Acids and bases part 2

$$pH = -\log_{10}[H_3O^+]$$

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

a 25 ° C $K_W = [H_3O^+]\times[OH^-] = 1.0\times10^{-14}\ M^2$

$$pH + pOH = 14$$

Alcune immagini sono state prese e modificate da “Chimica” di Kotz, Treichel & Weaver, Edises 2007, III edizione

pH of a solution of a strong acid

$$HA\ (aq) + H_2O\ (l) \rightarrow A^-\ (aq) + H_3O^+\ (aq)$$

- in water $[H_3O^+]_w = [OH^-]_w = 1.0\times10^{-7}$ M.
- the strong acid HA is added, at a concentration = c_A
- since it is strong $[H_3O^+]_A = c_A$

- $[H_3O^+]_{total} = [H_3O^+]_w + [H_3O^+]_A = [H_3O^+]_w + c_A$ and $[OH^-]_{total} = [OH^-]_w$

- $Q = [H_3O^+]_{total}\,[OH^-]_{total} = ([H_3O^+]_w + c_A)\ [OH^-]_w > K_W$

- $K_W = ([H_3O^+]_w + c_A - x)\ ([OH^-]_w - x)$

- $x^2 - ([H_3O^+]_w + [OH^-]_w + c_A)\,x + c_A[OH^-]_w = 0$

$$x = \frac{[H_3O^+]_w + [OH^-]_w + c_A - \sqrt{c_A^2 + 4K_W}}{2}$$

$$[H_3O^+] = [H_3O^+]_w + c_A - x \quad \text{e} \quad [OH^-] = K_W / [H_3O^+]$$

Calculation of the pH of a solution of 0.1 M di HCl at 25 ° C

$$x = \frac{[H_3O^+]_w + [OH^-]_w + c_A - \sqrt{c_A^2 + 4K_W}}{2}$$

$$x = \frac{2.0 \cdot 10^{-7} + 0.1 - \sqrt{0.1^2 + 4 \cdot 10^{-14}}}{2} = 1.0 \cdot 10^{-7}\ \mathrm{M}$$

$$[H_3O^+] = [H_3O^+]_w + c_A - x = 1.0 \cdot 10^{-7} + 0.1 - 1.0 \cdot 10^{-7} = 0.1\ \mathrm{M}$$

$pH = -\log_{10}[H_3O^+] = -\log_{10} 0.1 = 1$ and $pOH = 14 - 1 = 13$

pH of a solution of a strong acid - approximation

$$HA\ (aq) + H_2O\ (l) \rightarrow A^-\ (aq) + H_3O^+\ (aq)$$

- in pure water $[H_3O^+]_w = [OH^-]_w = 1.0\times10^{-7}$ M.
- the strong acid HA is added, at a concentration = c_A
- since it is strong $[H_3O^+]_A = c_A$

When the concentration of C_A is much larger than $[H_3O^+]_w$ from water self-protolysis :

$$\boxed{pH = -\log_{10} c_A}$$

$$[H_3O^+]_{total} \approx c_A$$

pH of a solution of a strong base

$B\ (aq) + H_2O\ (l) \rightarrow BH^+\ (aq) + OH^-\ (aq)$

- in pure water $[OH^-]_w = 1.0\times10^{-7}$ M.
- the strong base B is added, at a concentration = c_B
- since it is strong $[OH^-]_B = c_B$

$$\boxed{pH = 14 - \log_{10} c_B}$$

$$[OH^-]_{total} \approx c_B$$

Range for the approximation $[H_3O^+]_{total} \approx c_A$ (or $[OH^-]_{total} \approx c_B$)

c_A (M)	$[H_3O^+]$ (M) (eq. 1)	pH (eq. 1)	$-\log_{10}[c_A]$
10^{-8}	1.05×10^{-7}	6.97	8.00
10^{-7}	1.62×10^{-7}	6.79	7.00
10^{-6}	1.01×10^{-6}	5.99	6.00
10^{-5}	10^{-5}	5.00	5.00
10^{-4}	10^{-4}	4.00	4.00
10^{-3}	10^{-3}	3.00	3.00
10^{-2}	10^{-2}	2.00	2.00
10^{-1}	10^{-1}	1.00	1.00
1	1	0.00	0.00

$c_A \geq 10^{-5}$ M

and

$c_B \geq 10^{-5}$ M

pH of a solution of a weak acid

A weak acid is partially dissociated in water

$HA\ (aq) + H_2O\ (l) \rightleftarrows A^-\ (aq) + H_3O^+\ (aq)$

We have for species in solution: HA, A^-, H_3O^+ e OH^-.

$$\begin{cases} K_A = \dfrac{[A^-]\cdot[H_3O^+]}{[HA]} & \text{Law of mass action for the acid} \\ K_W = [H_3O^+]\cdot[OH^-] & \text{Law of mass action for water} \\ c_A = [HA]+[A^-] & \text{Law of mass conservation for the acid} \\ [H_3O^+] = [A^-]+[OH^-] & \text{Law of mass conservation for water} \end{cases}$$

As in the previous case, the presence of the acid decreases water self-protolysis

One can calculate that:

$$K_A = \frac{[H_3O^+]\cdot\left([H_3O^+]-\frac{K_W}{[H_3O^+]}\right)}{c_A-[H_3O^+]+\frac{K_W}{[H_3O^+]}}$$

That can be rearranged to give:

$$[H_3O^+]^3 + K_A[H_3O^+]^2 - (K_A c_A + K_W)\cdot[H_3O^+] - K_A K_W = 0$$

This expression allows to calculate the pH of a solution of a weak acid.

It can be simplified

The same is valid for a weak base substituting $[OH^-]$ to $[H_3O^+]$ and c_B to c_A

Approximations

If c_A is not too small and the acid is not too weak ($K_A > 10^{-14}$):

$[H_3O^+]_{tot} \approx [H_3O^+]_{acid}$ and, since

$[H_3O^+]_{acid} = [A^-]$ and $c_A \approx [HA]$ substituting and solving for $[H_3O^+]$

$$K_A = \frac{[H_3O^+]\cdot[A^-]}{[HA]}$$

$$[H_3O^+]^2 = K_A\,(c_A - [H_3O^+])$$

⇓

$$\boxed{[H_3O^+] = \frac{-K_A + \sqrt{K_A^2 + 4K_Ac_A}}{2}}$$

$$HA\ (aq) + H_2O\ (l) \rightleftarrows A^-\ (aq) + H_3O^+\ (aq)$$

Approximations

if c_A is not too small and the acid is not too weak ($K_A > 10^{-14}$):

$[H_3O^+]_{tot} \approx [H_3O^+]_{acid}$ then: $[H_3O^+]_{acido} = [A^-]$

Since the acid is weak, $\alpha \ll 1$ then: $c_A \approx [HA]$

if we substitute and we solve for $[H_3O^+]$

$$K_A = \frac{[H_3O^+]\cdot[A^-]}{[HA]} \qquad [H_3O^+]\,[A^-] = K_A\,[HA]$$

Usin the approximations:

$$[H_3O^+]^2 = K_A\, c_A \qquad [H_3O^+] = \sqrt{K_A c_A}$$

If $[H_3O^+] \ll c_A$, it is negligible with respect to c_A:

$$K_A = \frac{[H_3O^+]^2}{c_A - A} \approx \frac{[H_3O^+]^2}{c_A}$$

$$[\mathrm{H_3O^+}] = \sqrt{\mathrm{K_A c_A}}$$

$\mathrm{c_A} \approx [\mathrm{HA}]$ $\alpha \ll 1$

And for a weak base:

$$[\mathrm{OH^-}] = \sqrt{\mathrm{K_B c_B}}$$

$\mathrm{c_B} \approx [\mathrm{B}]$ $\alpha \ll 1$

Range of application for these approximations

Calculated pH for acetic acid 25 ° C (K_A =1.8·10^{-5} M)

[acid] (M)	pH (eq. 1)	pH (eq. 2)	pH (eq. 3)
10^{-7}	6.793	7.002	5.872
10^{-6}	6.018	6.022	5.372
10^{-5}	5.145	5.145	4.872
10^{-4}	4.464	4.463	4.372
10^{-3}	3.902	3.901	3.872
10^{-2}	3.382	3.381	3.372
10^{-1}	2.875	2.875	2.872
10^{-0}	2.373	2.373	2.372

$$c_A \geq 10^{-4}\ \mathrm{M}$$

And for bases

$$c_B \geq 10^{-4}\ \mathrm{M}$$

$$\text{eq.1}\quad [H_3O^+]^3 + K_A[H_3O^+]^2 - (K_A c_A + K_W)\cdot[H_3O^+] - K_A K_W = 0$$

$$\text{eq.2}\quad [H_3O^+] = \frac{-K_A + \sqrt{K_A^2 + 4K_A c_A}}{2}$$

$$\text{eq.3}\quad [H_3O^+] = \sqrt{K_A c_A}$$

Used to solve problems

The strength of an acid or base increases as K_A o K_B increase

In chemistry and biochemistry we use a logarithmic scale to compare acids and bases.

$$\mathrm{HA\ (aq) + H_2O\ (l) \rightleftarrows A^- \ (aq) + H_3O^+\ (aq)} \qquad K_A = \frac{[H_3O^+]\cdot[A^-]}{[HA]}$$

$$pK_A = -\log_{10} K_A$$

$$\mathrm{B\ (aq) + H_2O\ (l) \rightleftarrows BH^+\ (aq) + OH^-\ (aq)} \qquad K_B = \frac{[OH^-]\cdot[BH^+]}{[B]}$$

$$pK_B = -\log_{10} K_B$$

examples

$$\mathrm{NH_3\ (aq) + H_2O\ (l) \rightleftarrows NH_4^+\ (aq) + OH^-\ (aq)}$$

$$K_B = \frac{[OH^-]\cdot[NH_4^+]}{[NH_3]} = 1.8\cdot 10^{-5}\,\mathrm{M}\ \ \text{a } 25\,°\mathrm{C} \rightarrow pK_B = -\log_{10}(1.8\cdot 10^{-5}) = 4.74$$

$$\mathrm{H_2CO_3\ (aq) + H_2O\ (l) \rightleftarrows HCO_3^-\ (aq) + H_3O^+\ (aq)}$$

$$K_A = \frac{[H_3O^+]\cdot[HCO_3^-]}{[H_2CO_3]} = 4.2\cdot 10^{-7}\,\mathrm{M}\ \ \text{a } 25\,°\mathrm{C} \rightarrow pK_A = -\log_{10}(4.2\cdot 10^{-7}) = 6.38$$

pK_A o pK_B decrease as the strength of an acid or a base increase

acid	formula	K_A (M)	pK
propanoic	CH_3CH_2COOH	$1.3\text{x}10^{-5}$	4.89
acetic	CH_3COOH	$1.8\text{x}10^{-5}$	4.74
methanoic	HCOOH	$1.8\text{x}10^{-4}$	3.74

strength increases

↓

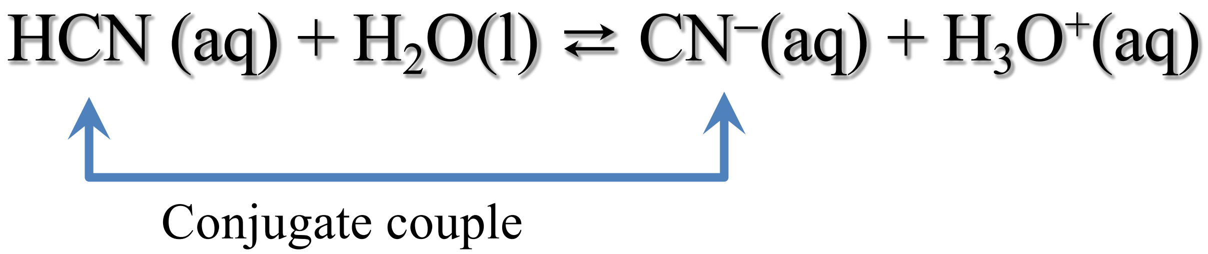
base	formula	K_A (M)	pK
aniline	$C_6H_5NH_2$	$4.0\text{x}10^{-10}$	9.40
ammonia	NH_3	$1.8\text{x}10^{-5}$	4.74
methylammine	CH_2NH_2	$5.0\text{x}10^{-4}$	3.30

strength increases

↓

Acids and bases part 3

Relationship between the ionization constants of an acid and its conjugate base



$$HCN\,(aq) + H_2O(l) \rightleftarrows CN^-(aq) + H_3O^+(aq)$$

Conjugate couple

The product between K_A of an acid and K_B of its conjugate base is K_W:

$$K_A\ K_B = K_W$$

$$pK_A + pK_B = 14$$

$HA\ (aq) + H_2O\ (l) \rightleftarrows A^-\ (aq) + H_3O^+\ (aq)$

$$K_A = \frac{[H_3O^+]\cdot[A^-]}{[HA]}$$

$A^-\ (aq) + H_2O\ (l) \rightleftarrows HA\ (aq) + OH^-\ (aq)$

$$K_B = \frac{[\mathrm{OH}^-]\cdot[AH]}{[A^-]}$$

$$K_A \cdot K_B = \frac{[H_3O^+]\cdot[A^-]}{[HA]} \bullet \frac{[\mathrm{OH}^-]\cdot[AH]}{[A^-]} = [H_3O^+]\cdot[OH^-] = K_W$$

