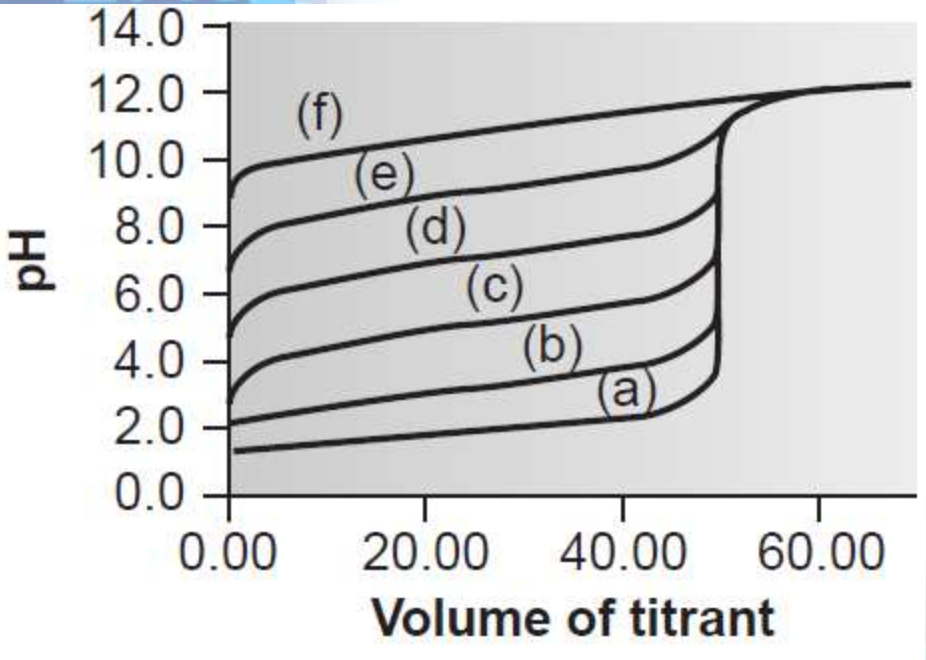
Analytical chemistry

Lecture № 16

ACID–BASE TITRATIONS PART II

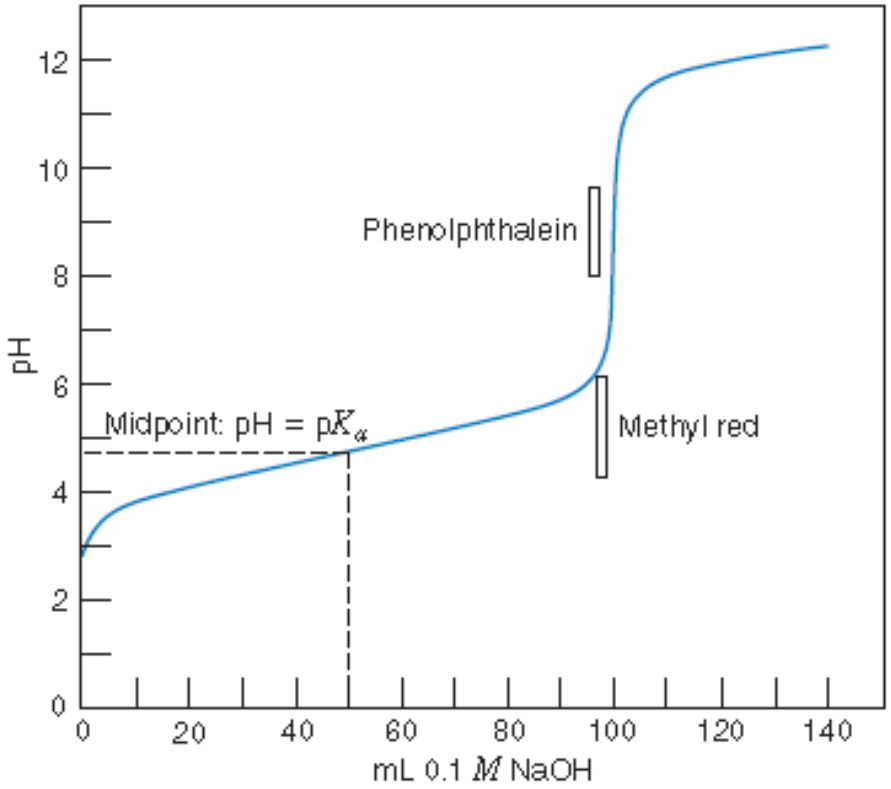
Neutralization Titration Curve of a Weak Acid with a Strong Base

The principal limitation to using a titration curve to locate the equivalence point is that an inflection point must be present. Sometimes, however, an inflection point may be missing or difficult to detect. Consider the influence of the acid dissociation constant, K_a, *on the titration curve for a weak* acid with a strong base titrant. The inflection point is visible, even if barely so, for acid dissociation constants larger than 10^{-9}, but is missing when K_a *is* 10^{-11}.



Titration curves for 50.00 mL of 0.100 M weak acid with 0.100 M strong base. The pK_a *of the weak acids are (a) 1, (b) 3, (c) 5,* (d) 7, (e) 9, (f) 11.

Titration Curves for Weak Acids



Titration curve for 100mL 0.1 *M HOAc versus 0.1 M* NaOH. Note that the equivalence point pH *is 8.73.*

The pH at the equivalence point is indeed located in basic medium. Its value depends on the *pKa value;*

$$HOAc + Na^+ + OH^- \rightarrow H_2O + Na^+ + OAc^-$$

- before the equivalence point, the reaction vessel contains the buffer constituted by the mixture of the remaining acid HA and of its conjugate form OAc^- resulting from the titration reaction. The pH value can be calculated from Henderson's relation:

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

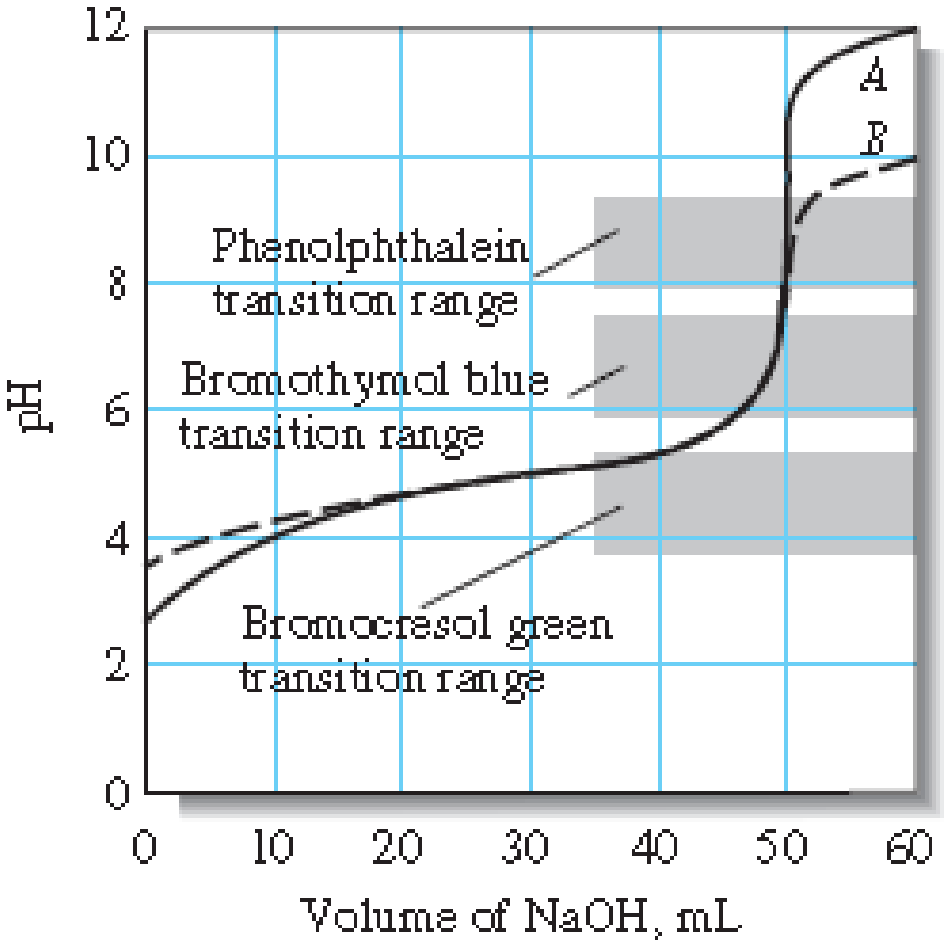
$$pH = pK_a + \log[CV/(C_0V_0 - CV)],$$

- at the equivalence point, all of the acid exists in its conjugate basic form OAc^-.

