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 !)

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

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

these 2 equilibria coexist in the same solution

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

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

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

Net hydrolytic event

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Hydrolysis

$$HCO_3^-{}_{aq} + \underbrace{H_3O^+ + OH^-}_{H_2O \text{ auto-protolysis}} \rightleftharpoons H_2CO_3 + H_2O + OH^-$$

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

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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**

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

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

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

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

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

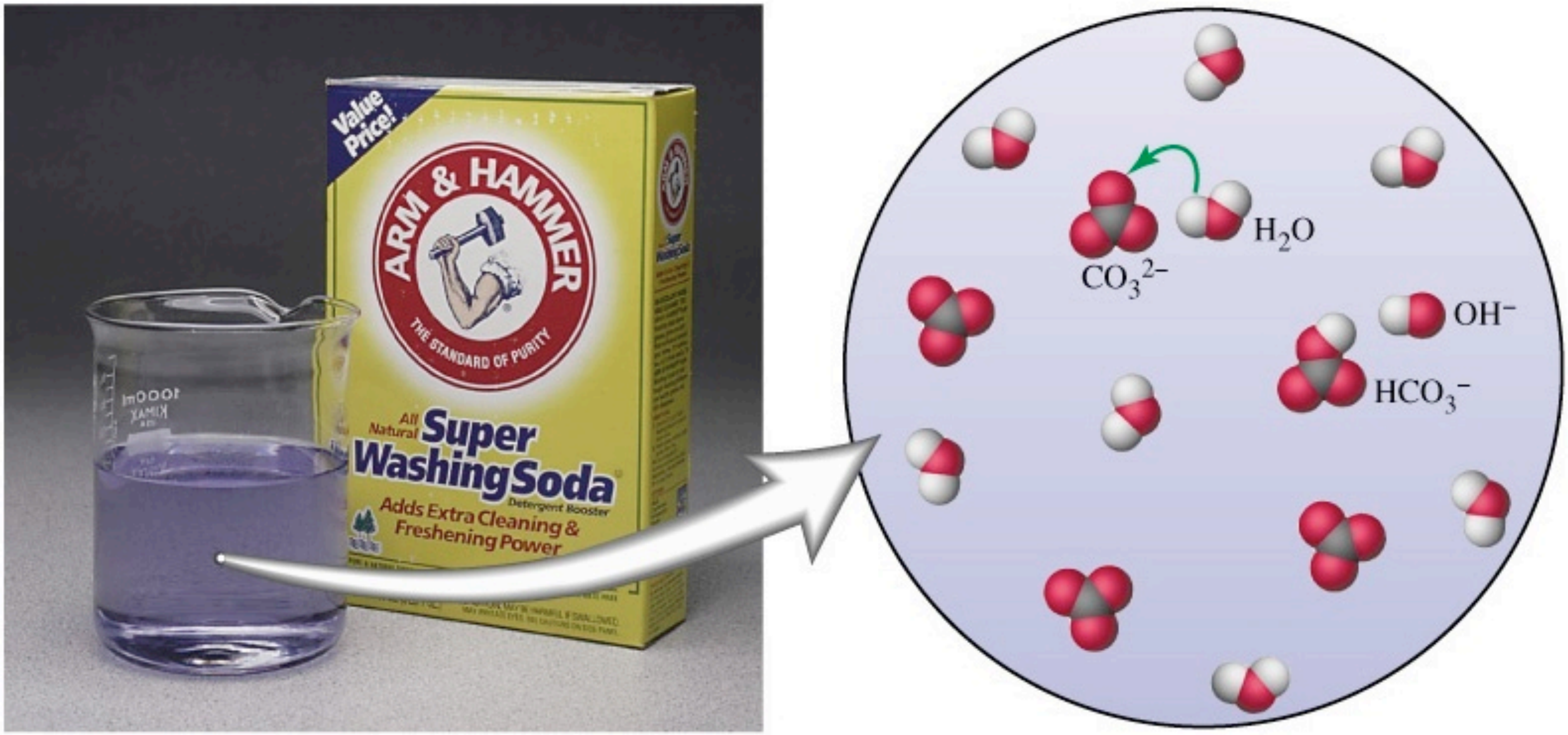
CH_3-HCOH-COOH
Lactic acid

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*

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Hydrolysis reactions (net)

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

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

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

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Basic (Alkaline) hydrolysis, *evaluating pH*

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

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

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

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*

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 !

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

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

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

Ki , Kw and Ka or Kb

Alkalyne hydrolysis

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

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

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

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

Acidic hydrolysis

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

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

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

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

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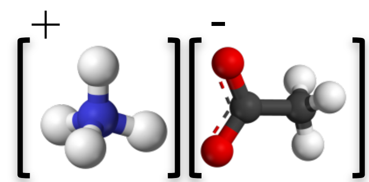
Ammonium acetate



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

both are conjugated **strong** species

The two equilibria coexist

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

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

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

If Ka = Kb ; pH = 7.0 neutral solution
if Ka > Kb ; pH < 7.0
if Ka < Kb ; pH > 7.0

$$[H_3O^+] = \sqrt{K_w \cdot \frac{K_a}{K_b}}$$

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…??]