Therefore K_B can be calculated: K_A/K_W

Interactions between the ionization constants of an acid and its conjugate base with H_2O at 25 ° C

$$\cancel{HCN}\ (aq) + H_2O\ (l) \rightleftarrows \cancel{CN^-}(aq) + H_3O^+(aq) \qquad K_A = 4.0x10^{-5}\ M$$

$$\cancel{CN^-}(aq) + H_2O\ (l) \rightleftarrows \cancel{HCN}\ (aq) + OH^-(aq) \qquad K_B = 2.5x10^{-10}\ M$$

$$2\ H_2O\ (l) \rightleftarrows H_3O^+(aq) + OH^-(aq) \qquad K_W = K_A K_B = 1.0x10^{-14}\ M^2$$

$$K_A \cdot K_B = \frac{[H_3O^+]\cdot[\cancel{CN^-}]}{[\cancel{HCN}]} \cdot \frac{[\cancel{HCN}]\cdot[OH^-]}{[\cancel{CN^-}]} = [H_3O^+]\cdot[OH^-] = K_W$$

$$\boxed{K_A\, K_B = K_W} \qquad \boxed{pK_A + pK_B = pK_W}$$

Therefore K_B can be calculated: K_A/K_W

pK of some acids and of their conjugate bases at 25 ° C: $14 = pK_A + pK_B$

forza dell’ acido crescente

Name of acid	acido	pK_A	base	pK_B	Name of base
hydronium	H_3O^+	0	H_2O	14	water
phosphoric	H_3PO_4	2.12	$H_2PO_4^-$	11.88	Dihydrogen phosphate
fluoridirc	HF	3.14	F^-	10.86	fluoride
acetic	CH_3COOH	4.74	CH_3COO^-	9.25	acetate
carbonic	H_2CO_3	6.38	HCO_3^-	7.62	Hydrogen carbonate
sulphidric	H_2S	7	HS^-	7	Hydrogen sulphide
Dihydrogen phosphate	$H_2PO_4^-$	7.21	HPO_4^{2-}	6.79	Hydrogen phosphate
ammonium	NH_4^+	9.25	NH_3	4.74	ammonia
cianidric	HCN	9.4	CN^-	4.6	cianide
Hydrogen carbonate	HCO_3^-	10.32	CO_3^{2-}	3.68	carbonate
Hydrogen phosphate	HPO_4^{2-}	12.44	PO_4^{3-}	1.56	phosphate
water	H_2O	14	OH^-	0	hydroxide

forza della base crescente

Types of acid-base reactions

We studied so far the reaction between acids and bases (strong and weak) with amphiprotic water has been studied. Acids and bases can react in water to form a salt.

$$\text{acid} + \text{base} \rightleftarrows \text{salt} + H_2O$$

type	example
strong acid + strong base	$HCl + NaOH \rightarrow NaCl + H_2O$
strong acid + weak base	$HCl + NH_3 \rightleftarrows NH_4Cl + H_2O$
weak acid + strong base	$CH_3COOH + NaOH \rightleftarrows CH_3COONa + H_2O$
weak acid + weak base	$CH_3COOH + NH_3 \rightleftarrows CH_3COONH_4 + H_2O$

Reaction between strong acid and strong base: **neutralization**

Strong acids and bases are 100 % ionized in solution:

$$HCl\ (aq) + H_2O \longrightarrow H_3O^+\ (aq) + Cl^-\ (aq)$$

$$NaOH\ (aq) \longrightarrow Na^+\ (aq) + OH^-\ (aq)$$

The net equation between HCl (strong acid) and NaOH (strong base) is :

$$H_3O^+\ (aq) + \cancel{Cl^-}\ (aq) + \cancel{Na^+}\ (aq) + OH^-\ (aq) \rightleftarrows 2\ H_2O\ (l) + \cancel{Na^+}\ (aq) + \cancel{Cl^-}\ (aq)$$

$$H_3O^+\ (aq) + OH^-\ (aq) \rightleftarrows 2\ H_2O\ (l)$$

$$K = \frac{1}{[H_3O^+]\cdot[OH^-]} = \frac{1}{K_W} = 1.0\cdot 10^{14}\,M^{-2}$$

The net ionic equation for the reaction of a strong acid with a strong base is always the union of a hydronium ion with a hydroxide ion to give water.
Since K = 1 / K_W, reagents are fully consumed to K = 1 / K_W, reagents are fully consumed to yield products. If an equal amount of moles of NaOH and HCl, are mixed, the result is a neutral NaCl solution (pH =7.0 at 25 ° C)

When the concentrations of strong acids and bases are much larger than $[H_3O^+]$ water self-ionization:

if $c_A = c_B$ $[H_3O^+] = 1.0\text{x}10^{-7}$ M and pH =7

If $c_A > c_B$ $[H_3O^+] = c_A - c_B$ and $\text{pH} = -\log_{10}(c_A - c_B) < 7$

if $c_A < c_B$ $[OH^-] = c_B - c_A$ and $\text{pOH} = -\log_{10}(c_B - c_A)$ $\text{pH} = 14 - \text{pOH} > 7$

Reaction between strong acid and weak base

The weak base is not 100 % ionized in solution:

$$HCl\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + Cl^-\ (aq)$$

$$H_3O^+\ (aq) + NH_3\ (aq) + \cancel{Cl^-}\ (aq) \rightleftarrows H_2O\ (l) + NH_4^+\ (aq) + \cancel{Cl^-}\ (aq)$$

The net reaction of HCl (strong acid) e NH_3 (weak base) is :

$$H_3O^+\ (aq) + NH_3\ (aq) \rightleftarrows H_2O\ (l) + NH_4^+\ (aq)$$

$$K = \frac{[NH_4^+]}{[H_3O^+]\cdot[NH_3]} = \frac{1}{K_A} = \frac{K_B}{K_W} = 1.8\cdot 10^9\ M^{-1}$$

In this reaction H_3O^+ is an acid stronger than NH_4^+ and NH_3 is a base stronger than H_2O. The reaction is strongly shifted toward the products.

Mixing equimolar amounts of a strong acid with a weak base produces a salt whose cation is the conjugate acid of the weak base. The solution becomes acid, with a pH depending on the K_A of the cation. The salt ammonium choride is formed: NH_4Cl.

Reaction between weak acid and strong base

In the reaction between a weak acid HCOOH, with a strong base NaOHnet ionic reaction is:

$$\mathrm{HCOOH\ (aq) + OH^{-}\ (aq) \rightleftarrows HCOO^{-}\ (aq) + H_2O\ (l)}$$

$$K = \frac{[\mathrm{HCOO^-}]}{[\mathrm{HCOOH}]\cdot[\mathrm{OH^-}]} = \frac{[\mathrm{HCOO^-}]\cdot[\mathrm{H_3O^+}]}{[\mathrm{HCOOH}]\cdot[\mathrm{OH^-}]\cdot[\mathrm{H_3O^+}]} = \frac{[\mathrm{HCOO^-}]\cdot[\mathrm{H_3O^+}]}{[\mathrm{HCOOH}]\cdot K_W} = \frac{K_A}{K_W}$$

$$K = \frac{K_A}{K_W} = \frac{1.8\cdot 10^{-4}}{1.0\cdot 10^{-14}} = 1.8\cdot 10^{10}\ \mathrm{M^{-1}}$$

In this reaction the hydroxide OH^- is a base stronger than formiate $HCOO^-$ and formic acid HCOOH is an acid stronger than water: the reaction is strongly shifted toward the product.

Mixing equimolar amounts of a strong acid with a weak base produces a salt whose cation is the conjugate acid of the weak base. The solution is basic with a pH that depends on the K_B of the anion.
The salt HCO_2Na (sodium formiate) is formed.

Reaction between weak acid and weak base

$CH_3COOH\ (aq) + NH_3\ (aq) \rightleftarrows CH_3COO^-\ (aq) + NH_4^+\ (aq)$

In this reaction product formation is favored since acetic acid is a stronger acid than the ammonium ion and ammonia is a stronger base than acetate: the reaction is strongly shifted to the right.

Mixing of equimolar amounts of a weak base with a weak acid produces a salt whose anion is the conjugated base of the weak acid and cation is the conjugate acid of the weak base. The pH depends on the values of K_A of the weak acid and of K_B of the weak base.
The salt ammonium acetate is formed $CH_3CO_2NH_4$

Chemistry of acids and bases 3

- Salt hydrolysis
- Buffer solutions
- Acid-base titrations

Hydrolytic equilibria

The aqueous solution of a salt obtained from an acid and a strong base contains the free ionic species that form the salt.

Base and acid (strong)	Salt solution	pH
$NaOH + HCl \longrightarrow NaCl + H_2O$	$NaCl\ (s) \rightarrow Na^+\ (aq) + Cl^-\ (aq)$	7
$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$	$NaNO_3\ (s) \rightarrow Na^+\ (aq) + NaNO_3^-\ (aq)$	7
$KOH + HClO_4 \longrightarrow KClO_4 + H_2O$	$KClO_4\ (s) \rightarrow K^+\ (aq) + ClO_4^-\ (aq)$	7
$KOH + HBr \longrightarrow KBr + H_2O$	$KBr\ (s) \rightarrow K^+\ (aq) + Br^-\ (aq)$	7
$Ca(OH)_2 + 2\ HCl \longrightarrow CaCl_2 + H_2O$	$CaCl_2\ (s) \rightarrow Ca^{2+}\ (aq) + 2\ Cl^-\ (aq)$	7

In these solutions there is no proton exchange because both cation (conjugated acid of the strong base) and anion (conjugated base of the strong acid) do not tend to release or subtract protons from water. The solution is therefore neutral.

We call hydrolysis those proton exchange reactions (acid-base) that are established in the aqueous solutions of salts formed by:

- weak acids and strong bases (which contain moderately strong conjugated bases and very weak conjugated acids): basic hydrolysis, pH > 7

- weak bases and strong acids (which contain moderately strong conjugated acids and very weak conjugated bases) : acid hydrolysis, pH > 7

- acids and bases both weak (which contain moderately strong conjugated acids and bases): basic, acid or neutral hydrolysis

As a result of these exchanges of protons with the aqueous amphiprotic solvent there is a variation in the concentration of $[H_3O^+]$ and $[OH^-]$ (pH)

$$NH_4Cl\ (s) \longrightarrow NH_4^+\ (aq) + Cl^-\ (aq)$$

$$NH_4^+\ (aq) + H_2O\ (l) \rightleftarrows NH_3\ (aq) + H_3O^+\ (aq)$$

Salt formed by weak acids and strong bases : basic hydrolysis

The dissociation of the salt CA is followed by the protonation equilibrium of the anion A^-, which is a moderately strong Brønsted base.

$$CA\ (aq) \rightarrow C^+\ (aq) + A^-\ (aq)$$

$$A^-\ (aq) + H_2O\ (l) \rightleftarrows HA\ (aq) + OH^-\ (aq)$$

$$CH_3COONa\ (aq) \rightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$$

$$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftarrows CH_3COOH\ (aq) + OH^-\ (aq)$$

$$KCN\ (aq) \rightarrow K^+\ (aq) + CN^-\ (aq)$$

$$CN^-\ (aq) + H_2O\ (l) \rightleftarrows HCN\ (aq) + OH^-\ (aq)$$

$$KNO_2\ (aq) \rightarrow K^+\ (aq) + NO_2^-\ (aq)$$

$$NO_2^-\ (aq) + H_2O\ (l) \rightleftarrows HNO_2\ (aq) + OH^-\ (aq)$$

Due to the hydrolytic equilibrium, the solution is enriched with OH^- ions.

The equilibrium constant of this equilibrium is called hydrolysis constant K_i:

$$A^- \text{ (aq)} + H_2O \text{ (l)} \rightleftarrows HA \text{ (aq)} + OH^- \text{ (aq)}$$

$$K_i = \frac{[HA]\cdot[OH^-]}{[A^-]}$$

K_i is directly related to K_A of the weak acid that is formed:

$$K_i = \frac{[HA]\cdot[OH^-]}{[A^-]} = \frac{[HA]\cdot[OH^-]}{[A^-]}\cdot\frac{[H_3O^+]}{[H_3O^+]} = \frac{K_W}{K_A}$$

$$K_i = \frac{K_W}{K_A}$$

$$[OH^-] = \sqrt{K_i c_S} = \sqrt{\frac{K_W}{K_A} c_S}$$

The weaker the acid and the higher the salt concentration, the more basic is the resulting solution.

Alkaline hydrolisis pH determination formula

$$K_i = \frac{[HA]\cdot[OH^-]}{[A^-]} = \frac{[HA]\cdot[OH^-]}{[A^-]}\cdot\frac{[H_3O^+]}{[H_3O^+]} = \frac{K_W}{K_A}$$

$$\boxed{K_i = \frac{K_W}{K_A}}$$

The OH^- arising from water self-protolysis are negligible: $[OH^-]=[HA]$

And if we consider that

A^- is a weak base: $[A^-]=c_s$

Rearranging K_i

$$\boxed{[OH^-] = \sqrt{K_i c_S} = \sqrt{\frac{K_W}{K_A} c_S}}$$

$$[OH^-]^2 = Ki\ c_s$$

Salt formed by weak base and strong acid : acid hydrolysis

The dissociation of the salt BHA is followed by the deprotonation equilibrium of the cation BH, which is a moderately strong Brønsted acid.

$$\mathrm{BHA\ (aq) \rightarrow BH^{+}\ (aq) + A^{-}\ (aq)}$$

$$\mathrm{BH^{+}\ (aq) + H_2O\ (l) \rightleftarrows B\ (aq) + H_3O^{+}\ (aq)}$$

$$\mathrm{NH_4Cl\ (s) \rightarrow NH_4^{+}\ (aq) + Cl^{-}\ (aq)}$$

$$\mathrm{NH_4^{+}\ (aq) + H_2O\ (l) \rightleftarrows NH_3\ (aq) + H_3O^{+}\ (aq)}$$

$$\mathrm{C_6H_5NH_3Cl\ (s) \rightarrow C_6H_5NH_3^{+}\ (aq) + Cl^{-}\ (aq)}$$

$$\mathrm{C_6H_5NH_3^{+}\ (aq) + H_2O\ (l) \rightleftarrows C_6H_5NH_2\ (aq) + H_3O^{+}\ (aq)}$$

Due to the hydrolytic equilibrium, the solution is enriched with H_3O^+ ions.