$$[A^-] = C_0V_0/(V_0 + V_{ep}).$$

$$pH_{ep} = 1/2\ pK_w + 1/2\ pK_a + 1/2 \log[C_0V_0/(V_0 + V_{ep})],$$

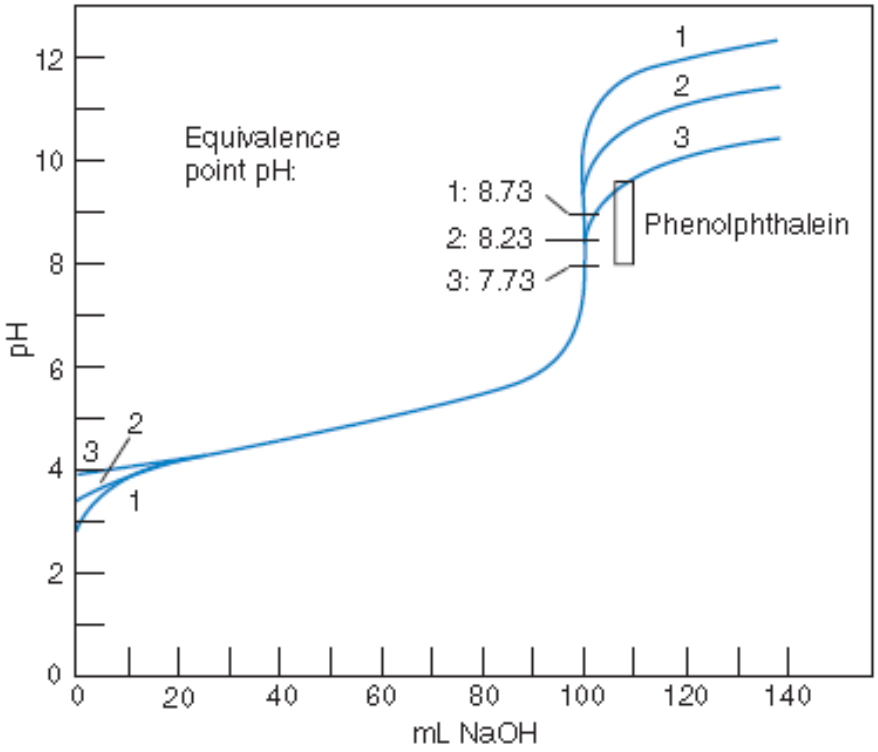
- after the equivalence point, two bases remain: OH− and A−. The latter, which is a weak base, is of little importance with respect to the former because of the repression of the ionization of the weak base by the strong base OH−.



Curve for the titration of acetic acid with sodium hydroxide. Curve A: 0.1000 M acid with 0.1000 M base. Curve B: 0.001000 M acid with 0.001000 M base.

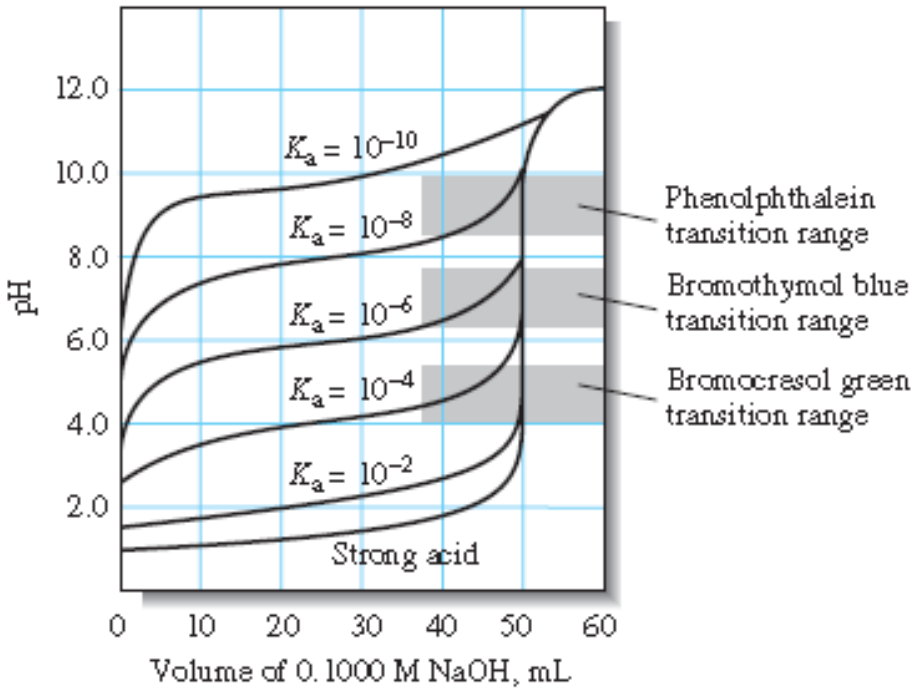
the initial pH values are higher and the equivalence-point pH is lower for the more dilute solution (Curve *B).*
At intermediate titrant volumes, however, the pH values differ only slightly because of the buffering action of the acetic acid/sodium acetate system that is present in this region.

bromocresol green is totally unsuited for titration of 0.1000 M acetic acid. Bromothymol blue does not work either because its full color change occurs over a range of titrant volume from about 47 mL to 50 mL of 0.1000 M base. On the other hand, an indicator exhibiting a color change in the basic region, such as phenolphthalein, provides a sharp end point with a minimal titration error.



Curve 1: 0.1 *M HOAc and 0.1 M* NaOH.
Curve 2: 0.01 *M HOAc and 0.01 M NaOH.*
Curve 3: 0.001 *M HOAc and 0.001 M NaOH.*

Obviously, phenolphthalein could not be used as an indicator for solutions as dilute as 10^{-3} *M (curve 3). Note that the equivalence point pH decreases as the weak* acid system becomes more dilute



The effect of acid strength (dissociation constant) on titration curves.

Generally, for titrations at significant concentrations (ca. 0.1 *M), acids with Ka values as low as* 10^{-6} *can be titrated accurately with a visual* indicator.

We see that

• each acid has its own curve. Since titration conditions are identical from one acid to the next, their different behavior is necessarily due to their difference in strength (pK_a);

• the pH-change intervals at the equivalence point are not identical. The change is weaker with the weaker acid;

• for all acids, the equivalence point is located in basic medium. Its accurate pH value depends on the acid. The weaker the acid is, the higher the pH value will be at the equivalence point;

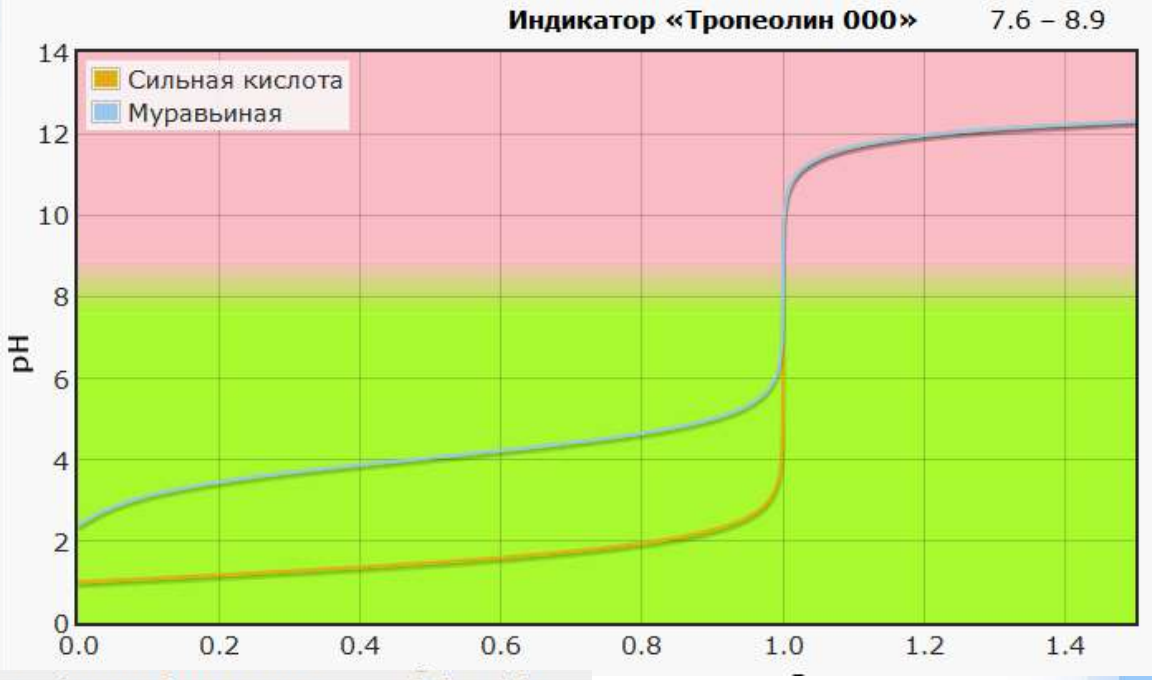
• after the equivalence point, the curves can be superimposed;

