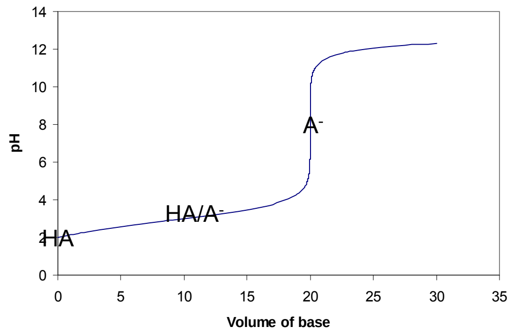
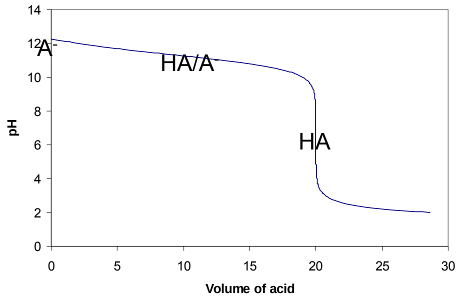
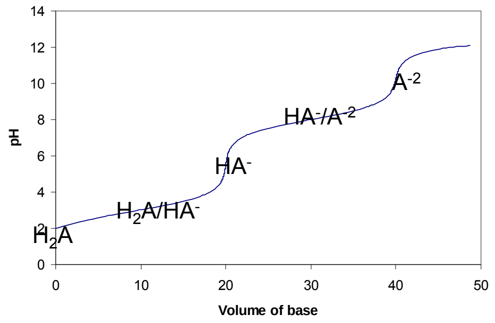
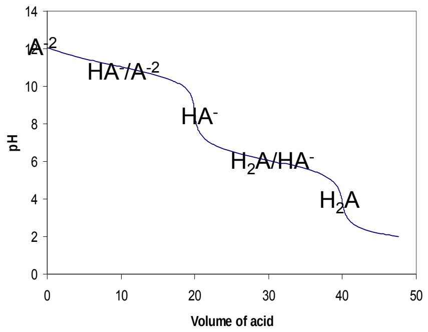
Acid – Base Titrations

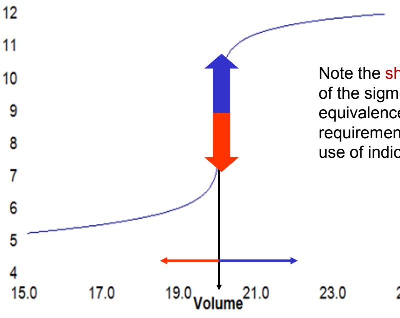








Perfect Acid-Base Indicator



Note the sharp rise/drop of the sigmoid at the equivalence point; requirement for the use of indicators.

Equivalence point

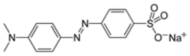
<u>Acid-base indicators</u>:

The materials used as indicators in acid- base titrations are, very weak organic acids or bases.

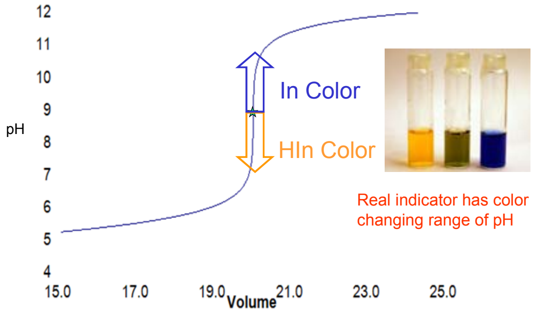
The conjugate pair of such compounds. exhibit different colors.

$HIn + H_2O \rightleftharpoons In^- + H_3O^+$ ⇔ pK_{HIn}
acid color — base color

$In + H_2O \rightleftharpoons InH^+ + HO^-$
base color — acid color



Perfect Acid-Base Indicator



Real indicator has color changing range of pH

Equivalence point

http://upload.wikimedia.org/wikipedia/commons/7/7d/Bromothymol_blue_colors.jpg

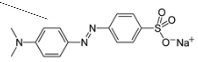
$$HIn + H_2O = In^- + H_3O^+$$

If HIn is in an acidic solution it exists mainly as Hin; color of Hin = acid color.

If HIn is in a basic solution, it exists mainly as In; color of In⁻ = base color.

Consider HIn case; $HIn + H_2O = In^- + H_3O^+$

$$K_{a,in} = \frac{[In^-][H^+]}{[HIn]};$$



$$[H^+] = K_{a,In}\frac{[HIn]}{[In^-]}$$

During the acid base titration [H⁺] changes, i.e. pH changes (low ↔ high); and the pH varies rapidly at the end point.