The complete dissociation of BHA salt is accompanied by the deprotonation equilibrium of the BH^+ cation, which is a moderately strong Brønsted acid.

Acid hydrolisis pH determination formula

$$K_i = \frac{[B]\cdot[H_3O^+]}{[BH^+]} = \frac{[B]\cdot[H_3O^+]}{[BH^+]}\cdot\frac{[OH^-]}{[OH^-]} = \frac{K_W}{K_B}$$

$$K_i = \frac{K_W}{K_B}$$

The H_3O^+ arising from water self-protolysis are negligible: $[H_3O^+]=[HA]$
And if we consider that
BH^+ is a weak acid: $[BH^+]=c_s$

Rearranging K_i

$$[H_3O^+]^2=Ki\ c_s$$

$$[H_3O^+] = \sqrt{K_i c_S} = \sqrt{\frac{K_W}{K_B}c_S}$$

The hydrolysis constant K_i:

$$BH^+ (aq) + H_2O (l) \rightleftarrows B (aq) + H_3O^+ (aq)$$

K_i is related to K_B of the weak base that is formed:

$$K_i = \frac{[B]\cdot[H_3O^+]}{[BH^+]} = \frac{[B]\cdot[H_3O^+]}{[BH^+]} \cdot \frac{[OH^-]}{[OH^-]} = \frac{K_W}{K_B}$$

$$K_i = \frac{K_W}{K_B}$$

$$[H_3O^+] = \sqrt{K_i c_S} = \sqrt{\frac{K_W}{K_B} c_S}$$

The weaker the base and the higher the salt concentration, the more acidic is the resulting solution.

Salt formed from a weak acid and base: hydrolysis

The full dissociation of the salt BHA is accompanied by the dissociation of BH^+ and by protonation of A^-

$$BHA\ (aq) \rightarrow BH^+\ (aq) + A^-\ (aq)$$

$$BH^+\ (aq) + H_2O\ (l) \rightleftarrows B\ (aq) + H_3O^+\ (aq)$$

$$A^-\ (aq) + H_2O\ (l) \rightleftarrows HA\ (aq) + OH^-\ (aq)$$

$$H_3O^+\ (aq) + OH^-\ (aq) \rightleftarrows 2\ H_2O\ (l)$$

$$BH^+\ (aq) + A^-\ (aq) \rightleftarrows B\ (aq) + HA\ (aq)$$

As usual we neglect hydrogen and hydroxide ions coming from water dissociation if the salt concentration is not too small.

$$BH^+ (aq) + A^- (aq) \rightleftarrows B (aq) + HA (aq)$$

$$K_i = \frac{K_W}{K_A^{HA} \cdot K_B^{B}}$$

$$[H_3O^+] = \sqrt{\frac{K_A^{HA}}{K_B^{B}} \cdot K_W}$$

$$K_A^{HA} = K_B^{B} \quad \rightarrow \quad pH = 7$$

if: $$K_A^{HA} > K_B^{B} \quad \rightarrow \quad pH < 7$$

$$K_A^{HA} < K_B^{B} \quad \rightarrow \quad pH > 7$$

Exercise 13. Calculate the pH of a 0.2 M of Na Acetate solution ($K_A = 1.8 \cdot 10^{-5}$ M a 25 ° C)

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$CH_3COONa\ (aq) \rightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$

$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftarrows CH_3COOH\ (aq) + OH^-\ (aq)$

We will have an alkaline hydrolisis

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We will have an alkaline hydrolisis

$$[OH^-] = \sqrt{K_i \cdot c_S} = \sqrt{\frac{K_W}{K_A} c_S} = \sqrt{\frac{1 \cdot 10^{-14}}{1.8 \cdot 10^{-5}} \cdot 0.2} = 1.05 \cdot 10^{-5}\ \text{M}$$

$$pOH = 4.98 \quad \rightarrow \quad pH = 14 - 4.98 = 9.02$$

Exercise 14. Calculate the pH of 0.1 M ammonium chloride solution ($K_B = 1.8 \cdot 10^{-5}$ M a 25 ° C)

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$$NH_4Cl\ (s) \longrightarrow NH_4^+\ (aq) + Cl^-\ (aq)$$

$$NH_4^+\ (aq) + H_2O\ (l) \rightleftarrows NH_3\ (aq) + H_3O^+\ (aq)$$

We have an acid hydrolysis

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$$NH_4^+\ (aq) + H_2O\ (l) \rightleftarrows NH_3\ (aq) + H_3O^+\ (aq)$$

We have an acid hydrolysis

$$[H_3O^+] = \sqrt{K_i \cdot c_S} = \sqrt{\frac{K_W}{K_B} \cdot c_S} = \sqrt{\frac{1 \cdot 10^{-14}}{1.8 \cdot 10^{-5}} \cdot 0.1} = 7.45 \cdot 10^{-6}\ M$$

$$pH = 5.12$$

Exercise 15. Calculate the pH of a 0.05 M ammonium fluoride solution (ammonia $K_B = 1.8 \cdot 10^{-5}$ M; HF $K_A = 7.2 \cdot 10^{-4}$ M at 25 ° C)

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$$NH_3F\ (aq) \rightarrow NH_4^+\ (aq) + F^-\ (aq)$$

$$NH_4^+\ (aq) + H_2O\ (l) \rightleftarrows NH_3\ (aq) + H_3O^+\ (aq)$$

$$F^-\ (aq) + H_2O\ (l) \rightleftarrows HF\ (aq) + OH^-\ (aq)$$

$$H_3O^+\ (aq) + OH^-\ (aq) \rightleftarrows 2\ H_2O\ (l)$$

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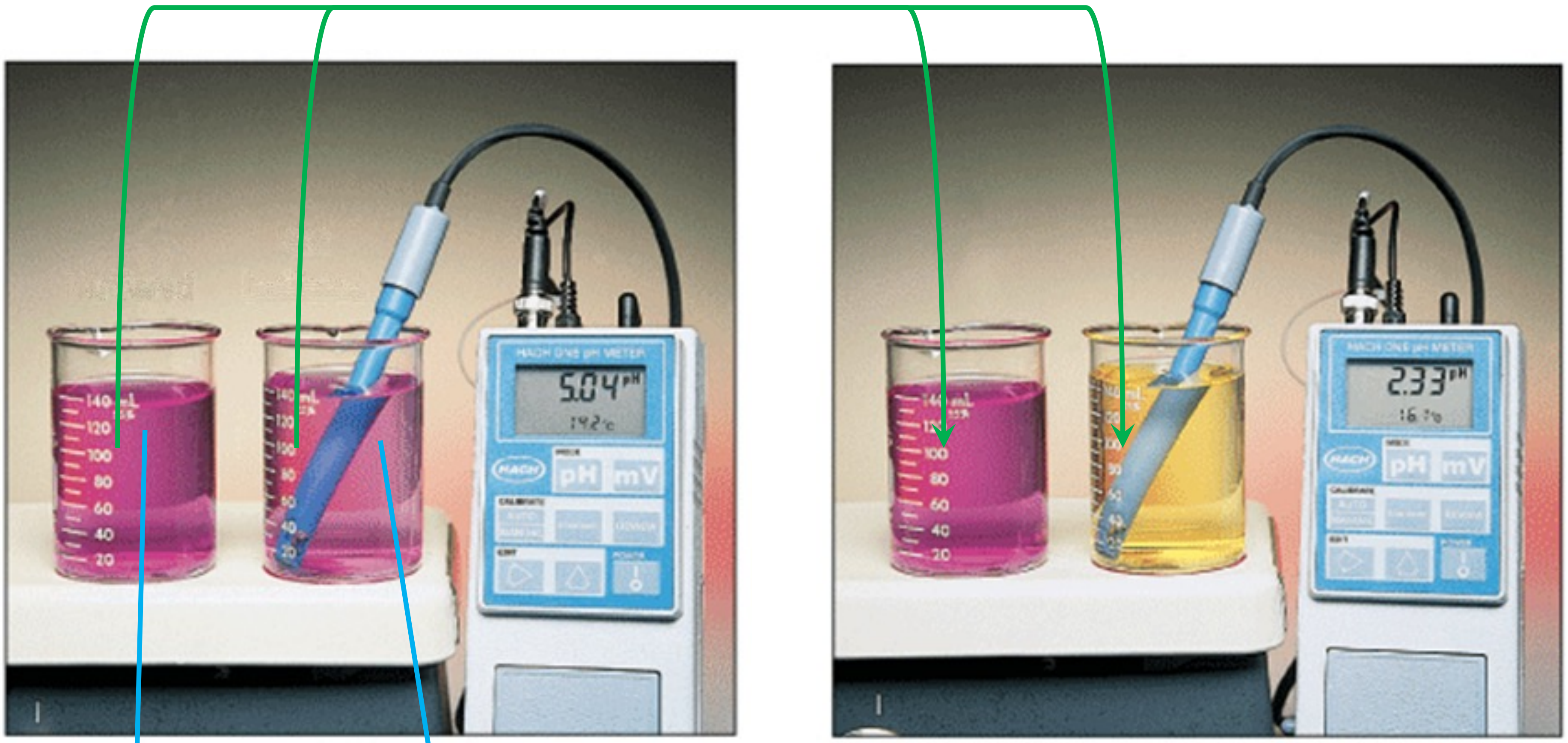
$NH_4^+\ (aq) + F^-\ (aq) \rightleftarrows NH_3\ (aq) + HF\ (aq)$

$$[H_3O^+] = \sqrt{\frac{K_A^{HF}}{K_B^{NH_3}}\cdot K_W} = \sqrt{\frac{7.2\square 10^{-4}}{1.8\square 10^{-5}}\cdot 1.0\cdot 10^{-14}} = 6.32\cdot 10^{-7}\ \text{M}$$

pH = 6.20

Controlling pH: Buffer solutions

+ HCl to both solutions

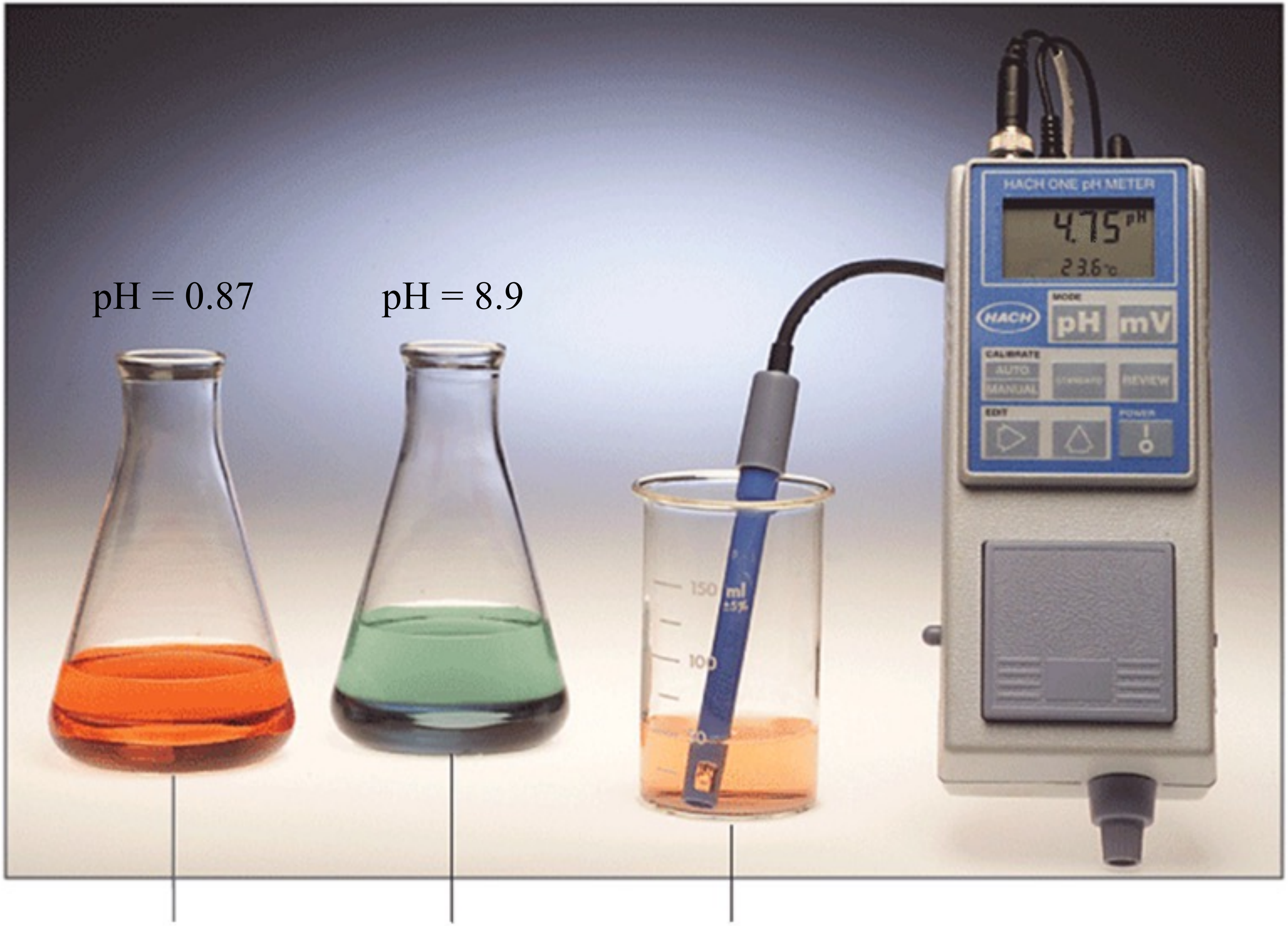


Buffered solution
pH 5.04

Not buffred solution
pH 5.04

After the addition of HCl, the pH of the buffered solution does not change (or changes slightly), while the non-buffered solution drops to pH 2.33. The buffered solution hampers pH variations.