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

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

acid base product

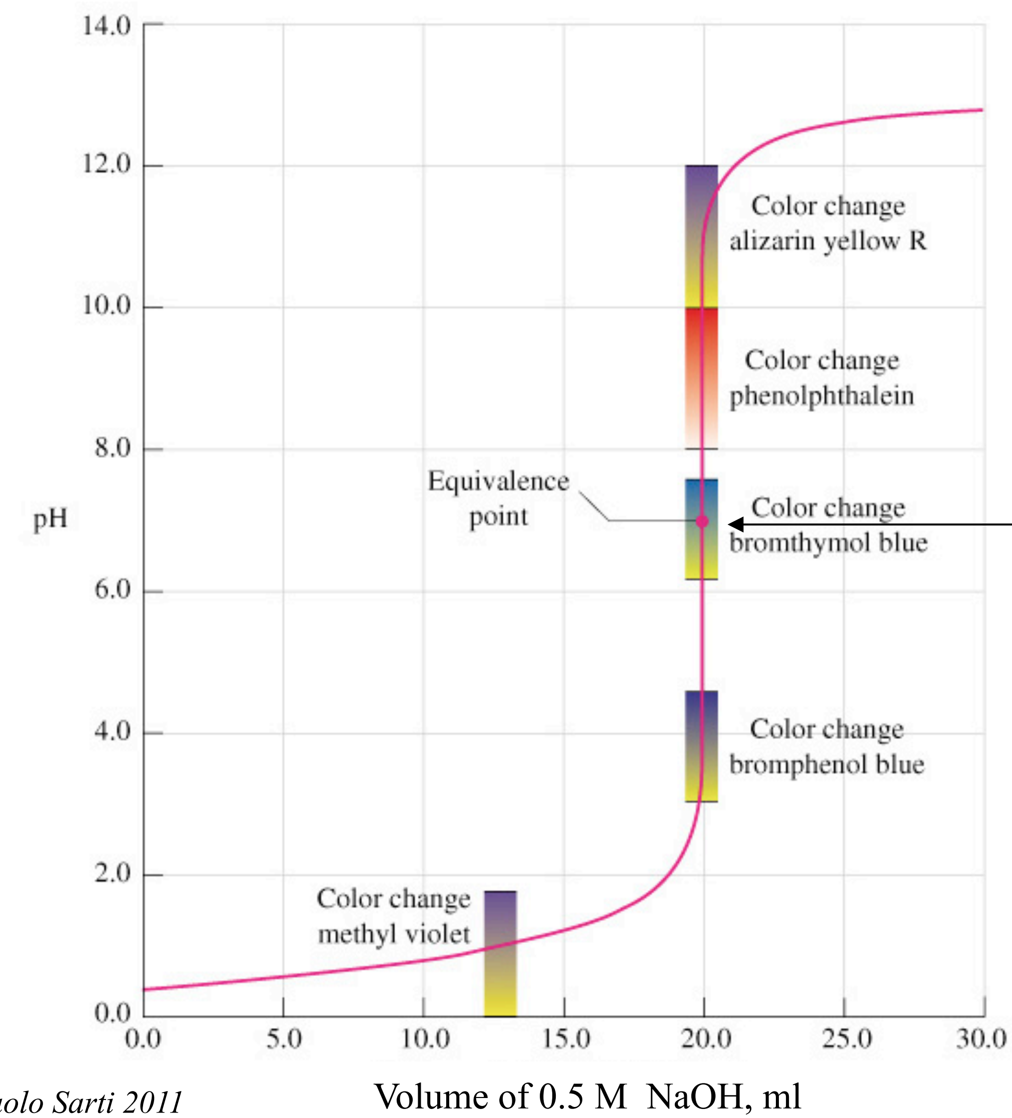
$$\Delta G < 0 \; = \; -15 \text{ Kcal/mol}$$

							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

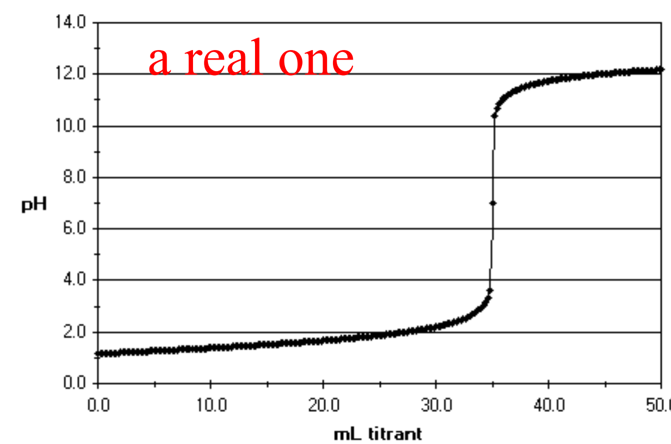
ACID-BASE titration

Strong acid & strong base

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



Equivalence
pH = 7.0



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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*