As the pH changes rapidly the quotient in the latter equation should change rapidly as well. Thus the ratio,

$$\frac{[HIn]}{[In^-]}$$

will change rapidly, giving a color change. It is a finite ratio.

For the human eye to detect a color change, the ratio $\frac{[HIn]}{[In^-]}$ must change by *<u>at least</u>* 100 times (up or down).

$$[H^+] = K_a\frac{[HIn]}{[In^-]}$$

∴ [H⁺] must change <u>at least</u> by 100 fold to detect a color change.

i.e. pH = (-log[H⁺]); must change by 2 at the eq. pt.

If ind. is in an acidic solution it exists mainly as Hin; color = acid color. (ratio =10, minimum)

If ind. is in a basic solution, it exists mainly as In; color = base color. (ratio = 0.1, minimum)

$$HIn + H_2O = In^- + H_3O^+$$

$$K_{HIn} = \frac{[In^-][H^+]}{[HIn]};$$

$$[H^+] = K_{HIn}\frac{[HIn]}{[In^-]}$$

$$pH = pK_{HIn} + \log\frac{[In^-]}{[HIn]}$$

pH (acidic) = pK_{HIn} + log(1/10) = $pK_{HIn} - 1$
pH (basic) = pK_{HIn} + log(10) = $pK_{HIn} + 1$

color change range = $pK_{HIn} \pm 1$ *pH range of indicator*.

This range can change with temperature, ionic strength, solvents, colloidal particles, etc.

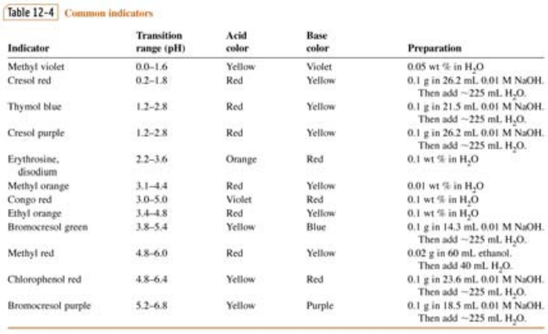


Table 12-4 Common indicators

Indicator	Transition range (pH)	Acid color	Base color	Preparation
Methyl violet	0.0–1.6	Yellow	Violet	0.05 wt % in H_2O
Cresol red	0.2–1.8	Red	Yellow	0.1 g in 26.2 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Thymol blue	1.2–2.8	Red	Yellow	0.1 g in 21.5 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Cresol purple	1.2–2.8	Red	Yellow	0.1 g in 26.2 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Erythrosine, disodium	2.2–3.6	Orange	Red	0.1 wt % in H_2O
Methyl orange	3.1–4.4	Red	Yellow	0.01 wt % in H_2O
Congo red	3.0–5.0	Violet	Red	0.1 wt % in H_2O
Ethyl orange	3.4–4.8	Red	Yellow	0.1 wt % in H_2O
Bromocresol green	3.8–5.4	Yellow	Blue	0.1 g in 14.3 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Methyl red	4.8–6.0	Red	Yellow	0.02 g in 60 mL ethanol. Then add 40 mL H_2O.
Chlorophenol red	4.8–6.4	Yellow	Red	0.1 g in 23.6 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Bromocresol purple	5.2–6.8	Yellow	Purple	0.1 g in 18.5 mL 0.01 M NaOH. Then add ~225 mL H_2O.

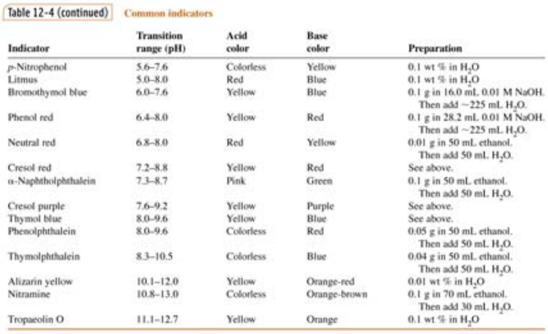
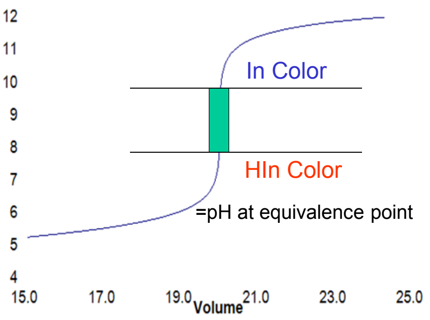