How do we prepare a buffer solution?



pH = 0.87

pH = 8.9

acetic acid
0.1 M

Na acetate
0.1 M

buffer

How do we prepare a buffer solution?

A buffer solution is an aqueous solution in which the pH does not vary appreciably upon small additions of strong acids or bases.

To make a buffer solution we have to satisfy two conditions:

- we need the simultaneous presence of two species: an acid capable of reacting with OH^- ions and a base capable reacting with H_3O^+ ion.
- The acid and the base must not react with each other.

A buffer solution is usually prepared from approximately equal amounts of a conjugated acid-base pair:

- a weak acid and its conjugate base (e.g. acetic acid and acetate ion)
- a weak base and its conjugate acid (e.g. ammonia and ammonium ion)

How does a buffer solution work?

In the acetic acid/acetate buffer, acetic acid (weak acid) is required to react and consume the added hydroxide ions :

CH_3COOH (aq) + OH^- (l) ⇄ CH_3COO^- (aq) + H_2O (aq)

$$K = \frac{[CH_3COO^-]}{[CH_3COOH]\cdot[OH^-]} = \frac{K_A}{K_W} = \frac{1.8\cdot10^{-5}}{1.0\cdot10^{-14}} = 1.8\cdot10^{9}\ M^{-1}$$

The equilibrium constant for the reaction is very large because the OH^- ion is a much stronger basis than acetate ($CH3COO^-$). This means that all OH^- ions, coming from an external source, are completely consumed.

Similarly, each hydronium ion added to the solution will react with the acetate ion present in the buffer.

CH_3COO^- (aq) + H_3O^+ (l) ⇄ CH_3COOH (aq) + H_2O (aq)

$$K = \frac{[CH_3COOH]}{[CH_3COO^-]\cdot[H_3O^+]} = \frac{1}{K_A} = \frac{1}{1.8\cdot10^{-5}} = 5.6\cdot10^{4}\ M^{-1}$$

The equilibrium constant for this reaction is very large, since the H_3O^+ ion is a much stronger acid than acetic acid (CH_3COOH).

Common buffers in laboratory practice

Weak acid	Conjugate base	K_A (M)	Buffering range pH
Acetic acid CH_3COOH	acetate CH_3COO^-	$1.8 \cdot 10^{-5}$	3.7–5.8
dhydrogen phosphate $H_2PO_4^-$	hydrogen phosphate HPO_4^{2-}	$6.2 \cdot 10^{-8}$	6.2–8.2
hydrogen carbonate HCO_3^-	carbonate CO_3^{2-}	$4.8 \cdot 10^{-11}$	9.3–11.3
hydrogen phosphate HPO_4^{2-}	phosphate PO_4^{3-}	$3.6 \cdot 10^{-13}$	11.3–13.3

Buffer system in the blood

- bicarbonate
- hemoglobin
- phosphate

The Henderson-Hasselbalch equation

$$pH = pK_A + \log_{10}\frac{[\text{coniugate base}]}{[\text{acid}]}$$

L.J. Henderson
(1878– 1942)

The pH of a buffer solution is controlled by two factors:

- the strength of the acid (indicated by K_A o pK_A)
- the relative amounts of the acid and of its conjugate base

The pH of a buffer solution is mainly determined by the value of pK_A and the fine pH control is achieved by modifying the relative amounts of conjugate base and acid.

$$if\ \frac{[\text{conjugate base}]}{[\text{acid}]} > 1 \rightarrow pH > pK_A$$

$$if\ \frac{[\text{conjugate base}]}{[\text{acid}]} = 1 \rightarrow pH = pK_A$$

$$if\ \frac{[\text{conjugate base}]}{[\text{acid}]} < 1 \rightarrow pH < pK_A$$

The Henderson-Hasselbalch Equation

In a buffer solution containing a weak acid HA and its conjugate base A^-:

$$HA\,(aq) + H_2O\,(l) \rightleftarrows A^-\,(aq) + H_3O^+\,(aq) \qquad K_A = \frac{[A^-]\cdot[H_3O^+]}{[HA]}$$

$$[H_3O^+] = K_A \cdot \frac{[HA]}{[A^-]} = K_A \cdot \frac{[\text{acid}]}{[\text{conjugate base}]}$$

Let’s use the co-logarithmic expression:

$$-\log_{10}[H_3O^+] = -\log_{10} K_A - \log_{10} \frac{[\text{acid}]}{[\text{conjugate base}]}$$

$$= -\log_{10} K_A + \log_{10} \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$pH = pK_A + \log_{10} \frac{[\text{conjugate base}]}{[\text{acid}]}$$

Preparing a buffer solution

We have two main conditions to satisfy:

- Control of pH: it has to be efficient at the desired pH. Use Henderson-Hasselbalch equation.

$$pH = pK_A + \log_{10}\frac{[\text{conjugate base}]}{[\text{acid}]}$$

First of all, on has to choose a a weak acid that has a K_A or pK_A close to the desired $[H_3O^+]$ or pH. The precise pH value is achieved adjusting the [conjugate base]/[acid] value.

- buffering power: the buffer solution has to compensate the amounts of acid or alkali added. E.g. in an acetate buffer we must have enough aceti acid to compensate for the acid which we foresee to be introduced.

A buffer solution is not effective, once the acid or conjuate base from the buffer is consumed.

Buffering power β

A buffer is at maximum efficacy pH is close to pK_A, i.e. when:

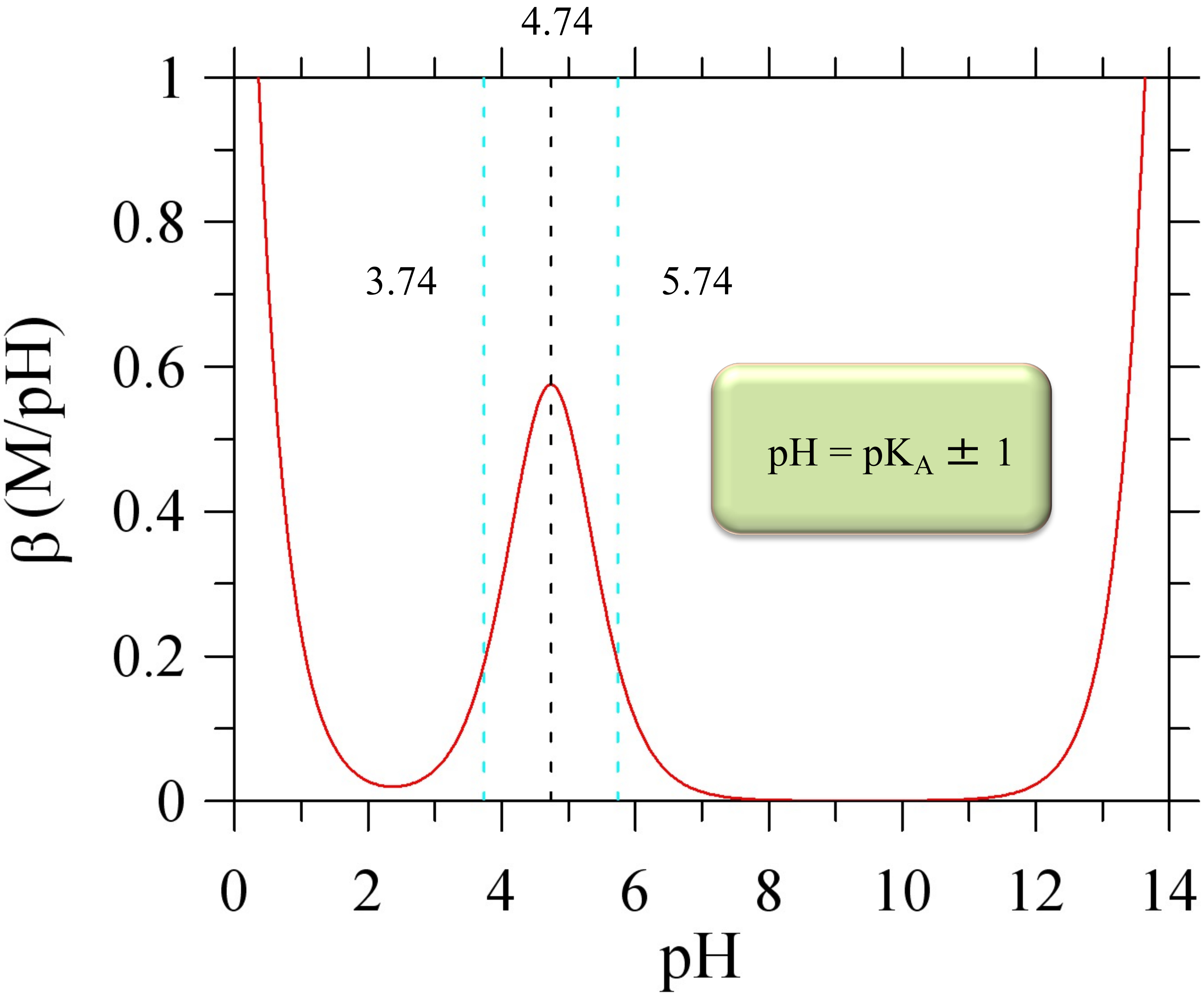
[acid] = [conjugate base]

The buffering power β is defined as the amount of base that leads to an increase of pH of 1.

$$\beta = \frac{dc_B}{dpH} = -\frac{dc_A}{dpH}$$

A buffer is efficient if $pH = pK_A \pm 1$

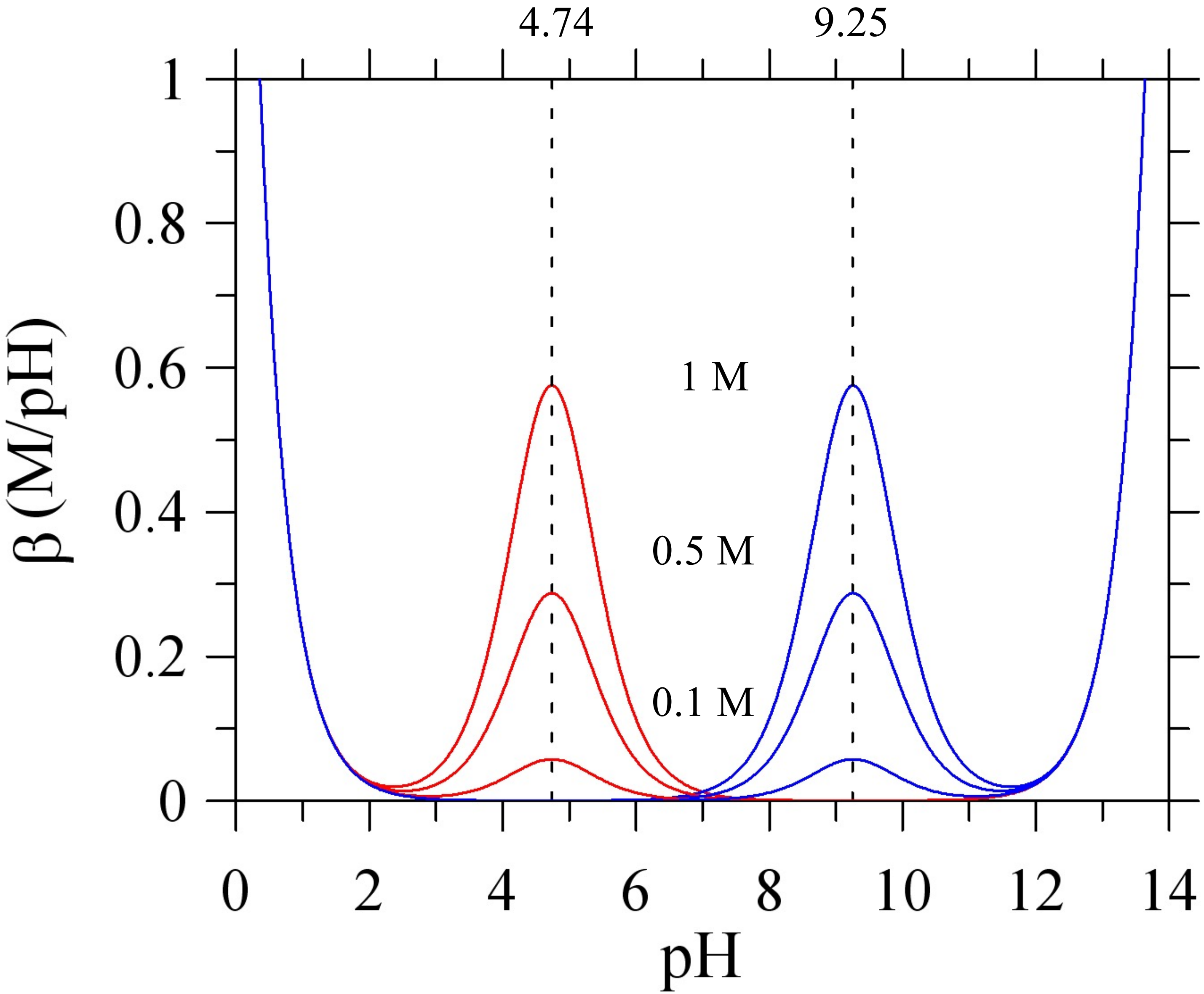
The acetic acid /acetate buffer $pK_A = 4.74$ ($c_A = 1$ M)