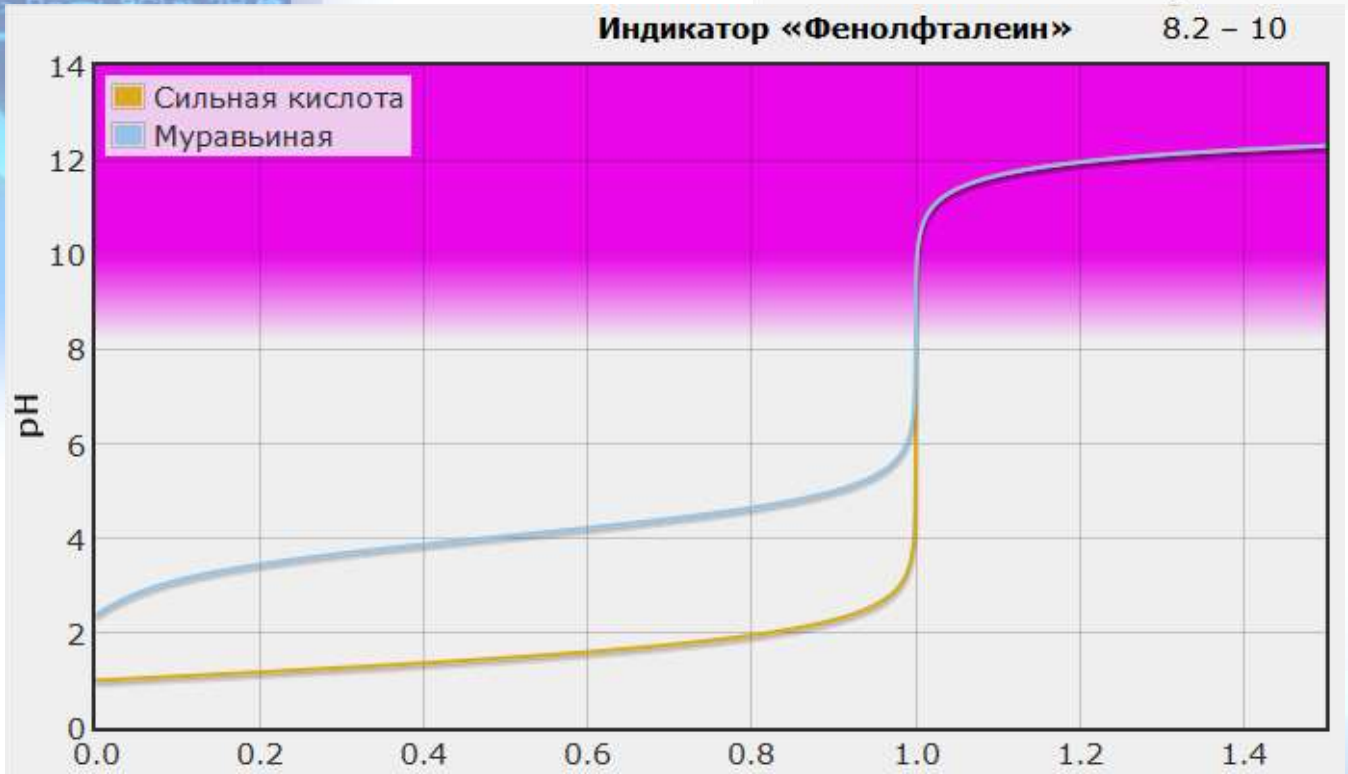
• the identical part of curves, located after the equivalence point, can be superimposed onto that obtained in the titration of a strong acid by a strong base under the same conditions of concentration and volume;

• before the equivalence point, the curves exhibit an S shape with an inflection point. This one is located at the half-neutralization, for which it appears that pH = pK_a.

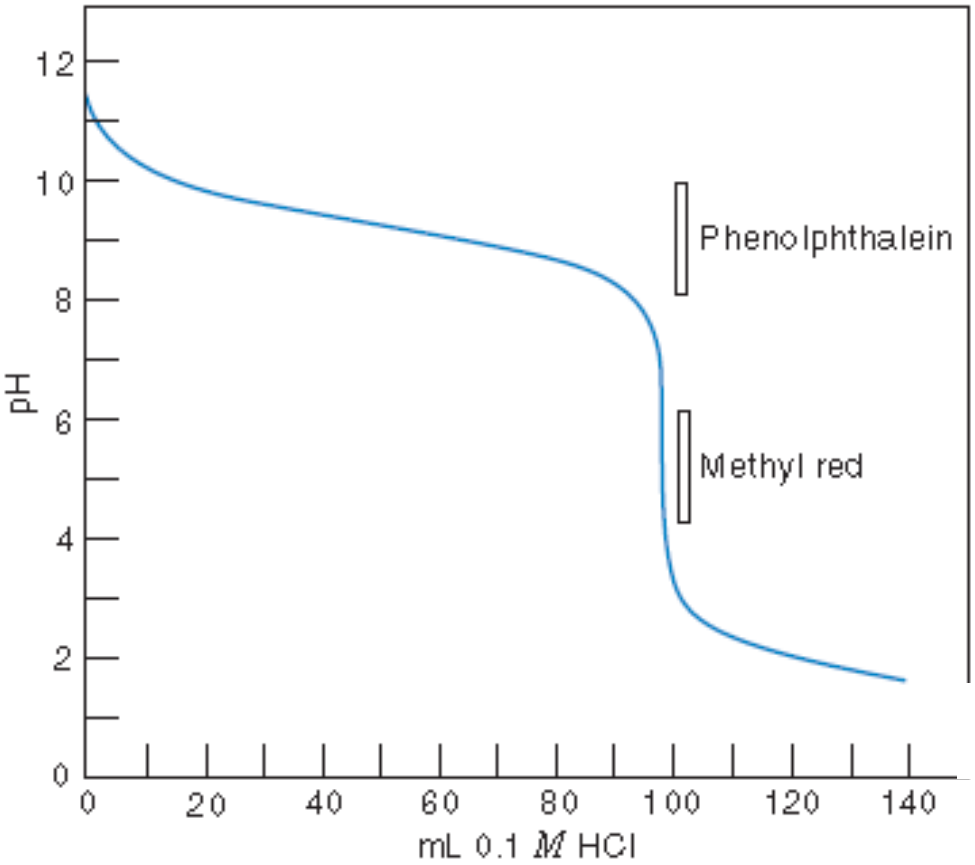
Practical Conclusions: Choice of the Indicator

We must use indicators whose color-change interval is located in basic pH values. Their choice depends on the *pK_a value of the acid. For example, for the titration of* acetic acid in the above conditions, pH=8.7 at the equivalence point. Using phenolphthalein, thymolphthalein, and thymol blue is satisfactory. For the second acid (*pK_a 7.00), pH = 9.9 at the equivalence point, only thymolphthalein is satisfactory.* (Recall that in this second example, the color-change interval is narrower than in the first one—see the curve's shape). For very weak acids (*pK_a > 7), no simple indicator* can be used. Only some mixtures of judiciously chosen indicators can be used. This is due to the fact that the pH change at the equivalence point is very weak.


Индикатор «Тропеолин 000» 7.6 – 8.9
Сильная кислота
Муравьиная
pH
0
2
4
6
8
10
12
14
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4


Индикатор «Фенолфталеин» 8.2 – 10
Сильная кислота
Муравьиная
pH
0
2
4
6
8
10
12
14
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

Titration of a Weak Base with a Strong Acid



Titration curve for 100mL 0.1 *M* NH_3 *versus 0.1 M* HCl.

The indicator for the titration must have a transition range within about pH 4 to 7. Methyl red meets this requirement. If phenolphthalein had been used as the indicator, it would have gradually lost its color between pH 10 and 8, before the equivalence point was reached.