Table 12-4 (continued) Common indicators

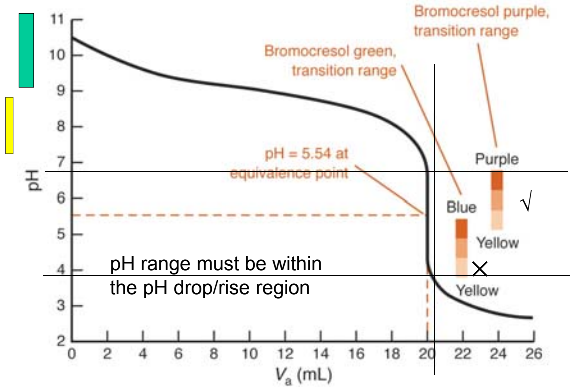
Indicator	Transition range (pH)	Acid color	Base color	Preparation
p-Nitrophenol	5.6–7.6	Colorless	Yellow	0.1 wt % in H_2O
Litmus	5.0–8.0	Red	Blue	0.1 wt % in H_2O
Bromothymol blue	6.0–7.6	Yellow	Blue	0.1 g in 16.0 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Phenol red	6.4–8.0	Yellow	Red	0.1 g in 28.2 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Neutral red	6.8–8.0	Red	Yellow	0.01 g in 50 mL ethanol. Then add 50 mL H_2O.
Cresol red	7.2–8.8	Yellow	Red	See above.
α-Naphtholphthalein	7.3–8.7	Pink	Green	0.1 g in 50 mL ethanol. Then add 50 mL H_2O.
Cresol purple	7.6–9.2	Yellow	Purple	See above.
Thymol blue	8.0–9.6	Yellow	Blue	See above.
Phenolphthalein	8.0–9.6	Colorless	Red	0.05 g in 50 mL ethanol. Then add 50 mL H_2O.
Thymolphthalein	8.3–10.5	Colorless	Blue	0.04 g in 50 mL ethanol. Then add 50 mL H_2O.
Alizarin yellow	10.1–12.0	Yellow	Orange-red	0.01 wt % in H_2O
Nitramine	10.8–13.0	Colorless	Orange-brown	0.1 g in 70 mL ethanol. Then add 30 mL H_2O.
Tropaeolin O	11.1–12.7	Yellow	Orange	0.1 wt % in H_2O

Ideal Acid-Base Indicator pK_{HIn}

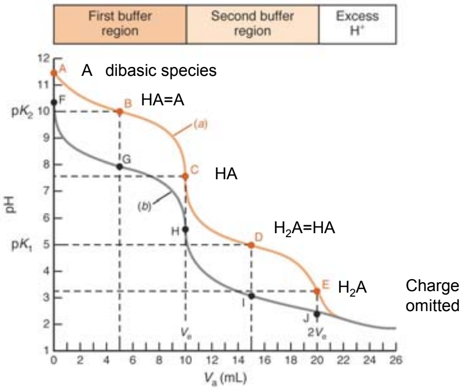


=pH at equivalence point

Equivalence point



pH range must be within the pH drop/rise region



A dibasic species

HA=A

HA

H_2A=HA

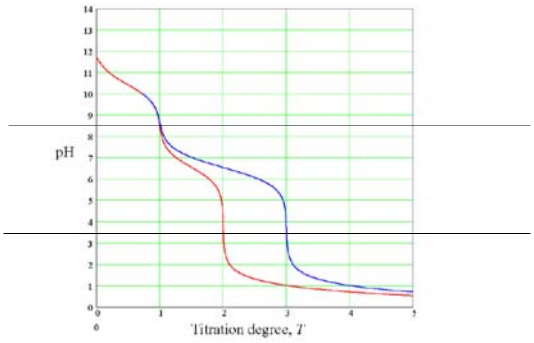
H_2A

Charge omitted

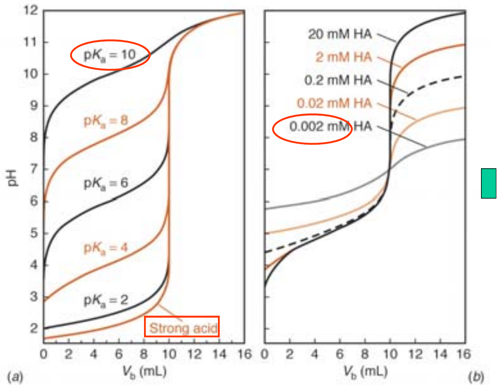
More basic site neutralized earlier in the reaction.