$pH = pK_A \pm 1$

Acetate buffer $pK_A = 4.74$ and ammonia buffer $pK_B = 9.25$

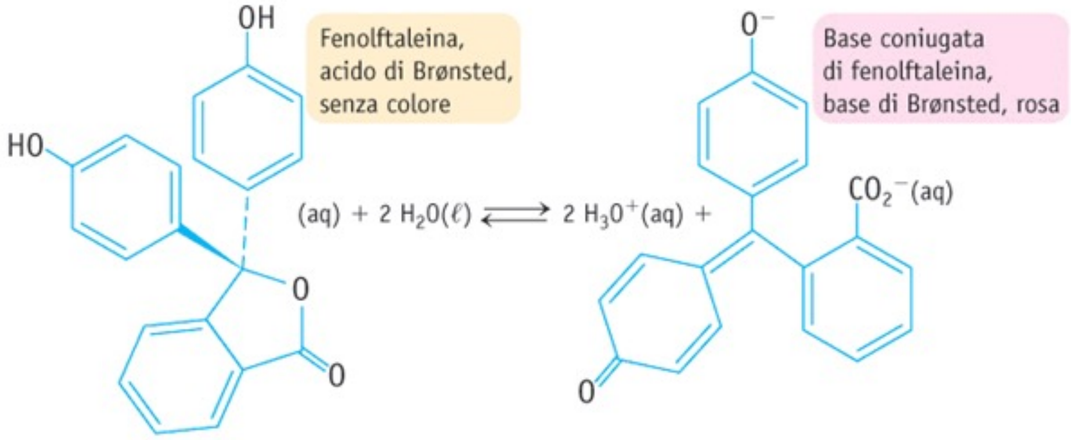
Buffering power decreases with buffer concentration



pH indicators

pH indicators

A pH indicator is a weak acid or a weak base in which protonated and deprotonated forms have different colours.



It is added in small quantities to a solution (to affect the least the pH) and it has different colours, depending on the pH of the solution.

If the indicator is a weak acid, we indicate as HInd (colour red) the protonated form and as con Ind^- (blue colour).
The indicator is in equilibrium in water:

$$\mathrm{HInd\ (aq) + H_2O\ (l) \rightleftarrows Ind^-\ (aq) + H_3O^+\ (aq)}$$

$$K_A = \frac{[\mathrm{Ind}^-]\cdot[\mathrm{H_3O^+}]}{[\mathrm{HInd}]} \qquad \frac{K_A}{[\mathrm{H_3O^+}]} = \frac{[\mathrm{Ind}^-]}{[\mathrm{HInd}]}$$

The ratio $[Ind^-]$ / [HInd] determines the colour of the solution. We can have three limit cases:

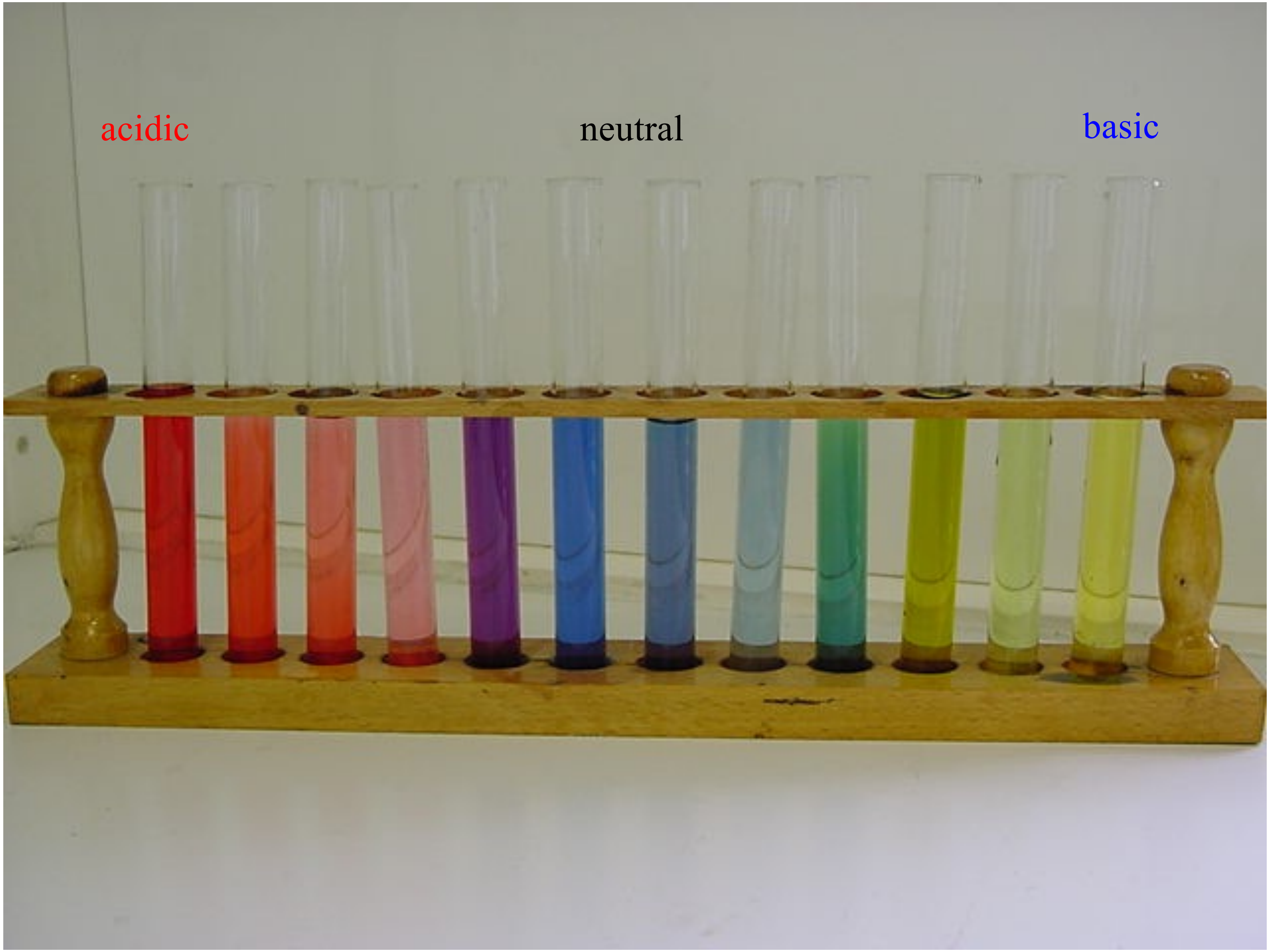
$[\mathrm{H_3O^+}] > K_A \rightarrow [\mathrm{HInd}] > [\mathrm{Ind}^-]$ red solution

$[\mathrm{H_3O^+}] = K_A \rightarrow [\mathrm{HInd}] = [\mathrm{Ind}^-]$ purple solution

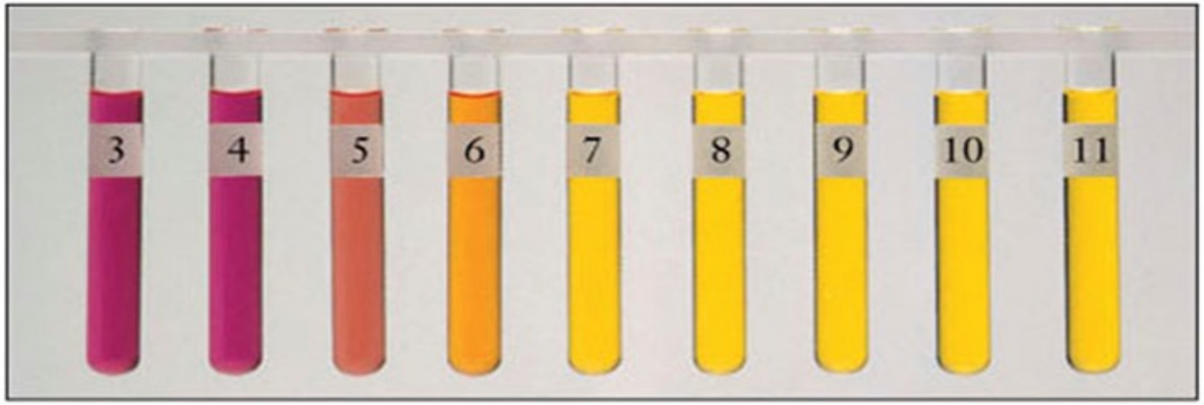
$[\mathrm{H_3O^+}] < K_A \rightarrow [\mathrm{HInd}] < [\mathrm{Ind}^-]$ blue solution

Each acidic indicator will be characterized by a K_A: in solution it will have the colour of the protonated form HInd if $pH < pK_A$. If $pH > pK_A$ the it will have the colour of the deprotonated species Ind^- .

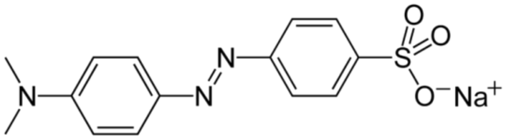
Anthocyanins from red cabbage

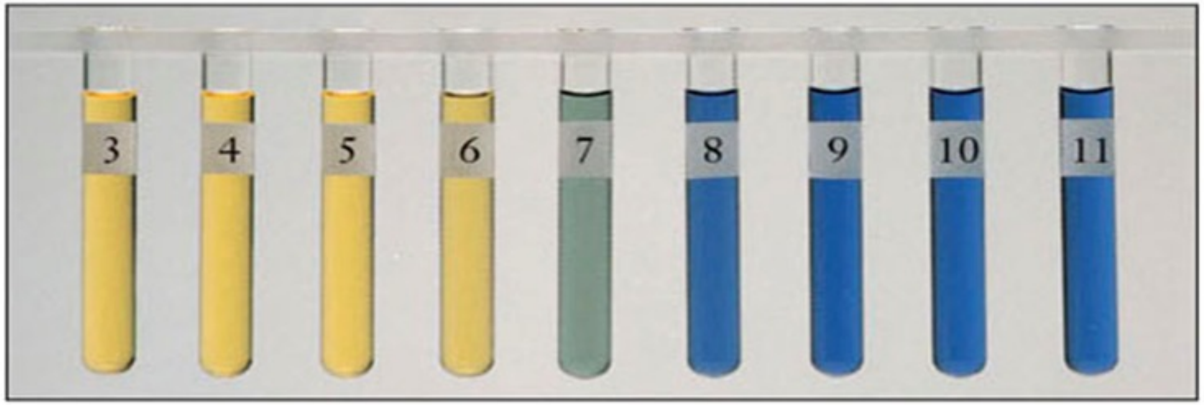


Colour change for some indicators:

