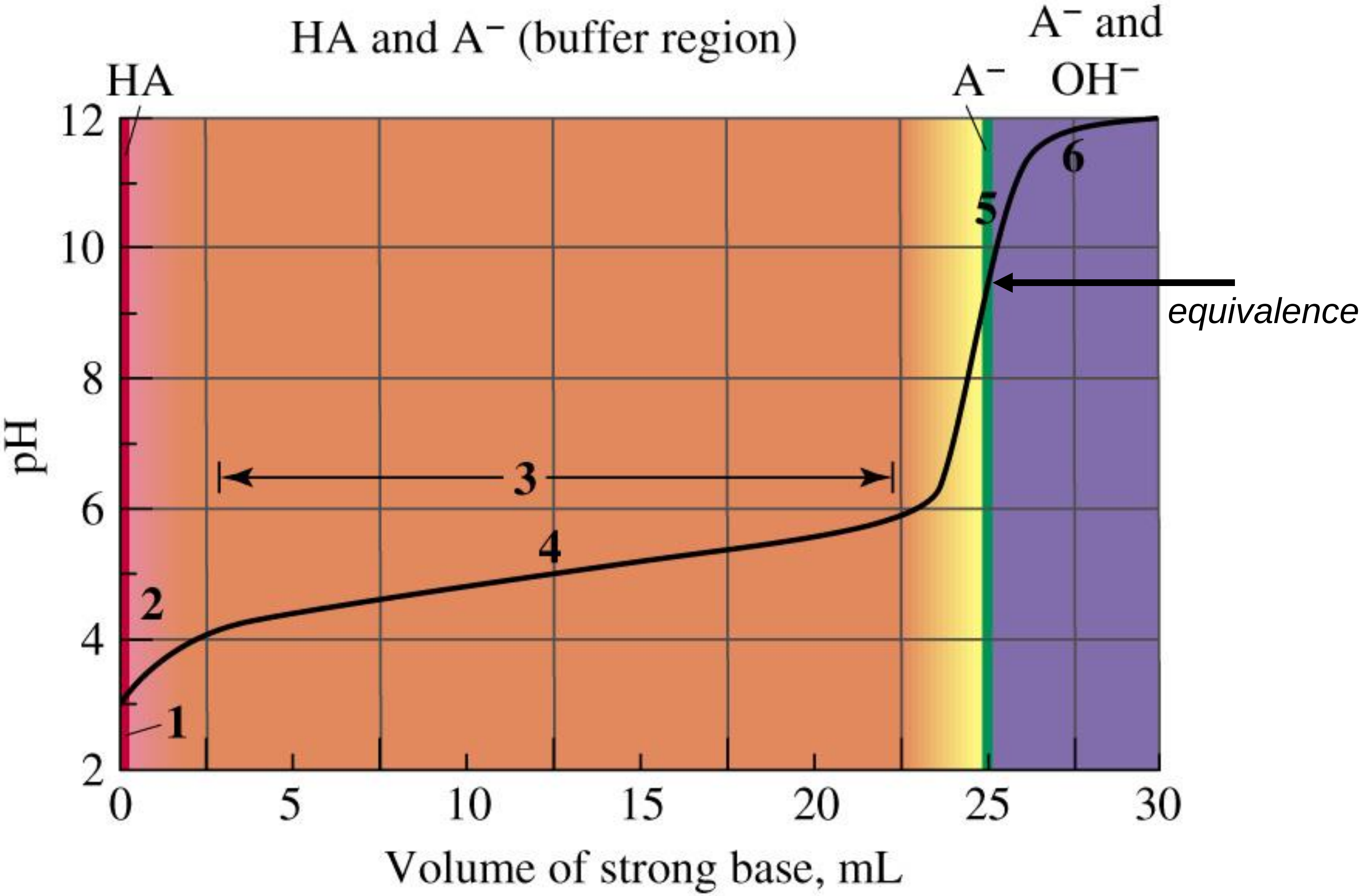
pH_{vir}= 6.0 - 7.6

pH_{vir}=3.2 - 4.4

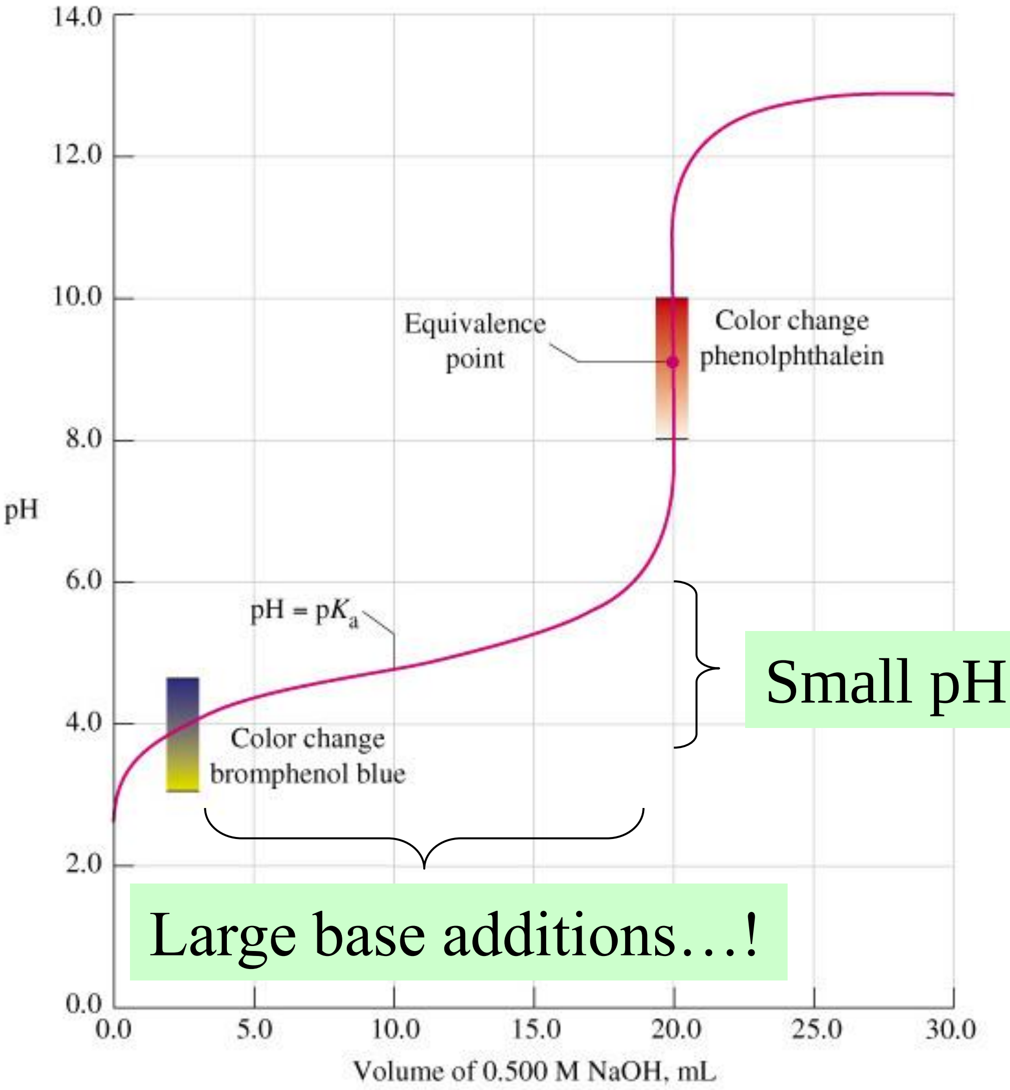
Volume of 0.5 M NaOH, ml

Equivalence
pH = 7.0

Small pH variations *vs* large amounts of base



Special condition when the acid is 50% neutralized



Small pH changes !

Large base additions…!

Buffer effect

H_2CO_3	$Ka_1 = 4 \times 10^{-7}$	$Ka_2 = 10^{-11}$
HCO_3^-	$Kb = 10^{-14}/ 4 \times 10^{-7} = 2.5 \times 10^{-8}$	