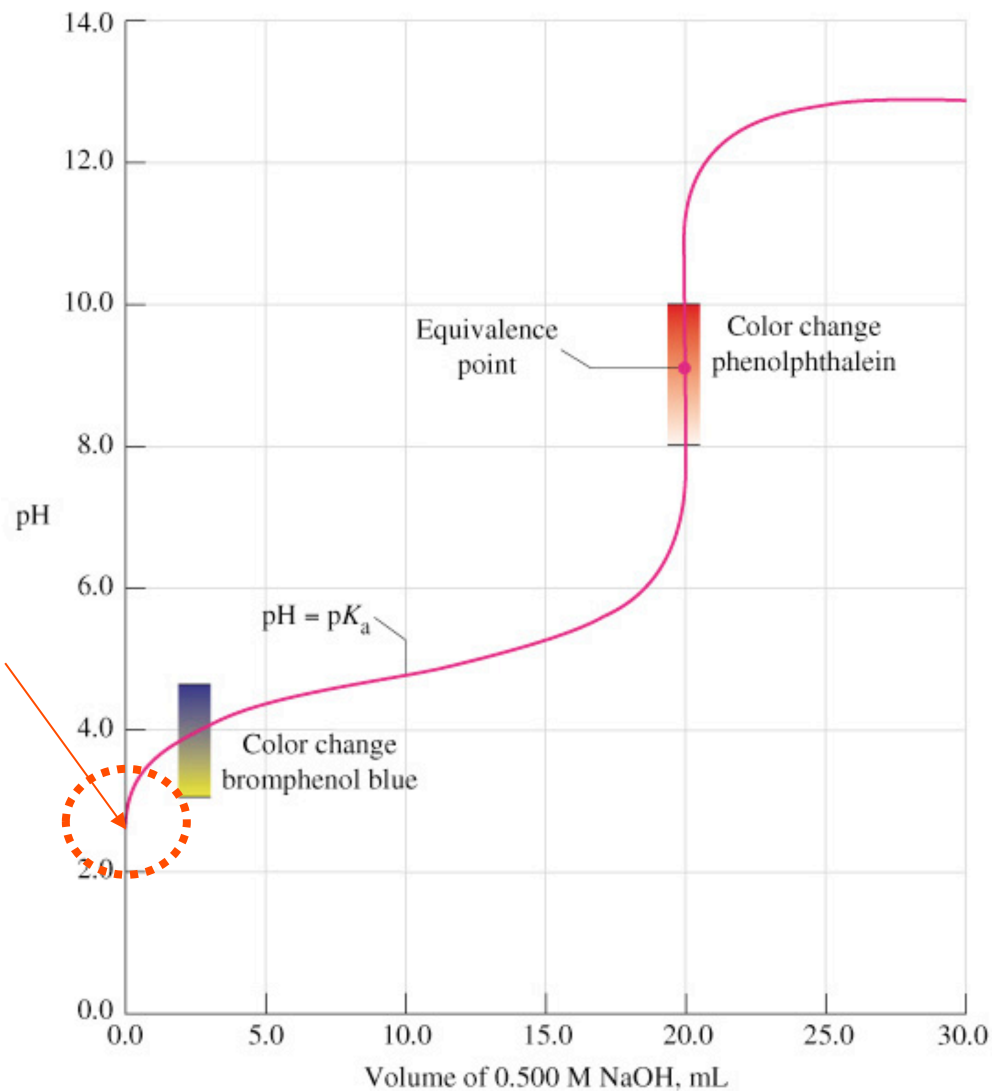
$$\boxed{[H^+] = \sqrt{Ka \times Ca}}$$

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

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

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*

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

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

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 $\approx$ Ca ed A$^-$ $\approx$ Cs.

Let's find H^+

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

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

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

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

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

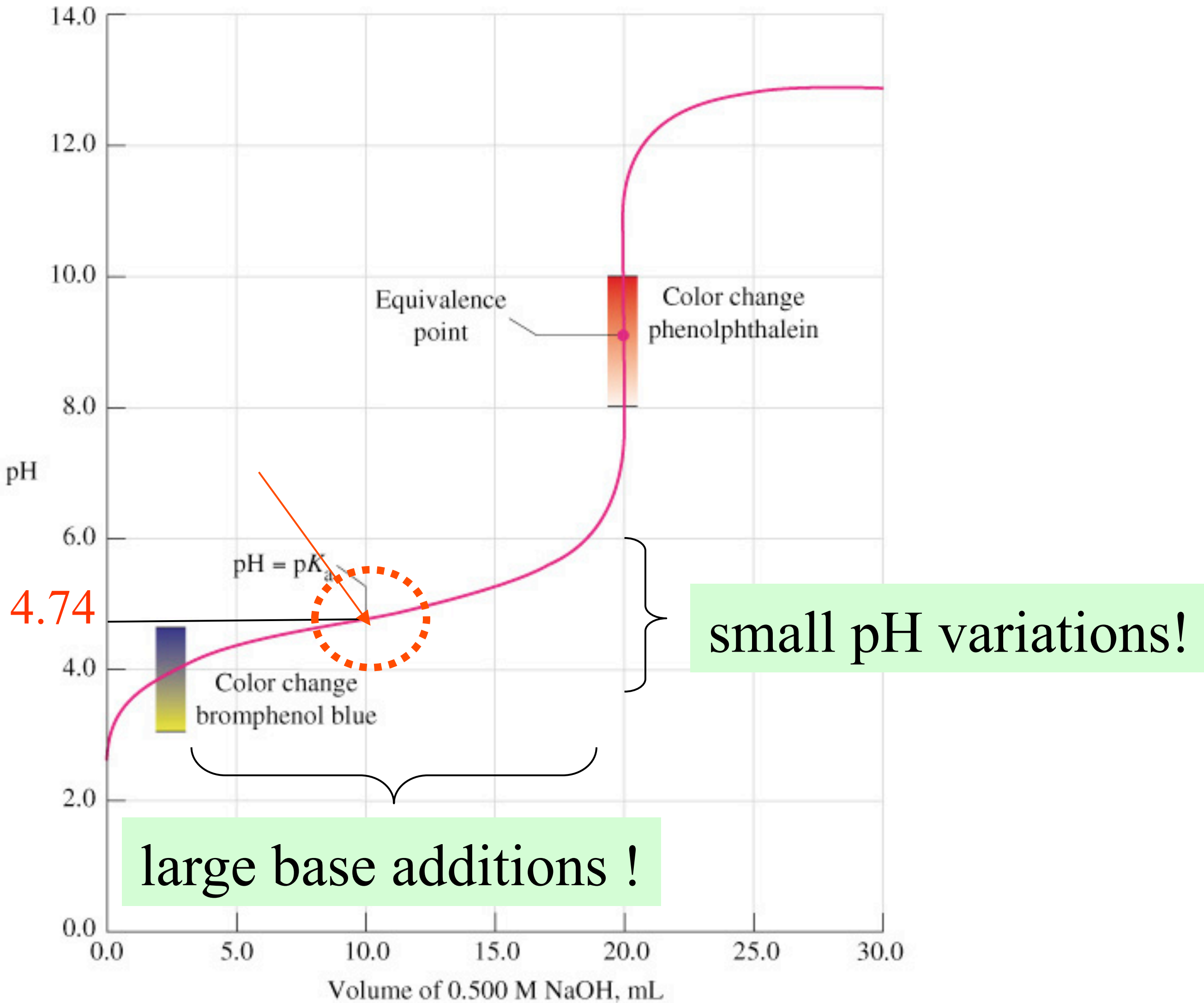
Eq. *Henderson Hasselbach* !!