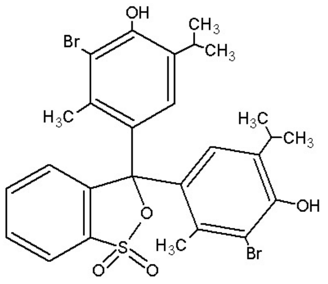


Methyl orange

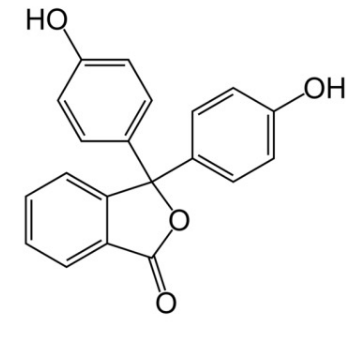




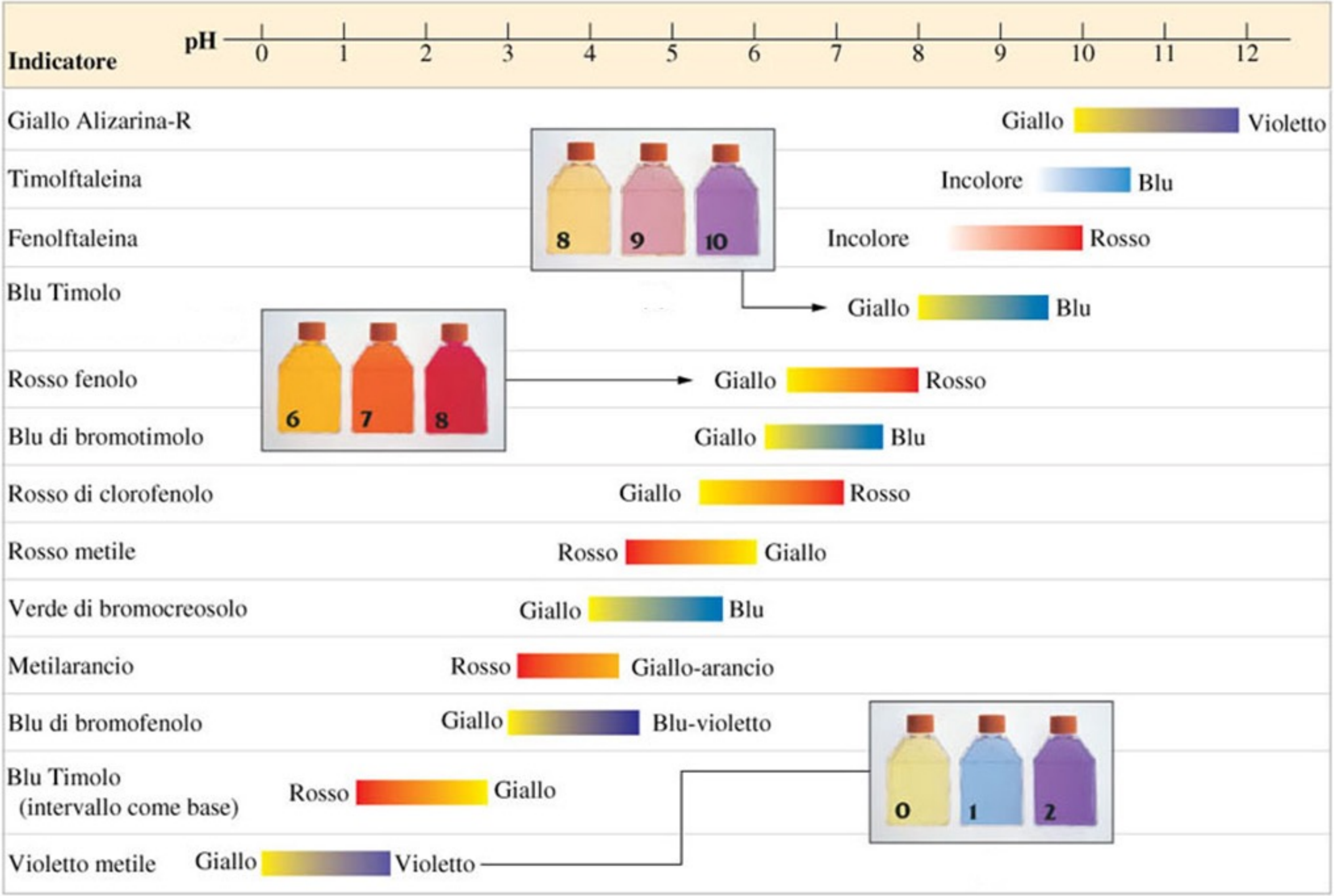
Bromothymol blue



Phenolphtalein

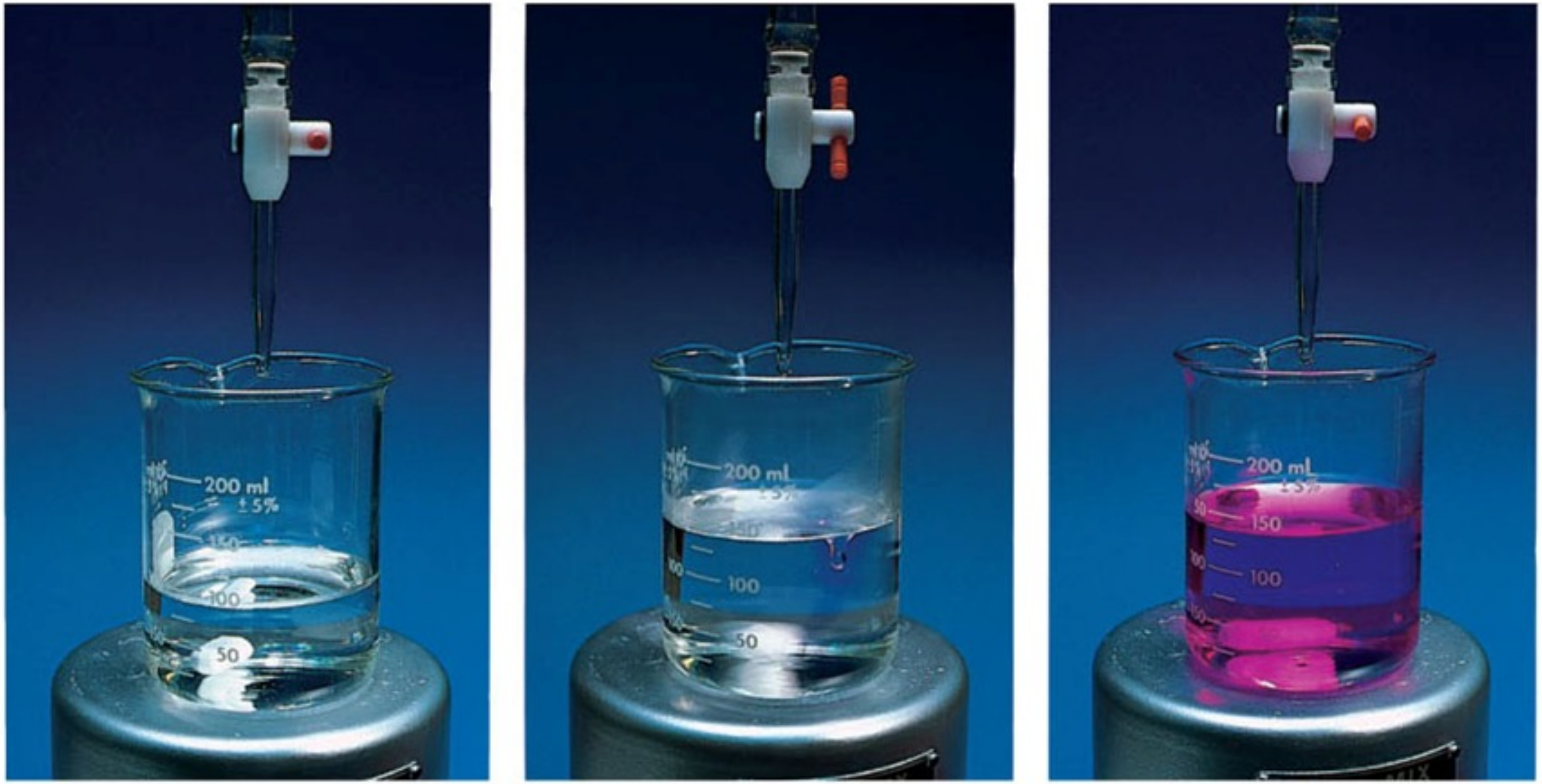


Some pH indicators and their pH range



Acid-base titration with phenolphtalein

In an acidic solution, phenolphthalein is colourless and it remains so as long as the colour-transition point is achieved. When the pH reaches 9 the solution starts to turn pink



Acid-base titrations

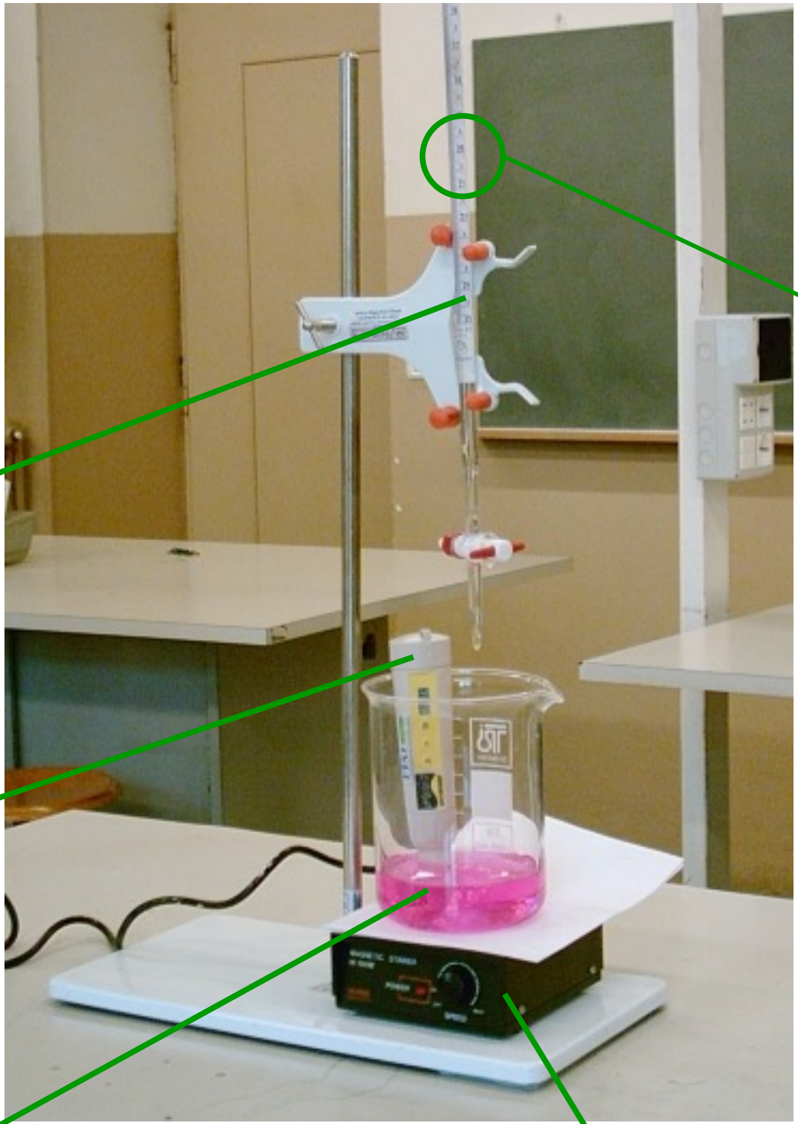
An acid-base titration allows one to determine the quantity of acid (or base) present in a solution by measuring the volume of a solution with a known concentration of base (or acid) necessary to achieve complete neutralization.

The acid solution to be titrated is introduced into a a flask and the base solution of known concentration is placed in a graduated burette above the container and added drop by drop until the acid is completely neutralized. From the volume of base added we can immediately calculate the number of moles of base necessary for neutralization

$$n_{Base} = \text{volume} \cdot \text{concentration}$$

This amounts corresponds to the acid present (for a monoprotic acid).
To appreciate neutralization one adds an indicator with turning poin at pH ≈ 7