1. CO_3^{-2},0.1M

2. CO_3^{-2},0.1M + HCO_3^- ,0.1M



More basic site neutralized earlier



Stronger acid/base, higher concentrations ~ sharper end points

pK_1=2.85
pK_2=5.70

To get sharp
pH drops the
ΔpK ~ 3 or higher

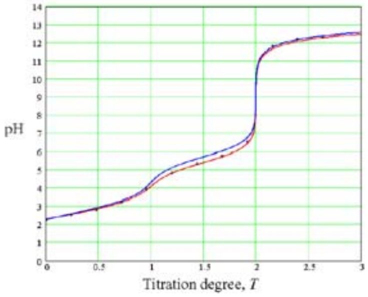


Figure 3. Titration of malonic acid with KOH: (a) without consideration of activity coefficients (blue curve), (b) with consideration of activity coefficients (red curve), and (c) experimental data (crosses).

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pK_1=3.13
pK_2=4.76
pK_3=6.40

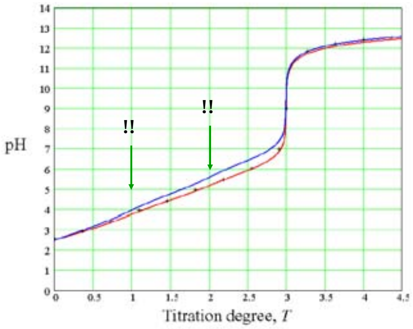

Figure 4. Titration of citric acid with KOH: (a) without consideration of activity coefficients (blue curve), (b) with consideration of activity coefficients (red curve), and (c) experimental data (crosses).

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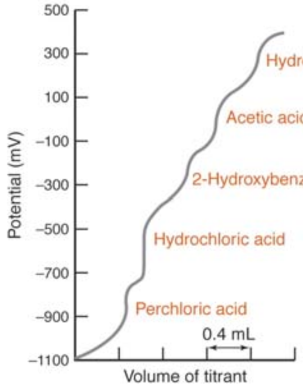
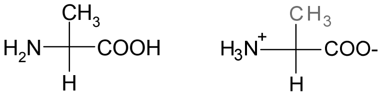


Titrating mixtures of acids

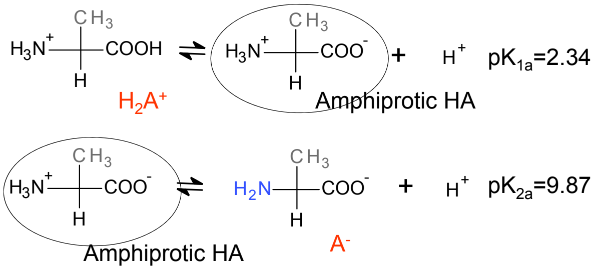
Potential proportional to pH

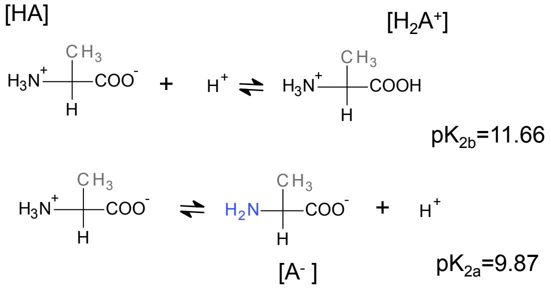
Amino acids:

Note: the '3' species



Zwitterion
electrically neutral





$$H_3N^+\text{–}CH(CH_3)\text{–}COO^- + H^+ \rightleftharpoons H_3N^+\text{–}CH(CH_3)\text{–}COOH \qquad pK_{2b}=11.66$$

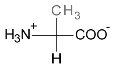
$$H_3N^+\text{–}CH(CH_3)\text{–}COO^- \rightleftharpoons H_2N\text{–}CH(CH_3)\text{–}COO^- + H^+ \qquad pK_{2a}=9.87$$

amphiprotic

$\boxed{[H_2A^+] \neq [A^-]}$

Isoionic point (pH): pH of pure neutral amino acid (neutral zwitterion) in aqueous solution.

A solution of **pure amino acid (HA**) is amphiprotic. The pH of such an amphiprotic species of formal concentration **F** is given by;

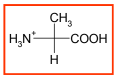


$$H_3N^+\text{–}CH(CH_3)\text{–}COO^-$$

$$[H^+] = \sqrt{\frac{K_{1a}K_{2a}F + K_{1a}K_w}{K_{1a} + F}}$$

Note: $[H_2A^+] \neq [A^-]$, in general; with $[H^+]$ from above eq. they can be calculated using the pK_a values of H_2A^+.