Example

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

50 %

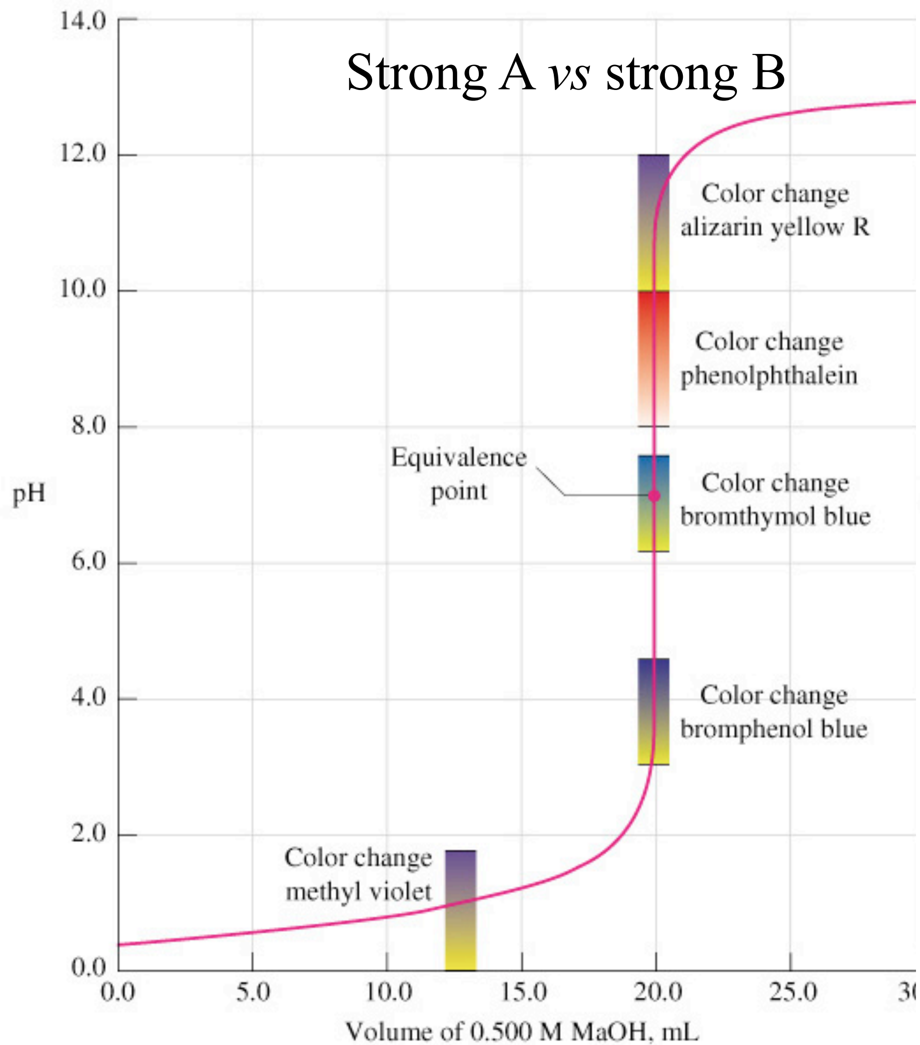
$$CH_3COOH + NaOH \longrightarrow H_2O + CH_3COONa$$

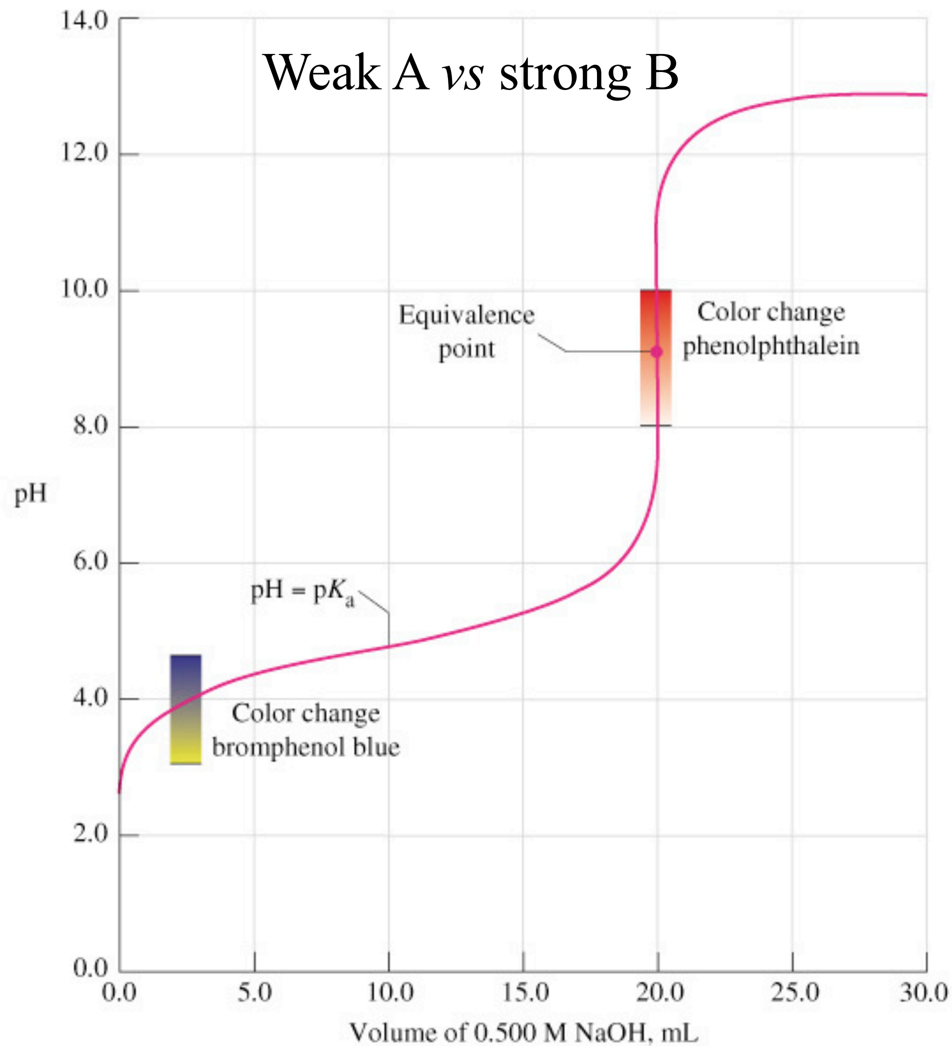


Buffering effect - buffer power…!