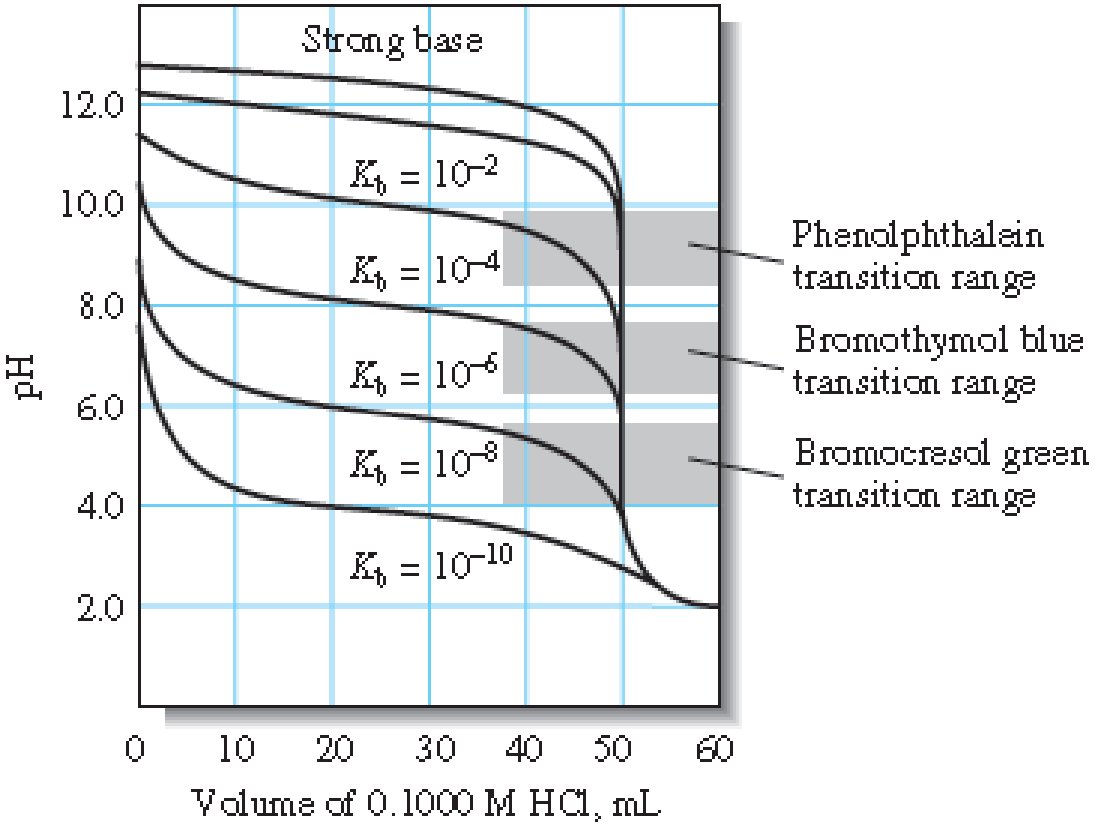
$$NH_3 + H^+ + Cl^- \rightarrow NH_4^+ + Cl^-$$

$$B + H_3O^+ \rightarrow BH^+ + H_2O$$

- before the equivalence point, the buffer BH+/B is present. This explains the S shape of the curve and the long flat portion about the half-neutralization;
- at exactly the equivalence point, the solution in the titration vessel is that of the weak acid BH+. Therefore, the pH value can be calculated by the relation

$$pH_{eq} = 1/2\ pK_a - 1/2 \log \left[C_0 V_0/(V_0 + V_{eq})\right]$$

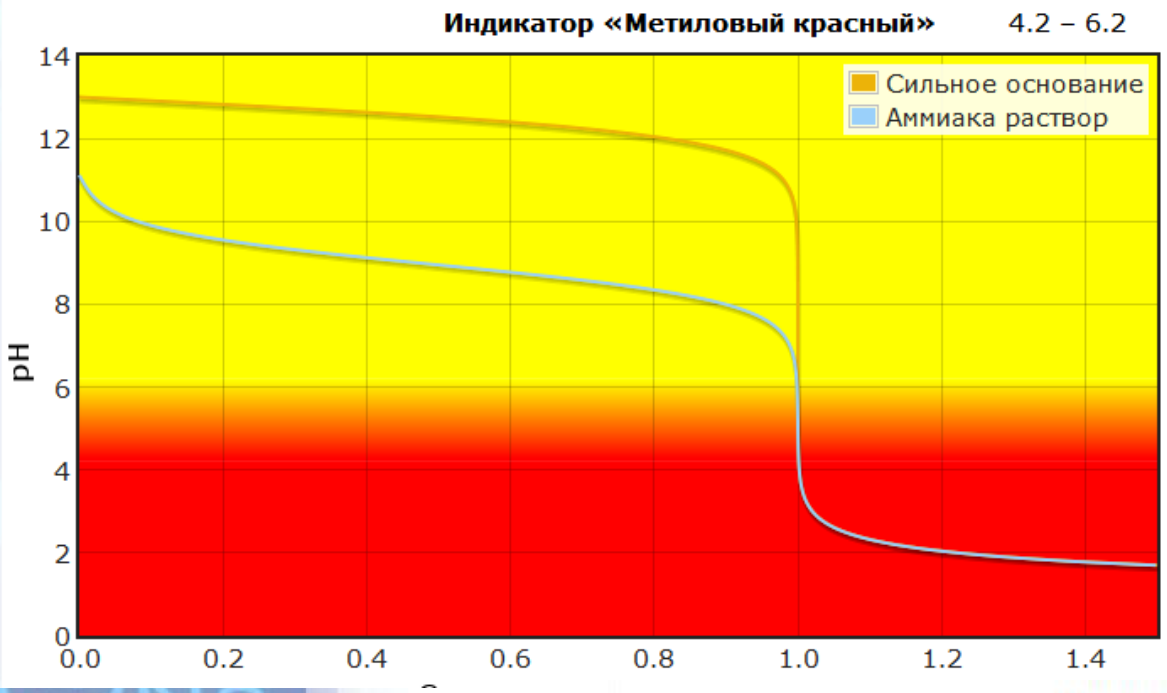
- beyond the equivalence point, the solution contains an excess of hydroxonium ions and the weak acid BH^+. Hydroxonium ions predominate due to the ionization repression of the weak acid.

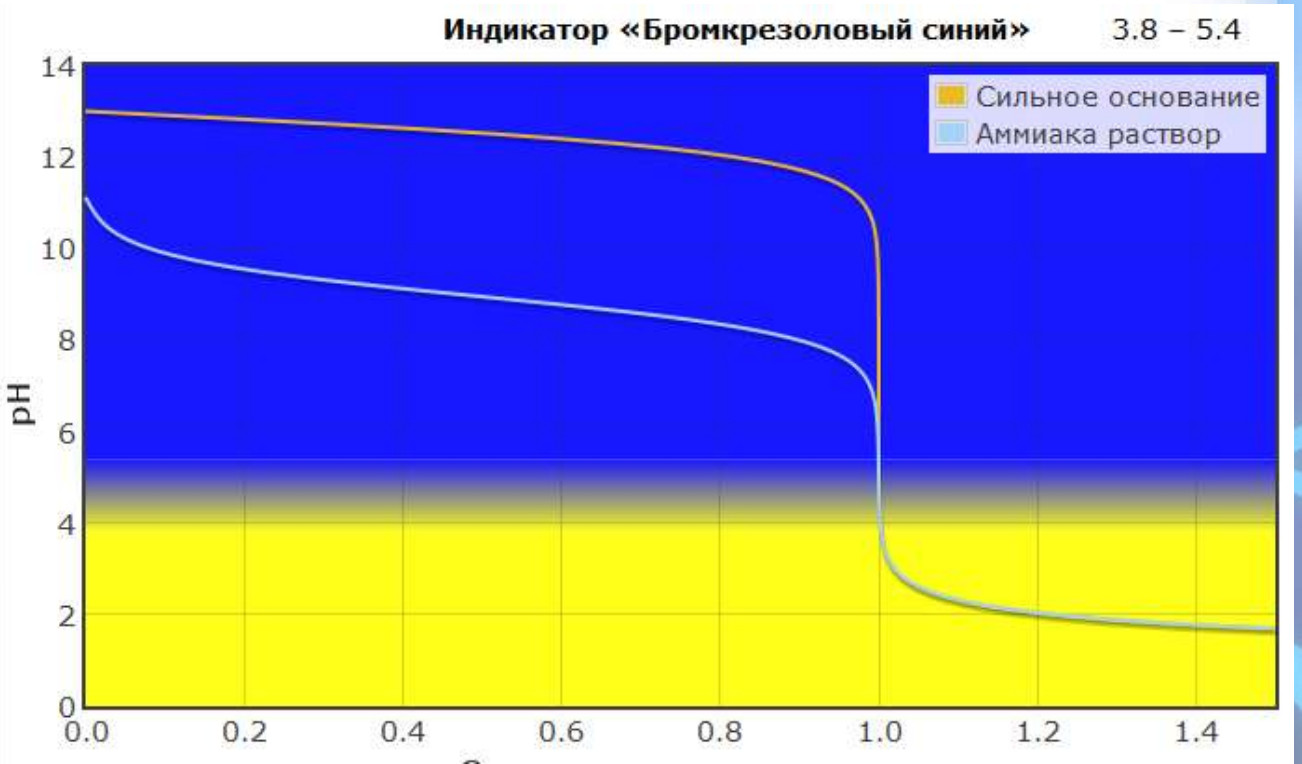


In titrations involving significant concentrations (ca. 0.1 M), one can accurately titrate a base with a K_b *of* 10^{-6} *using a visual indicator.*