Titration in paractice

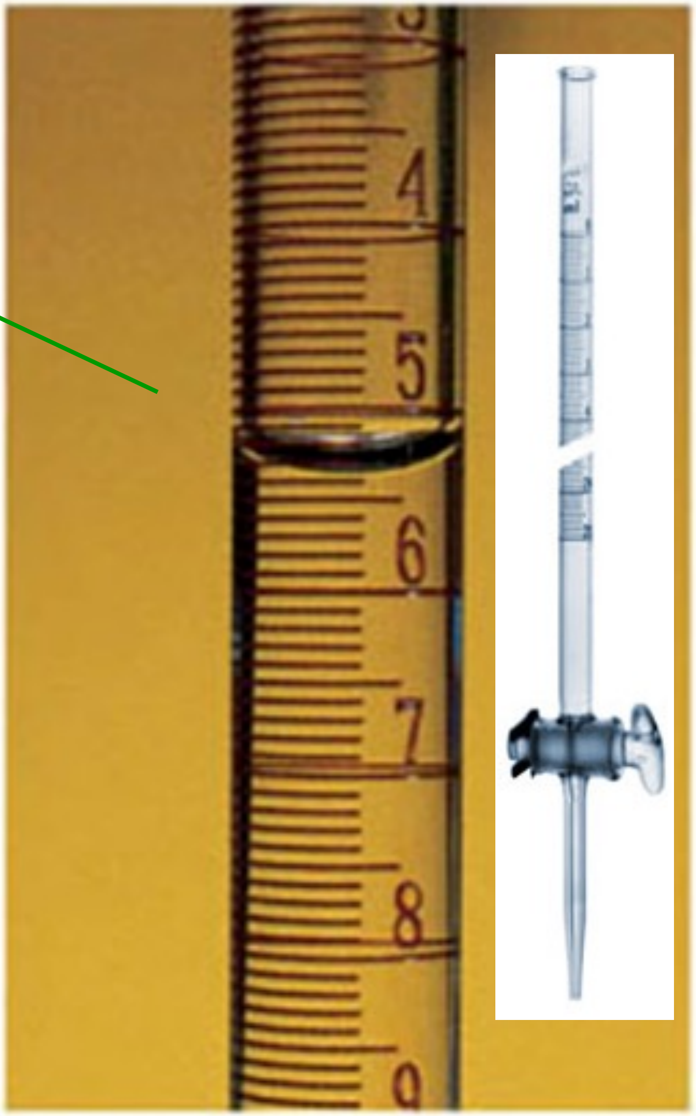


Burette filled with titrant

pH meter

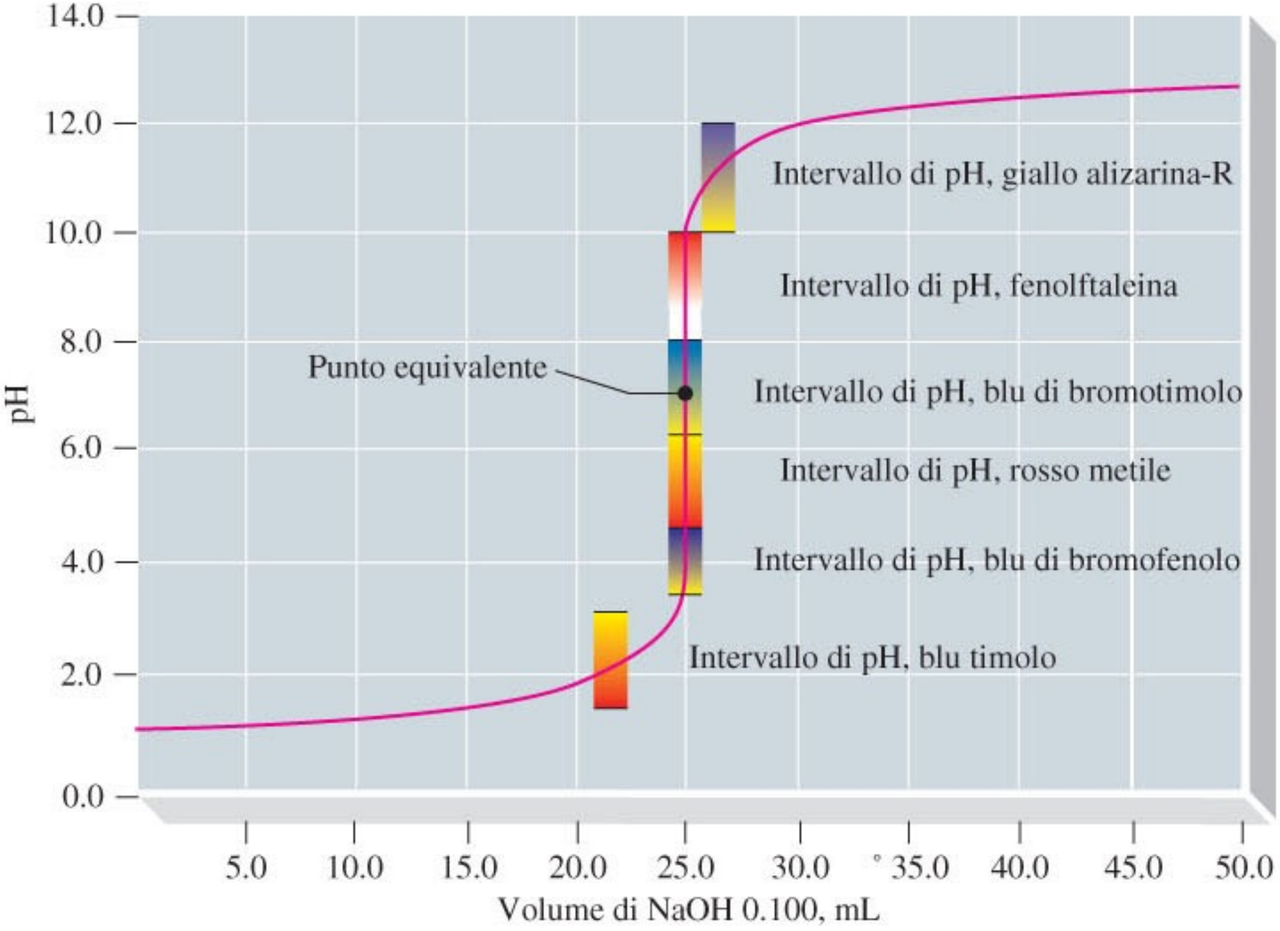
Soltion to be titrated + indicator

Magnetic stirrer



The volume of titrant must be masured accurately

An acid-base titration plot is a graph plotting the pH of an acid (or base) solution as a function of the volume of base (acid) added. The figure below shows the titration curve of 25ml of 0.1M HCl with 0.1M NaOH



The equivalence point of a titration is the point that corresponds to the addition of a stoichiometric amount of base (or acid). For an acid-base titration of strong electrolytes the equivalence point will be at pH=7.

Titration of a strong acid with a strong base

During titration the pH is calculated taking into account that the number of moles of base added neutralize the same number of moles of acid: the number of remaining moles of acid is divided by the total volume (which has increased compared to the initial value).

Initially we have a stron acid HA at concentration=c_A
pH = $-\log_{10}c_A$. If one adds the strong base B:
$HA\ (aq) + B\ (aq) \rightarrow BHA\ (aq) + H_2O\ (l)$

$$\boxed{\begin{aligned} n_A &= c_A \cdot V_{\text{initial}} \\ n_B &= c_B \cdot V_{\text{added}} \end{aligned}}$$

- as long as $n_A > n_B$

$$[H_3O^+] = \frac{n_A - n_B}{V_{iniziale} + V_{aggiunto}} = \frac{c_A \cdot V_{iniziale} - c_B \cdot V_{aggiunto}}{V_{iniziale} + V_{aggiunto}}$$

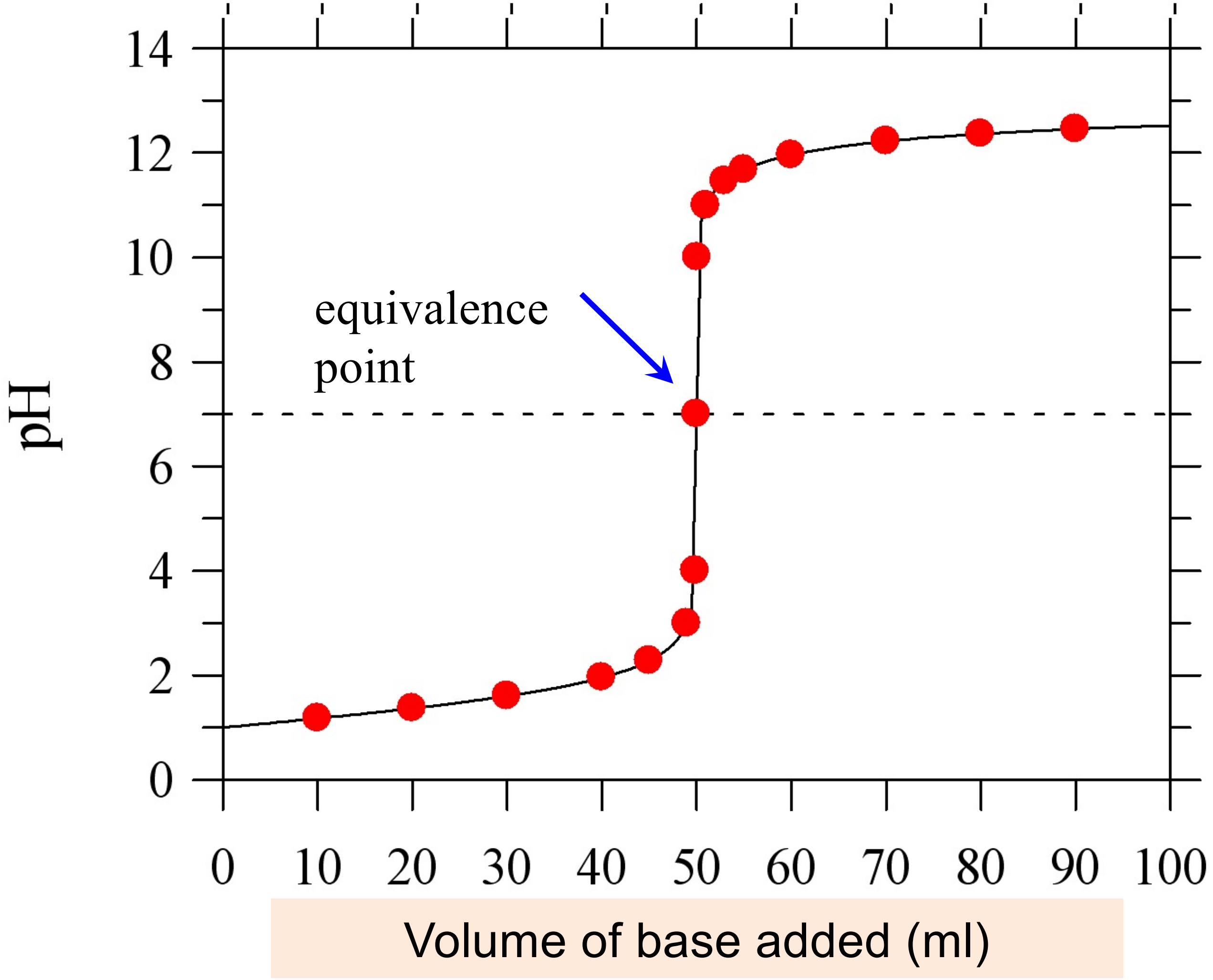
- when $n_A = n_B$, the base has completely neutralized the acid and pH = 7 (equivalence point)

- from that point on, adding further amounts of the base will cause: $n_A < n_B$

$$[OH^-] = \frac{n_B - n_A}{V_{iniziale} + V_{aggiunto}} = \frac{c_B \cdot V_{aggiunto} - c_A \cdot V_{iniziale}}{V_{iniziale} + V_{aggiunto}}$$

Titration of 50 ml di 0.1 M HCl with 0.1 M NaOH

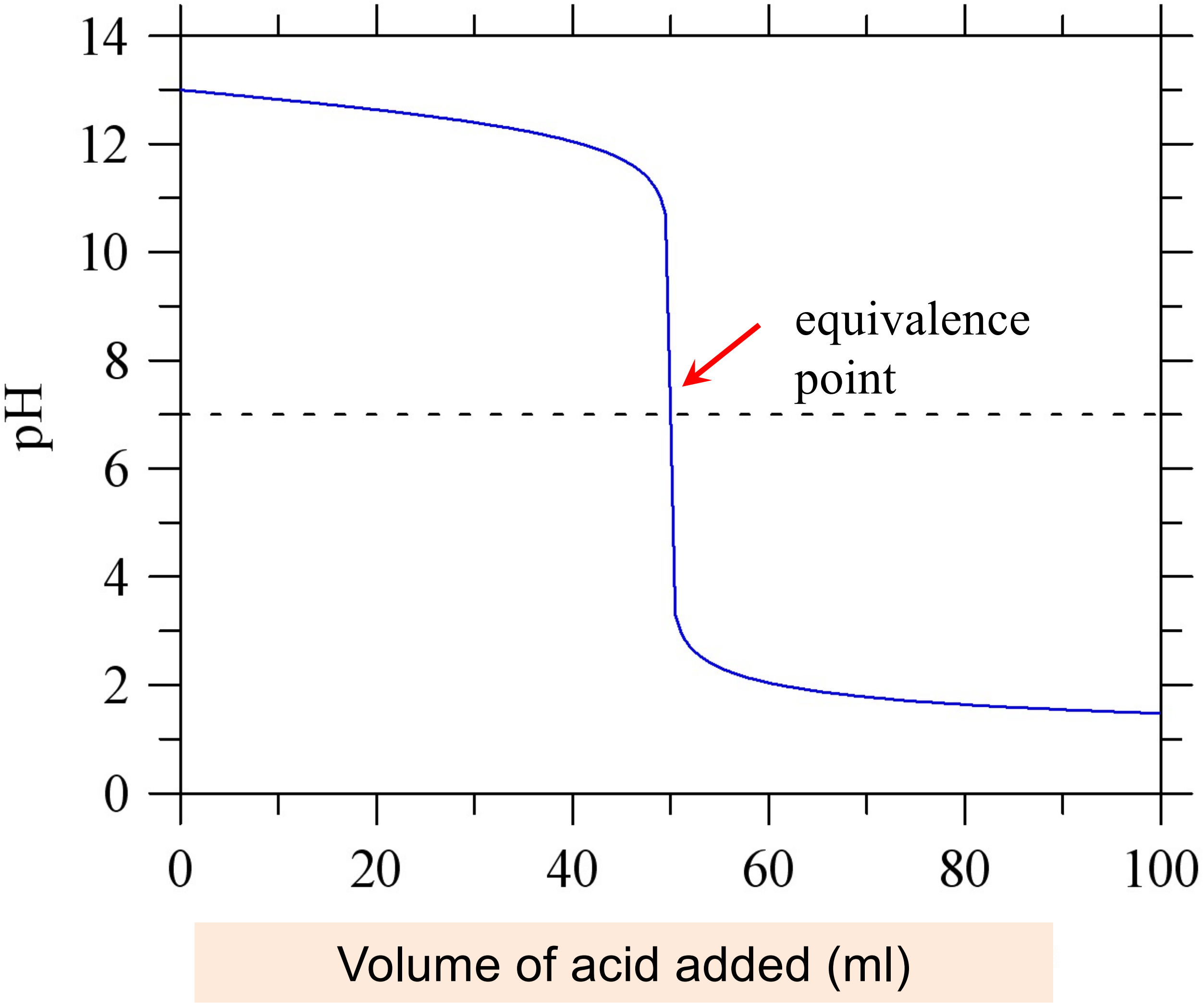
$\mathrm{HCl\ (aq) + NaOH\ (aq) \rightleftarrows NaCl\ (aq) + H_2O\ (l)}$



V (ml)	pH
0	1
10	1.1761
20	1.3680
30	1.6021
40	1.9542
45	2.2788
49	2.9956
49.9	3.9996
50	7.0000
50.1	9.9996
51	10.9957
53	11.4643
55	11.6778
60	11.9586
70	12.2218
80	12.3632
90	12.4559

Titration of 50 ml of 0.1 M NaOH con 0.1 M HCl

$\mathrm{NaOH\,(aq) + HCl\,(aq) \rightleftarrows NaCl\,(aq) + H_2O\,(l)}$



Problem: Calculate the pH of an aqueous soltion obtaine by mixing 40.0 g of NaOH (M = 40.0 g/mol) with 40.0 g of HBr (M = 80.9 g/mol) in a volume of solution of 1700 mL.