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

To be compared !





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

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

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

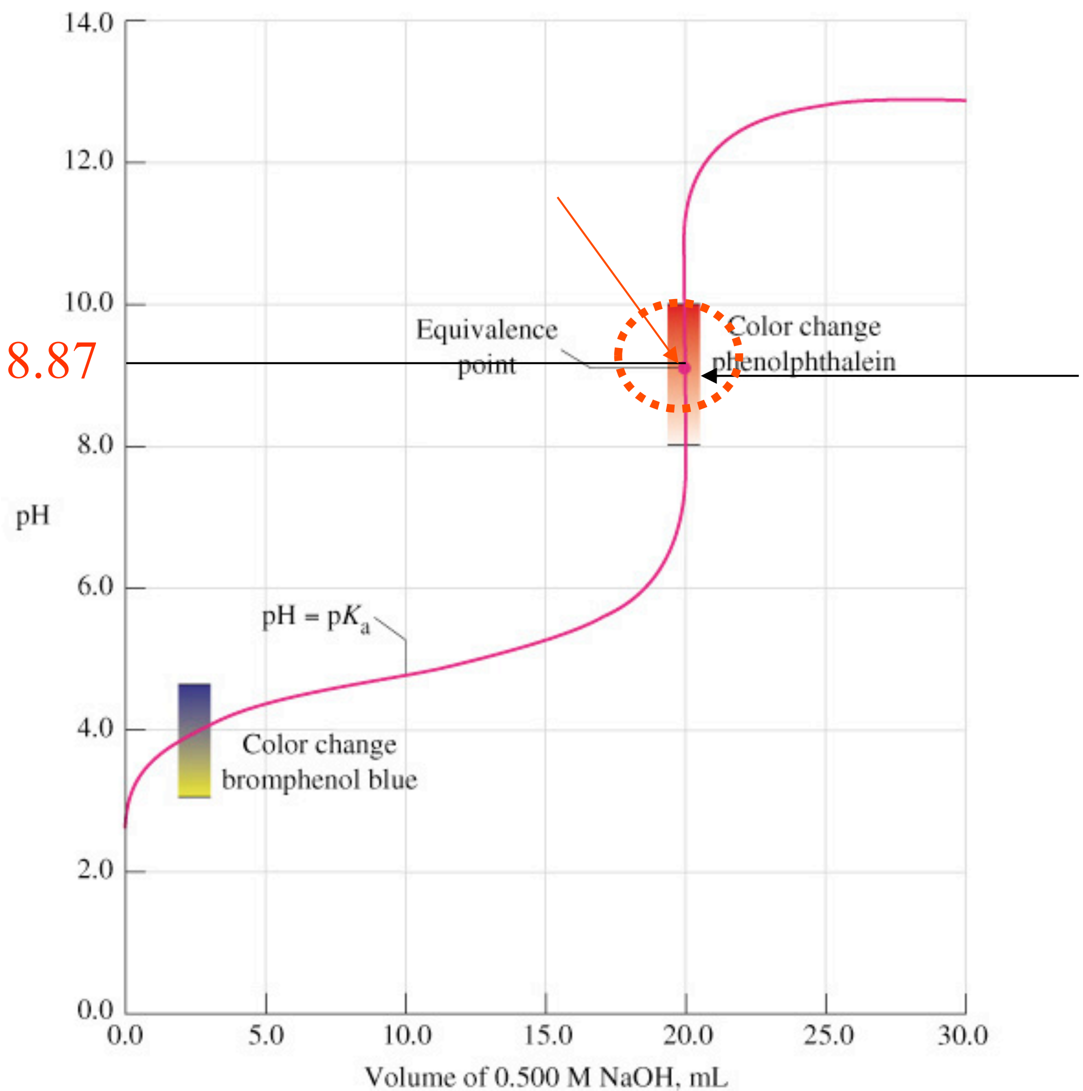
$$[OH^-] = \sqrt{1 \times 10^{-14} / 1.8 \times 10^{-5} \times 0.1}$$