Note: no approximations here!!



$$H_3N^+\text{–}CH(CH_3)\text{–}COOH$$

Equations for the calculation of pH at Isoionic point:

$$H_2A^+ = HA + H^+ \qquad K_{a1}$$

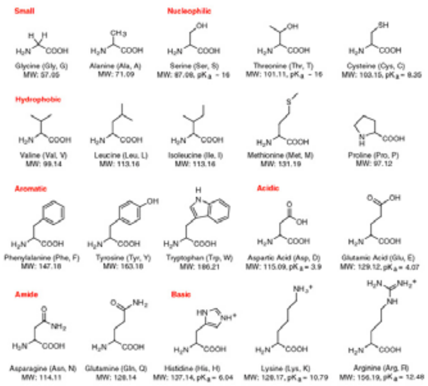
$$H_2A^+ = A^- + 2H^+ \qquad K_{a1}K_{a2}$$

$$H_2O = OH^- + H^+ \qquad K_w$$

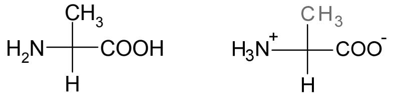
MB: $C_{HA} = [H_2A^+] + [HA] + [A^-]$

CB $[H^+] + [H_2A^+] = [OH^-] + [A^-]$ ←

Amino acids:

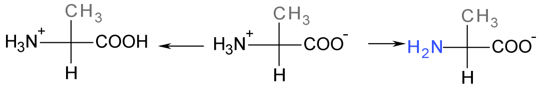


Amino acids:



$$H_2N\text{–}CH(CH_3)\text{–}COOH \qquad H_3N^+\text{–}CH(CH_3)\text{–}COO^-$$

Zwitterion
electrically neutral species with charged centers



$$H_3N^+\text{–}CH(CH_3)\text{–}COOH \leftarrow H_3N^+\text{–}CH(CH_3)\text{–}COO^- \rightarrow H_2N\text{–}CH(CH_3)\text{–}COO^-$$

Isoelectric point (pH): pH at which average charge of the polyprotic acid is zero.

i.e. $[H_2A^+] = [A^-]$, because zwitterion/amphiprotic species is neutral.

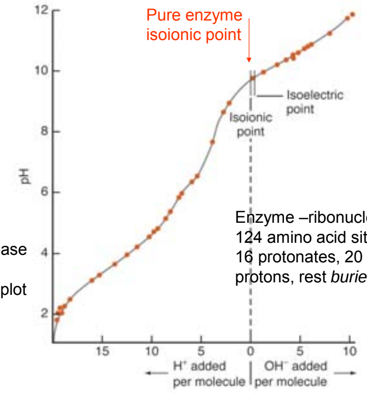
Eg. For alanine of 0.10M (isotonic, pure alanine);

$[H_2A^+]= 1.68\times10^{-5}$, $[A^-]= 1.76\times10^{-5}$

So, needed to add a little acid to the 0.10 M solution of pure alanine to bring to the isoelectric point.

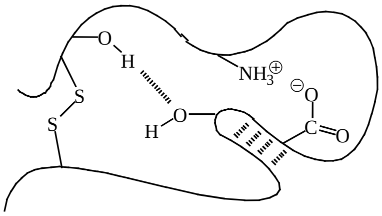
Calculation of Isoelectric point of an amino acid:

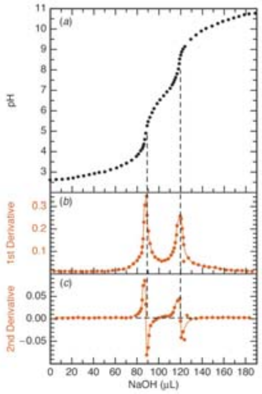
$$[H_2A^+] = \frac{[HA][H^+]}{K_{1a}}$$



Titratable acid/base groups and pK caclulated from plot

Enzyme –ribonuclease
124 amino acid sites
16 protonates, 20 ‘accessible’ protons, rest *buried.*

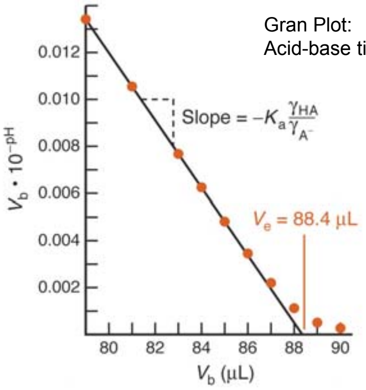




pH curve

1st Derivative

2nd Derivative



Gran Plot:
Acid-base titrations