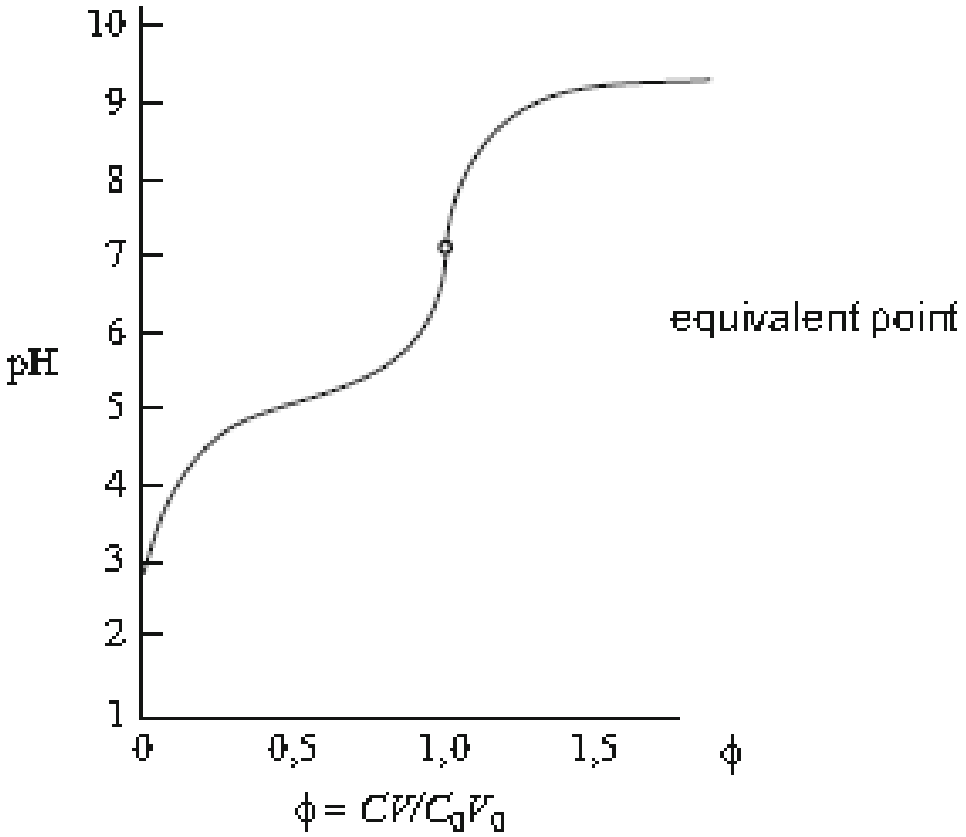
The effect of base strength (K_b) *on titration curves.*

When you titrate a weak base, use an indicator with a mostly acidic transition range. When titrating a weak acid, use an indicator with a mostly basic transition range.


Индикатор «Метиловый красный» 4.2 – 6.2
Сильное основание
Аммиака раствор
pH
0
2
4
6
8
10
12
14
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4


Индикатор «Бромкрезоловый синий» 3.8 – 5.4
Сильное основание
Аммиака раствор
pH
0
2
4
6
8
10
12
14
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

Titration of a Weak Acid with a Weak Base



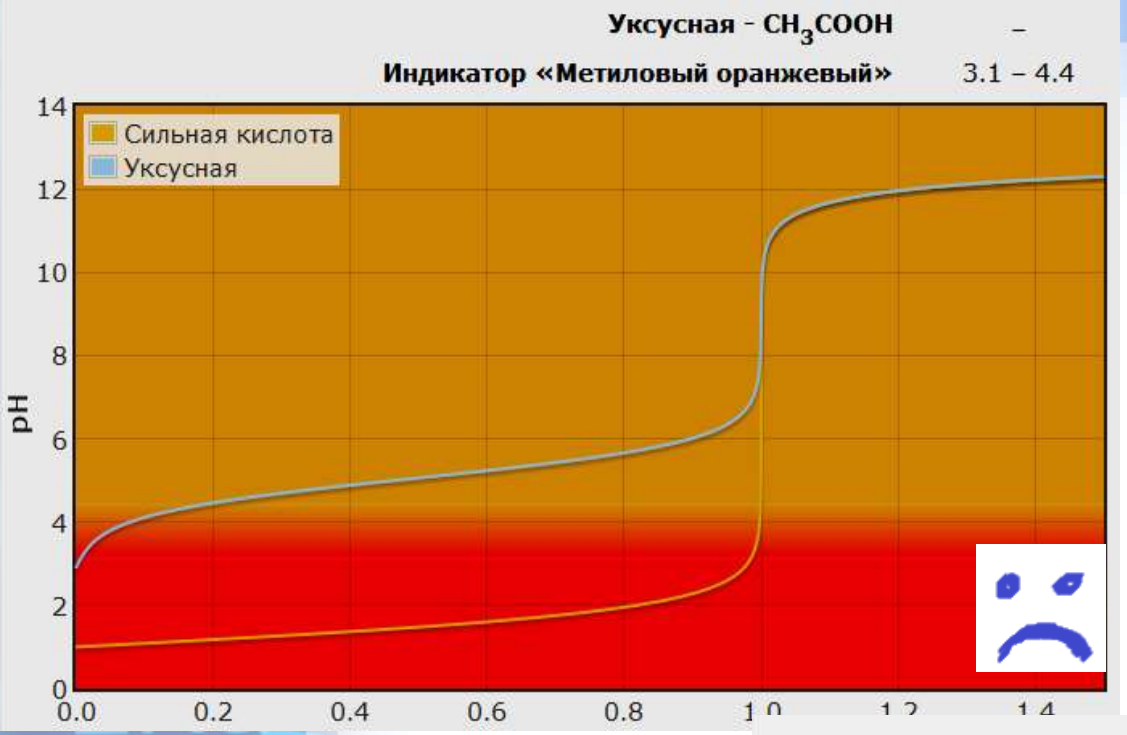
Titration curve of 0.1 mol/L acetic acid with 0.1 mol/L ammonia

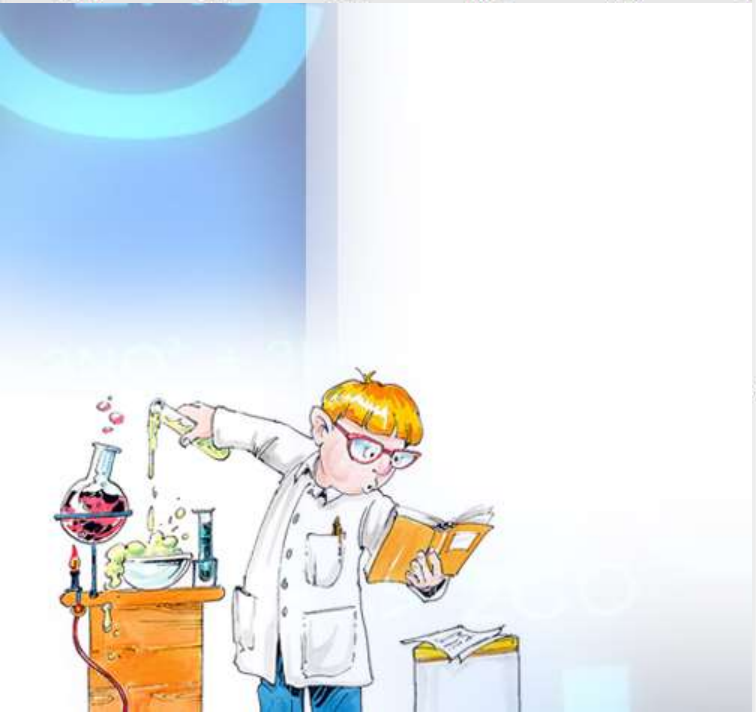
pH-metric detection of the equivalence point