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

pOH = 5.13 $\rightarrow$ pH = 14 – 5.13 = 8.87

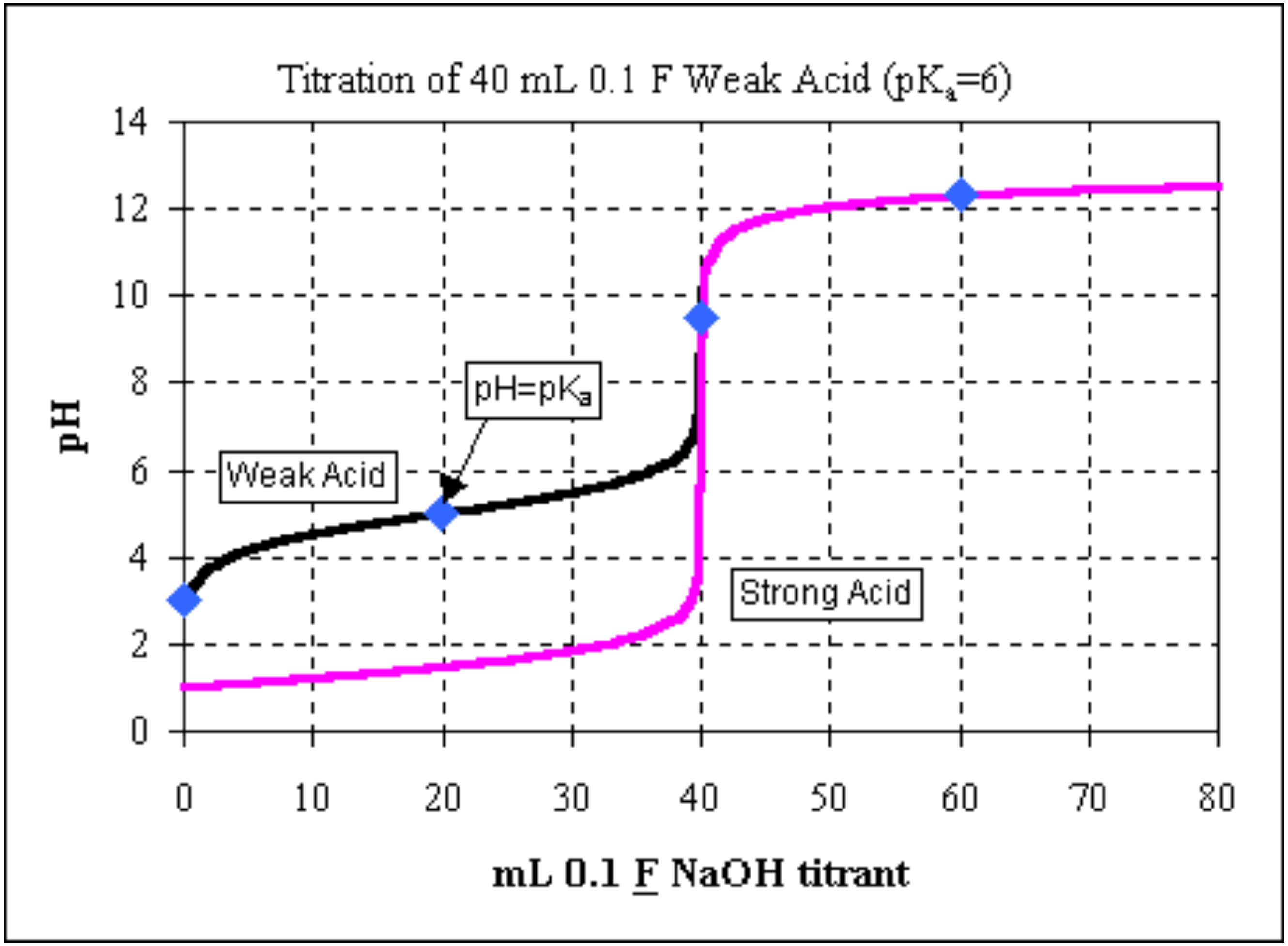
100 %

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

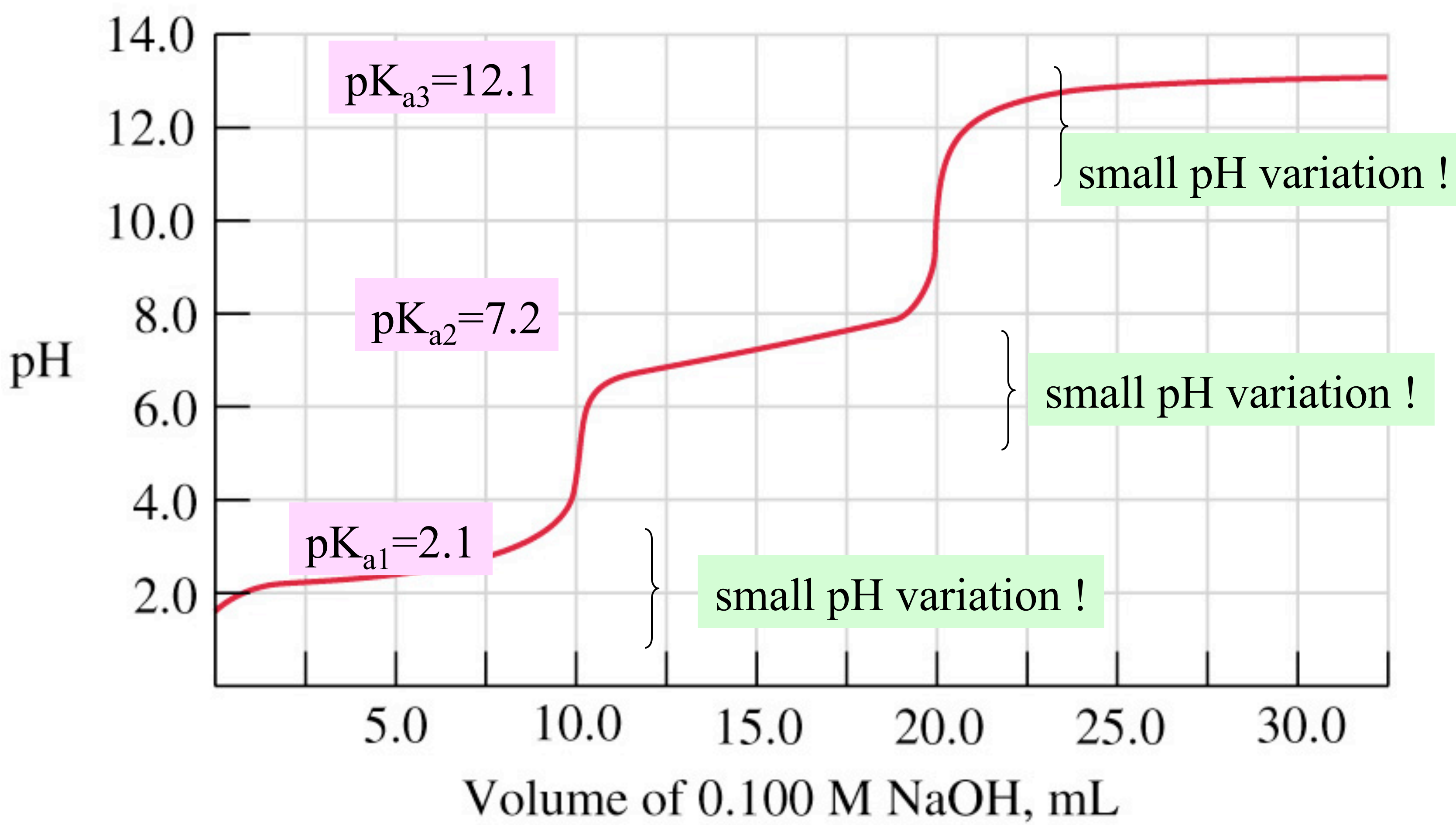


Equivalence point:
(<u>fully</u>) neutralised weak acid with strong base…

Comparing strong and weak acids



Polyprotic acid H_3PO_4



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
…..