$$n_{NAOH} = \frac{40.0\ \text{g}}{40.0\ \text{g}/\text{mol}} = 1.0\ \text{mol} \qquad n_{NAOH} = \frac{40.0\ \text{g}}{80.9\ \text{g}/\text{mol}} = 0.49\ \text{mol}$$

Hydrobromic acid is present in a smaller quantity (0.49 moles), and will react completely to neutralize 0.49 moles of NaOH::

$$NaOH + HBr \rightarrow NaBr + H_2O$$

The number of moles of remaining NaOH will be:

$$n_{NaOH} = 1.0 - 0.49 = 0.51\ \text{mol}$$

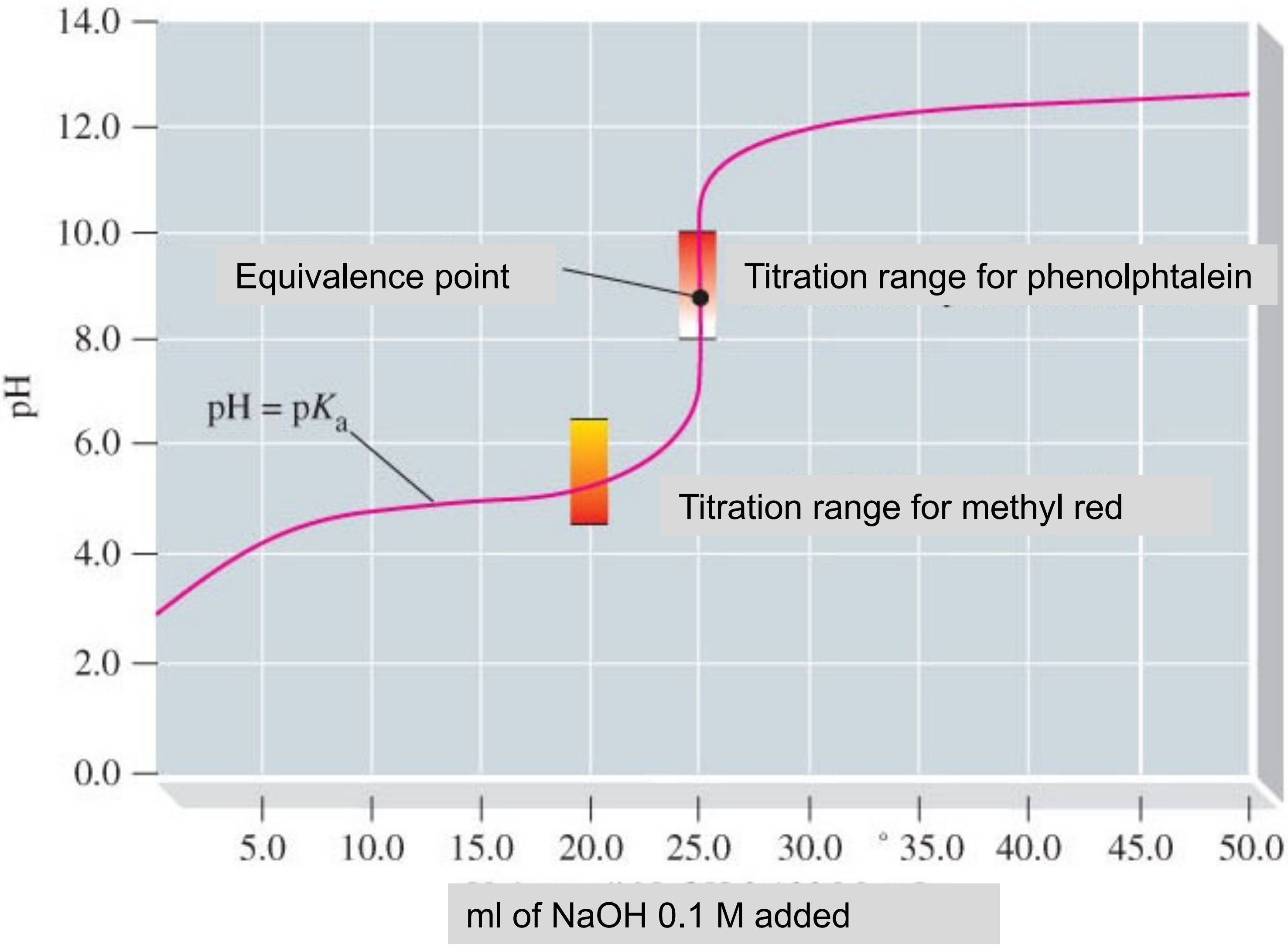
A concentration of: $c_{NAOH} = \frac{0.51\ \text{mol}}{1.7\ \text{L}} = 0.30\ \text{M}$

We will obtain a 0.30 M solution of NaOH. $[OH^-] = 0.30$ M, with

$pOH = -\log_{10} 0.30 = 0.52$ therefore $pH = 14 - 0.52 = 13.5$

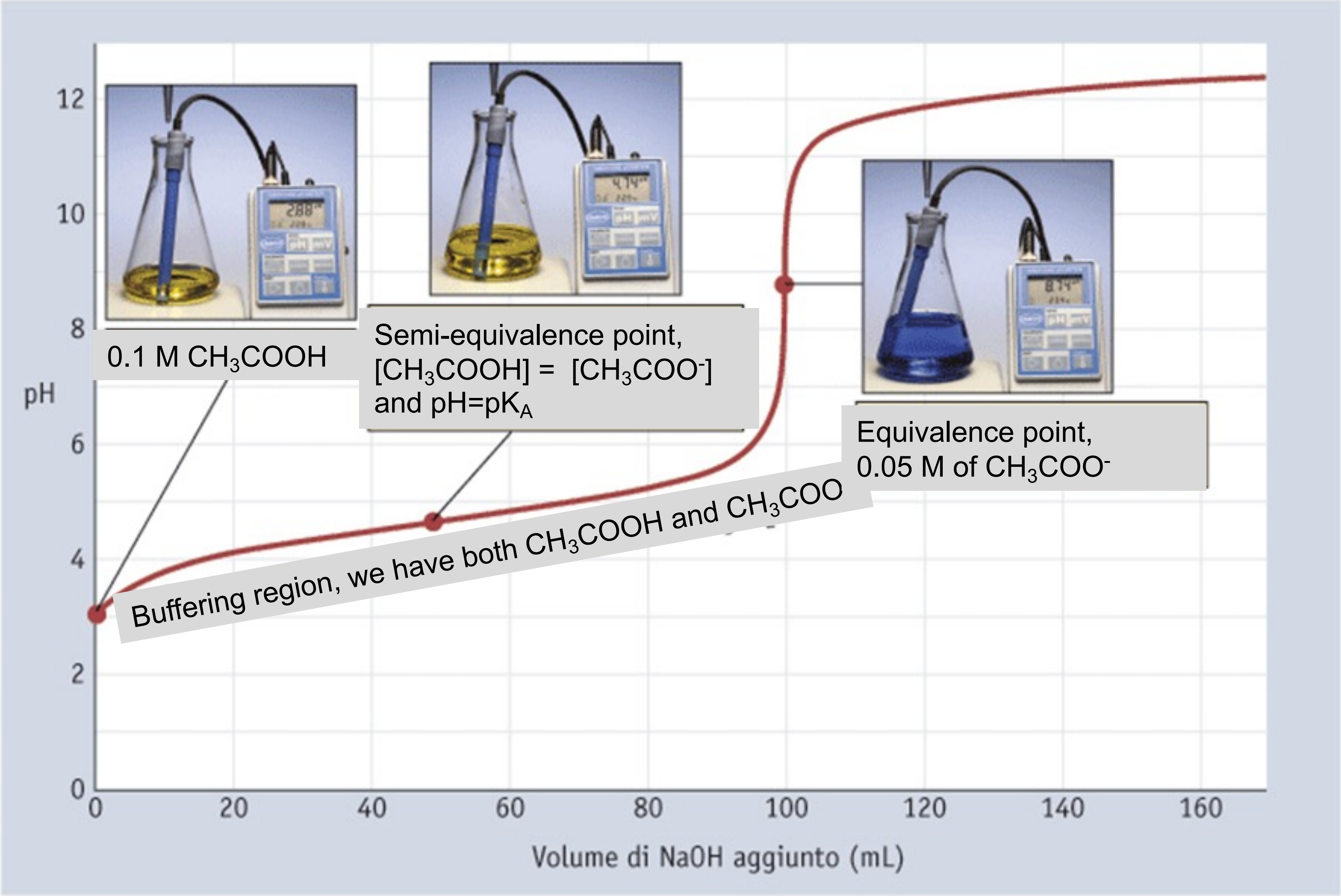
Titration of a weak acid with a strong base

The titration plot has a different shape. We report below the titration plot of 25ml of CH_3COOH 0.1M with NaOH 0.1M



Titration of a weak acid with a strong base

100 ml of acetic acid 0.1 M with NaOH 0.1 M.



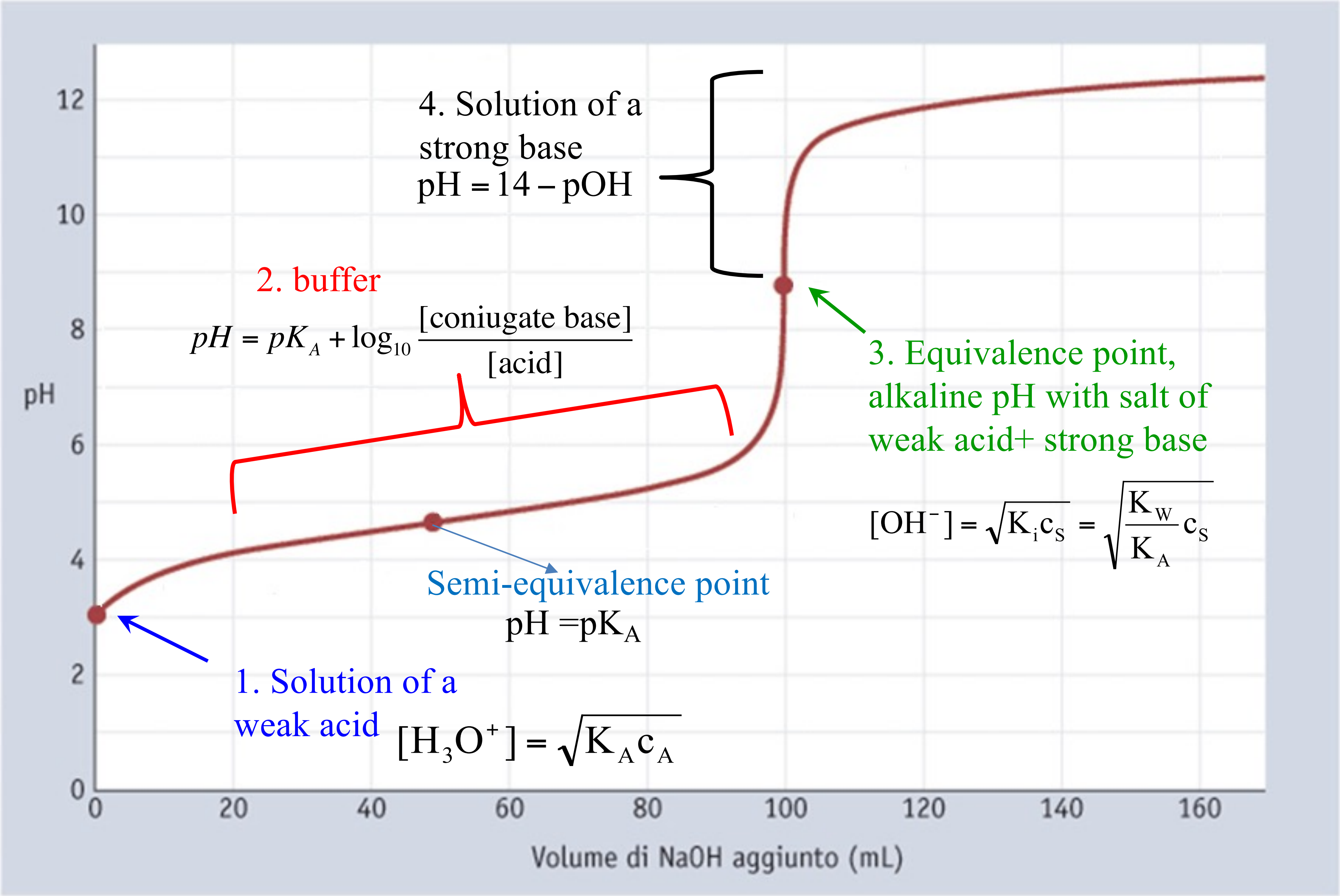
0.1 M CH_3COOH

Semi-equivalence point,
$[CH_3COOH] = [CH_3COO^-]$
and $pH=pK_A$

Equivalence point,
0.05 M of CH_3COO^-

Buffering region, we have both CH_3COOH and CH_3COO

The titration curve can be divided in four regions, where we calculate pH with different equations:



4. Solution of a strong base

$pH = 14 - pOH$

2. buffer

$$pH = pK_A + \log_{10}\frac{[\text{coniugate base}]}{[\text{acid}]}$$

3. Equivalence point, alkaline pH with salt of weak acid+ strong base

$$[OH^-] = \sqrt{K_i c_S} = \sqrt{\frac{K_W}{K_A} c_S}$$

Semi-equivalence point

$pH = pK_A$

1. Solution of a weak acid

$$[H_3O^+] = \sqrt{K_A c_A}$$

Titration of a weak acid ($pK_A = 4$) with a strong base in the presence of an indicator