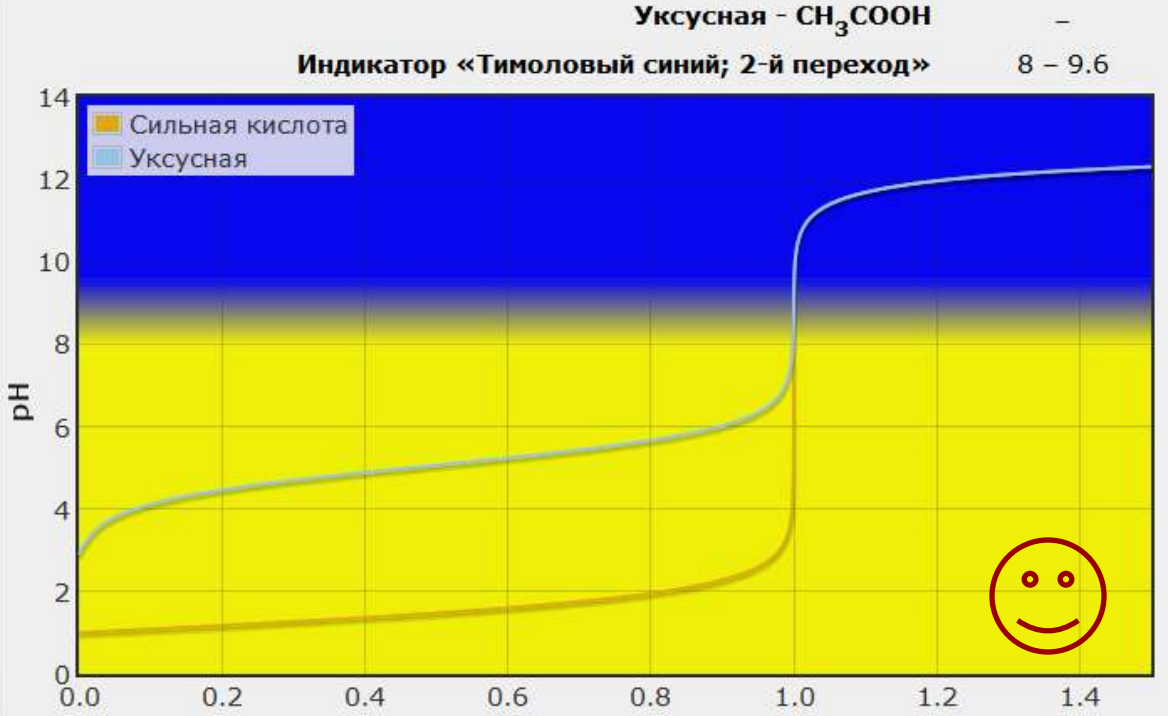
$$\text{acid}_1 + \text{base}_2 \rightleftharpoons \text{base}_1 + \text{acid}_2.$$

These titrations are seldom practiced because of the pH change near the equivalence point, which is very gradual. There is no sudden pH change . Because of this, the titration error may be high with neutralization indicators. They do not exhibit a sharp endpoint.

If it is the ratio K_{a1}/K_{a2} higher than 10^5 *that the titration's success.*

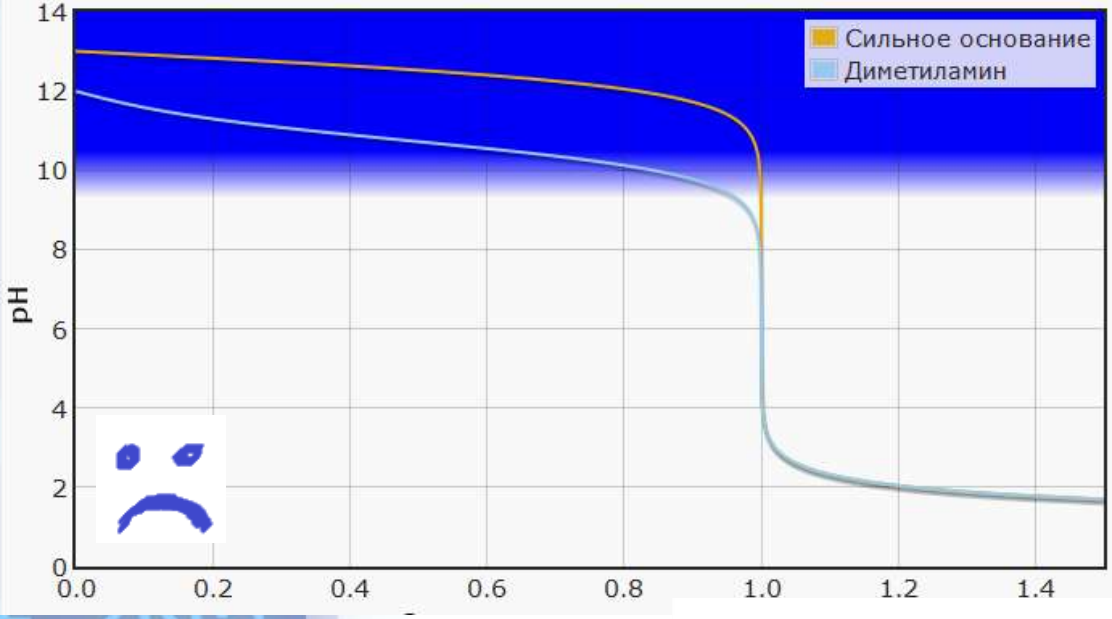

Уксусная - CH_3COOH
Индикатор «Метиловый оранжевый» 3.1 – 4.4
Сильная кислота
Уксусная
pH
0
2
4
6
8
10
12
14
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4




Уксусная - CH_3COOH
Индикатор «Тимоловый синий; 2-й переход» 8 – 9.6
Сильная кислота
Уксусная
pH
0
2
4
6
8
10
12
14
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