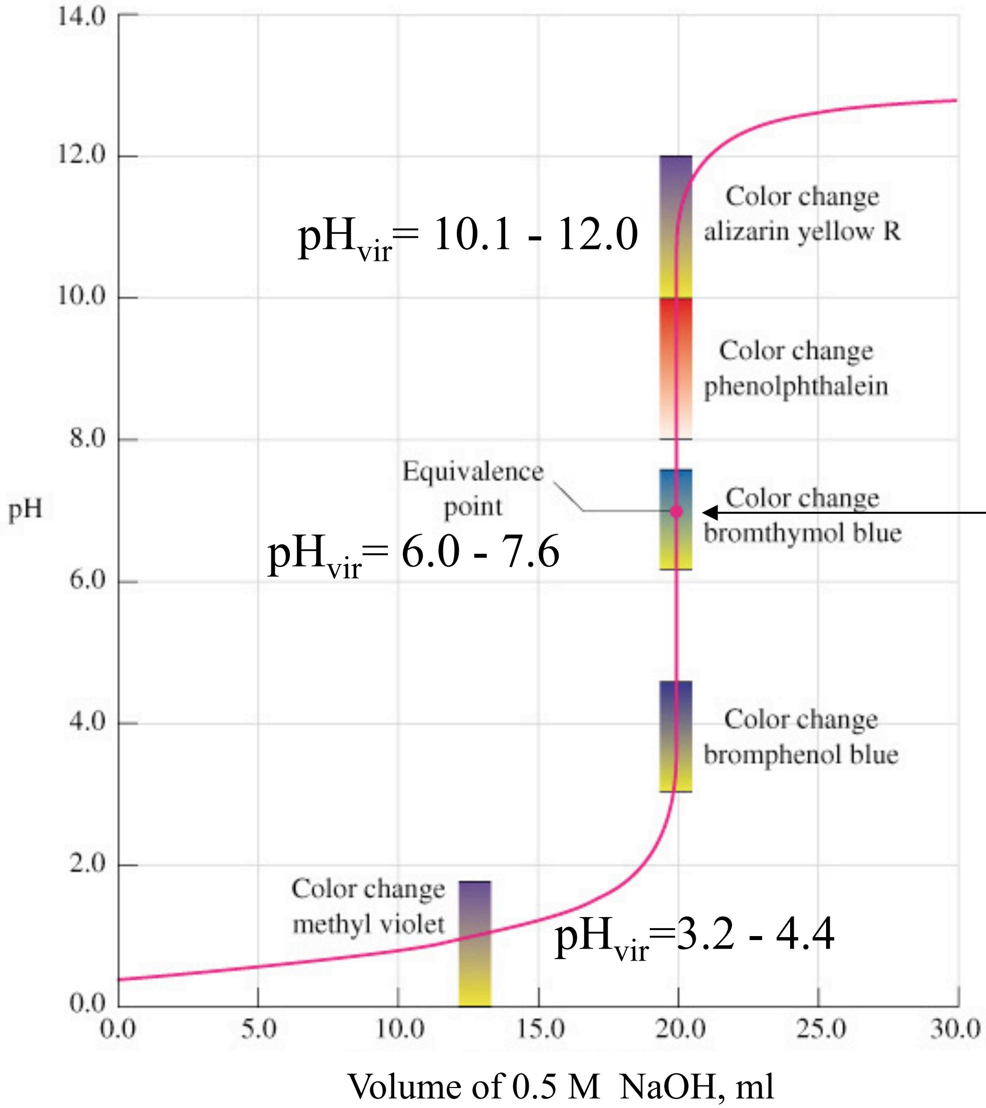
The pH value can be

- *worked out*
- *measured*

ACID – BASE titration

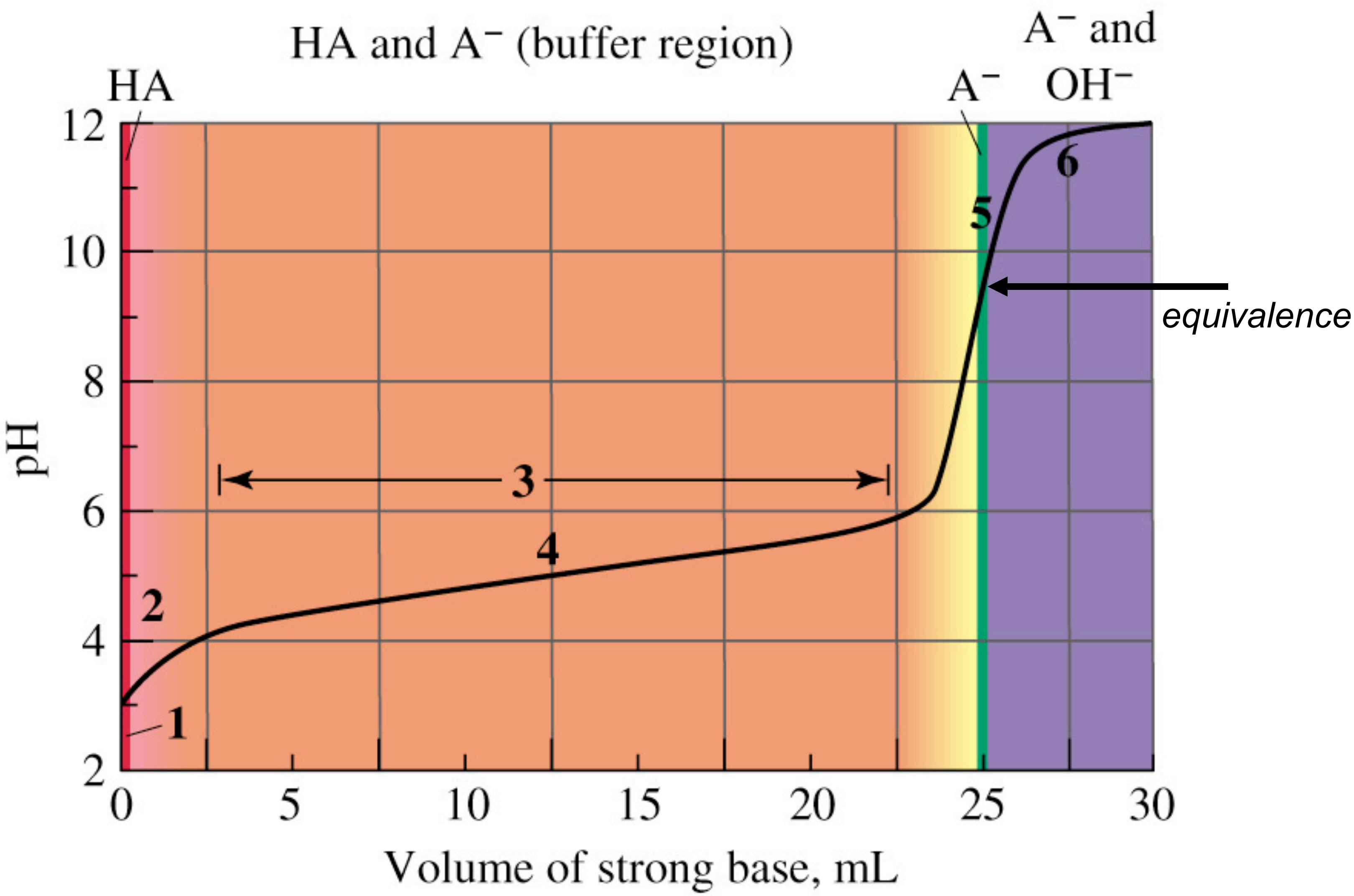
Strong acid + strong base

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

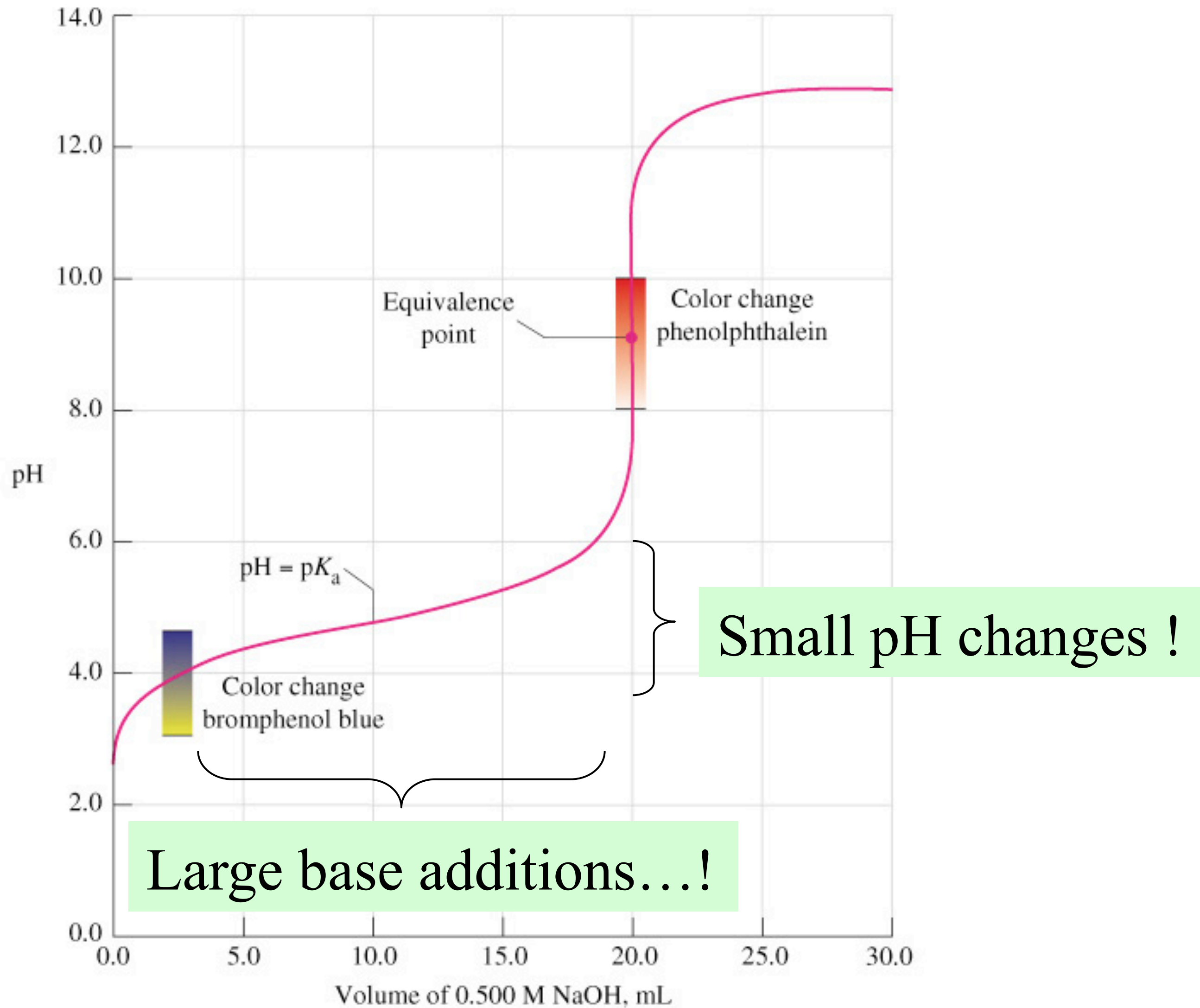


Equivalence
pH = 7.0

Small pH variations *vs* large amounts of base



Special condition when the acid is 50% neutralized



Buffer effect

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