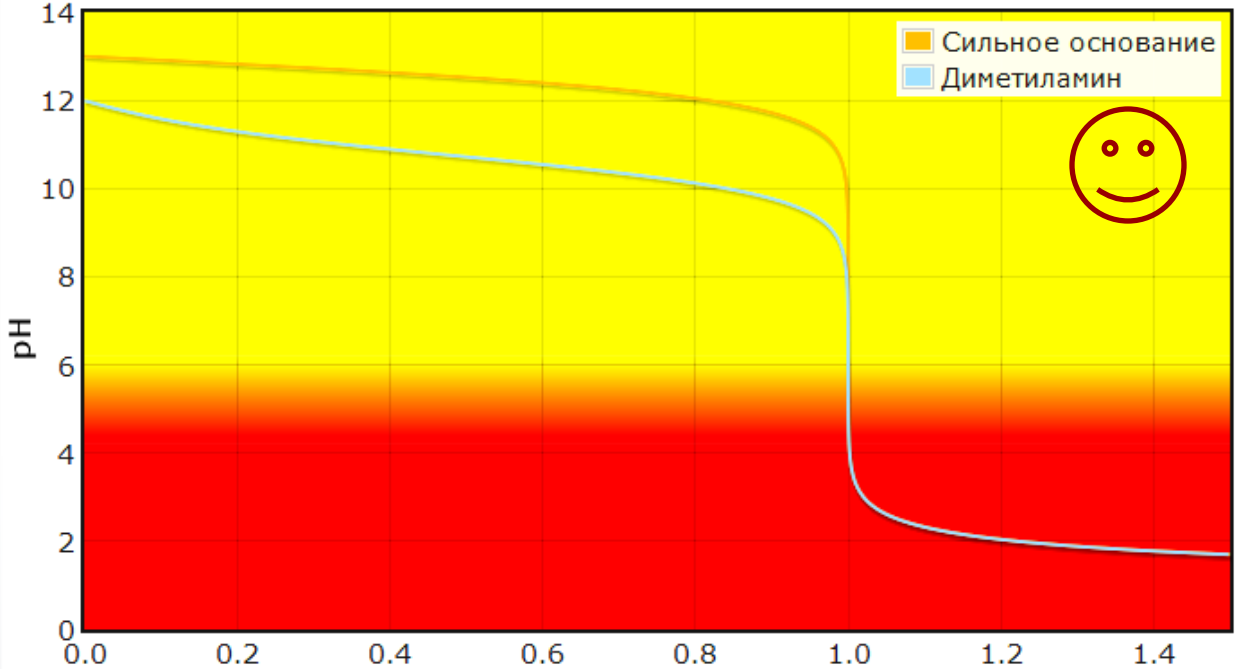
Диметиламин - $(CH_3)_2NH+H_2O$ –

Индикатор «Тимолфталеин» 9.3 – 10.5



Диметиламин - $(CH_3)_2NH+H_2O$ –

Индикатор «Метиловый красный» 4.2 – 6.2

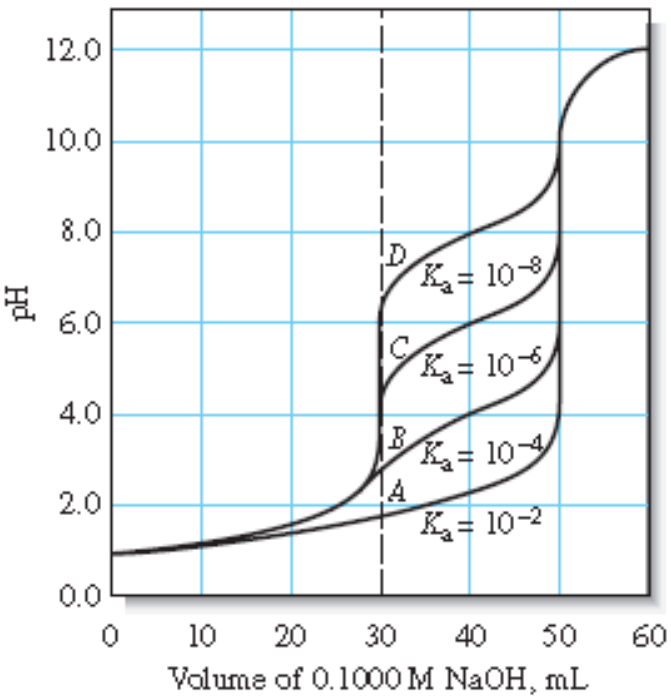


Complex Acid/Base Systems

We define **complex systems** as solutions made up of (1) two acids or two bases of different strengths, (2) an acid or a base that has two or more acidic or basic functional groups, or (3) an amphiprotic substance, which is capable of acting as both an acid and a base.

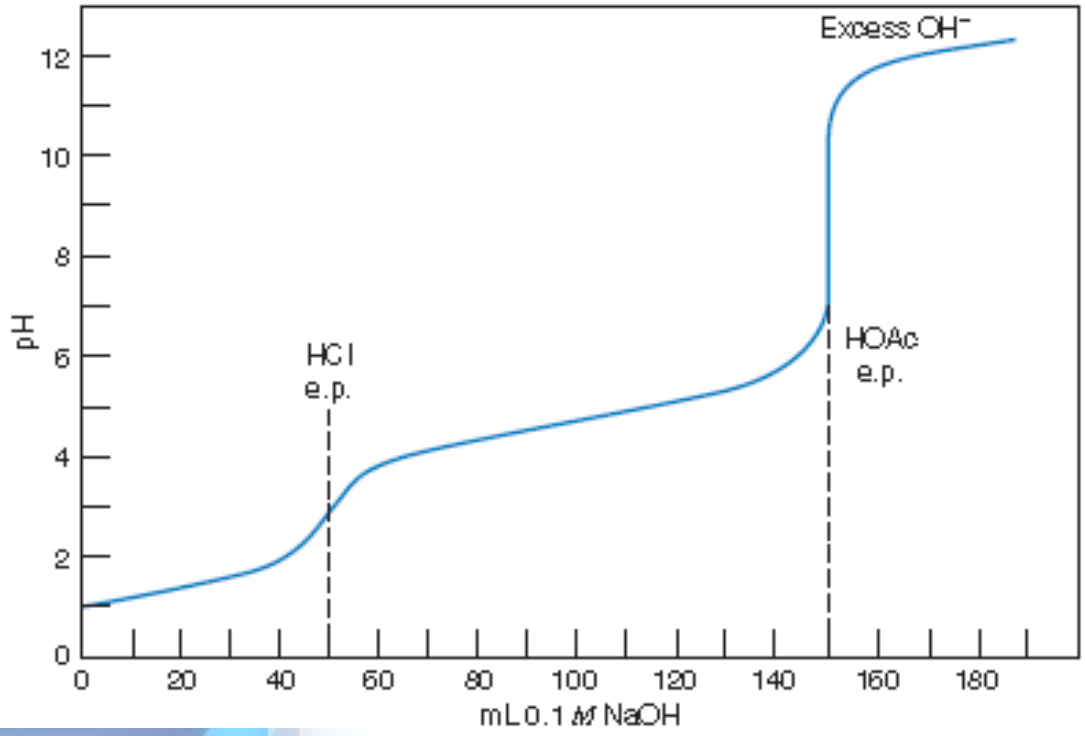
Mixtures of Strong and Weak Acids or Strong and Weak Bases

The composition of a mixture of a strong acid and a weak acid can be determined by titration with suitable indicators if the weak acid has a dissociation constant that lies between 10^{-4} and 10^{-8} and the concentrations of the two acids are of the same order of magnitude.



pH changes that occur during the titration of mixtures containing hydrochloric acid and several weak acids with different dissociation constants. Note that the rise in pH at the first equivalence point is small or essentially nonexistent when the weak acid has a relatively large dissociation constant (curves A and B). For titrations such as these, only the total number of millimoles of weak and strong acid can be determined accurately. Conversely, when the weak acid has a very small dissociation constant, only the strong acid content can be determined. For weak acids of intermediate strength there are usually two useful end points.

Curves for the titration of strong/weak acid mixtures with 0.1000 M NaOH. Each titration curve is for 25.00 mL of a solution that is 0.1200 M in HCl and 0.0800 M in the weak acid HA.



The stronger acid will titrate first and will give a pH break at its equivalence point. This will be followed by titration of the weaker acid and a pH break at its equivalence point.

Titration curve for 50mL of mixture of 0.1 *M HCl and 0.2 M HOAc with 0.1 M NaOH.*

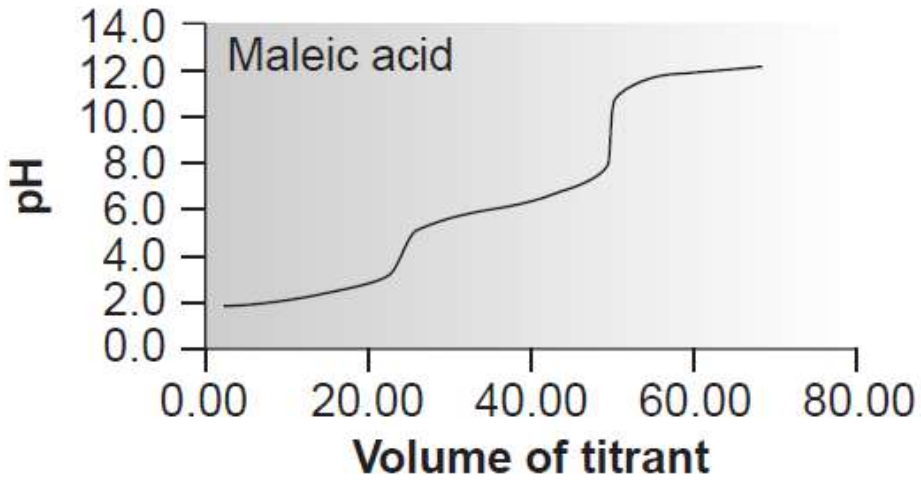
At the equivalence point for HCl, a solution of HOAc and NaCl remains, and so the equivalence point is acidic. Beyond the equivalence point, the OAc−/*HOAc buffer region is established, and this* markedly suppresses the pH break for HCl, leading to only a small pH change in the equivalence point of HCl, compared to when HCl is titrated in the absence of HOAc. The remainder of the titration curve is identical to the titration of HOAc.

If two strong acids are titrated together, there will be no differentiation between them, and only one equivalence point break will occur, corresponding to the titration of both acids. The same is true for two weak acids if their K_a *values are not* too different. For example, a mixture of acetic acid, $K_a = 1.75 \times 10^{-5}$, *and propionic* acid, $K_a = 1.3 \times 10^{-5}$, *would titrate together to give a single equivalence point.*

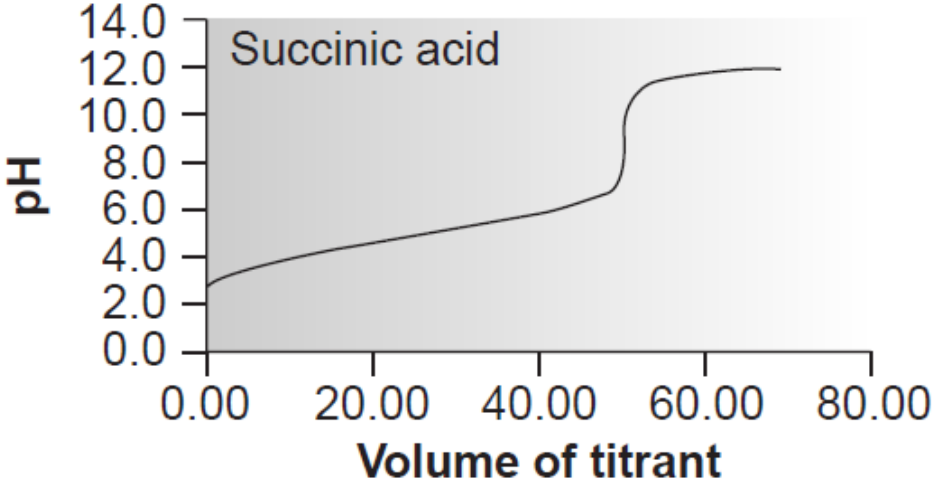
The construction of titration curves for mixtures of bases is analogous to that for mixtures of acids.

Polyfunctional Acids and Bases

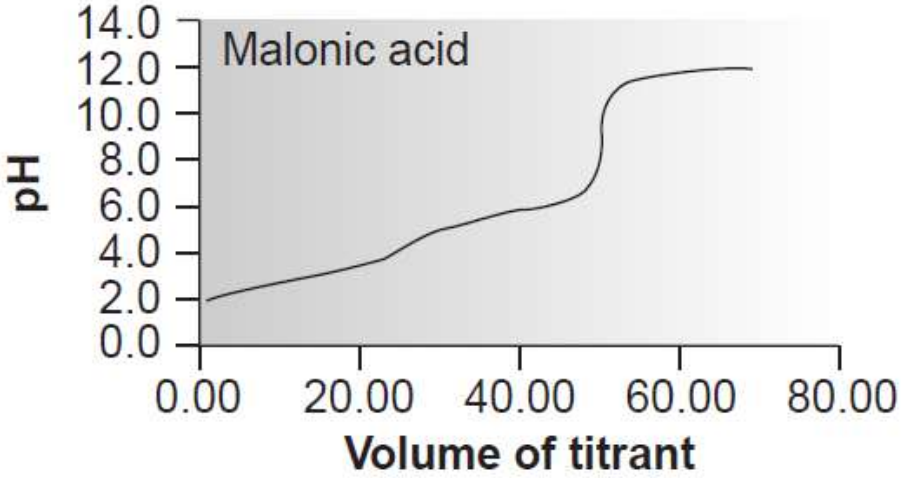
There are several species of interest in analytical chemistry that have two or more acidic or basic functional groups. These species are said to exhibit polyfunctional acidic or basic behavior. Generally, with a polyfunctional acid such as phosphoric acid (H_3PO_4), the protonated species (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}) differ enough in their dissociation constants that they exhibit multiple end points in a neutralization titration.



(a)



(c)



(b)

Titration curves for (a) maleic acid, pK_{a1}=*1.91,* pK_{a2}=*6.33; (b)malonic acid,* pK_{a1}=*2.85,* pK_{a2}=*5.70; (c) succinic acid,*pK_{a1}=*4.21,* pK_{a2}=*5.64. Titration curves are* for 50.00 mL of 0.0500 M acid with 0.100 M strong base. Equivalence points for all three titrations occur at 25.00 and 50.00 mL of titrant.

$$H_2A(aq) + OH^-(aq) \rightarrow HA^-(aq) + H_2O(\ell)$$

$$HA^-(aq) + OH^-(aq) \rightarrow A^{2-}(aq) + H_2O(\ell)$$

Two distinct inflection points are seen if reaction 1 is essentially complete before reaction 2 begins.

In general, separate inflection points are seen when successive acid dissociation constants differ by a factor of at least 500 (a Dp*Ka of at least 2.7).*

$pK_a = 1,25$ $\Delta pK_a = 3,02$ $pK_a = 4,27$

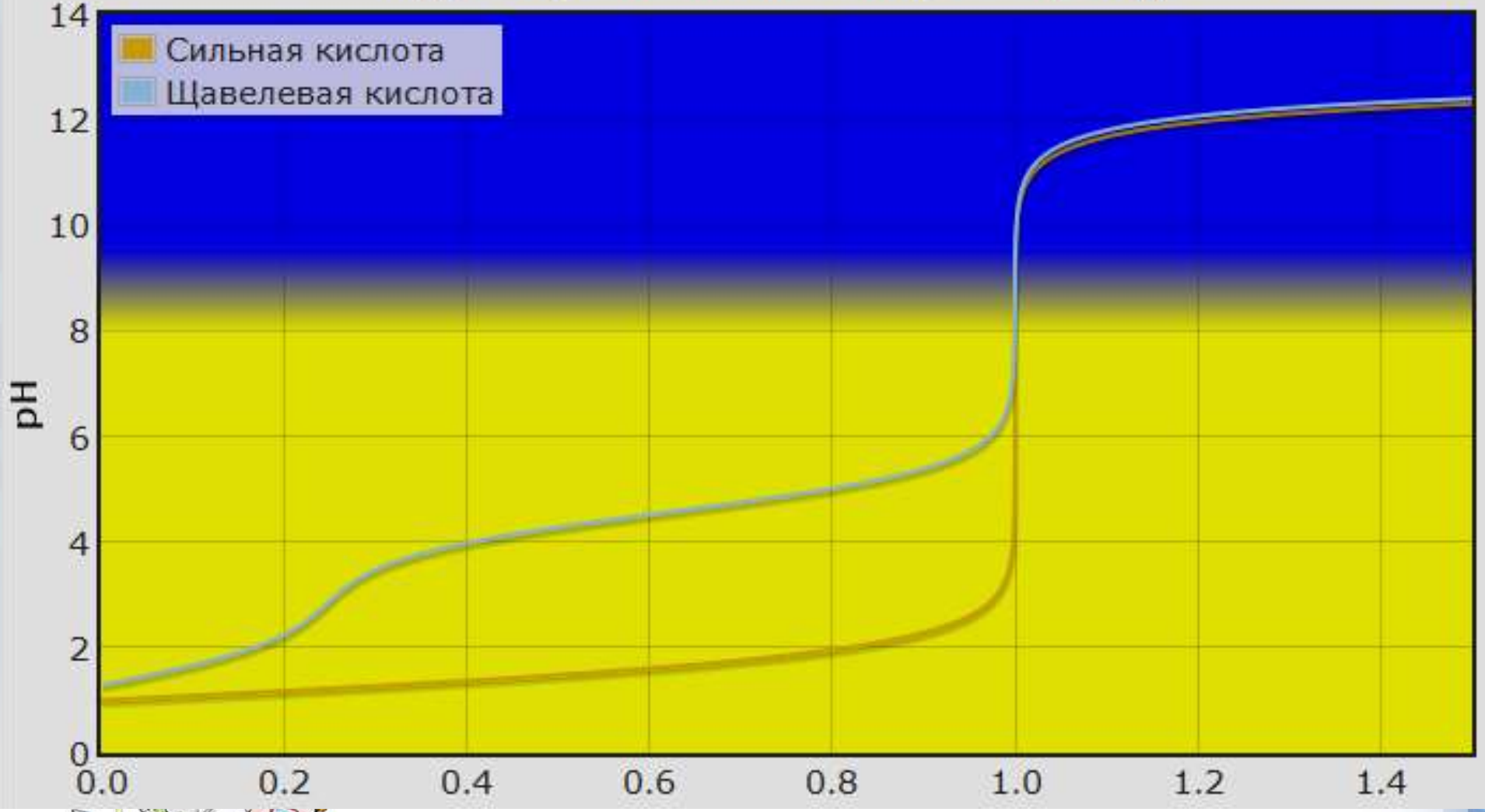
$$H_2C_2O_4 + NaOH \rightarrow NaHC_2O_4 + H_2O$$

$pK_a = 2,12$ $\Delta pK_a = 5,09$ $pK_a = 7,21$

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$$

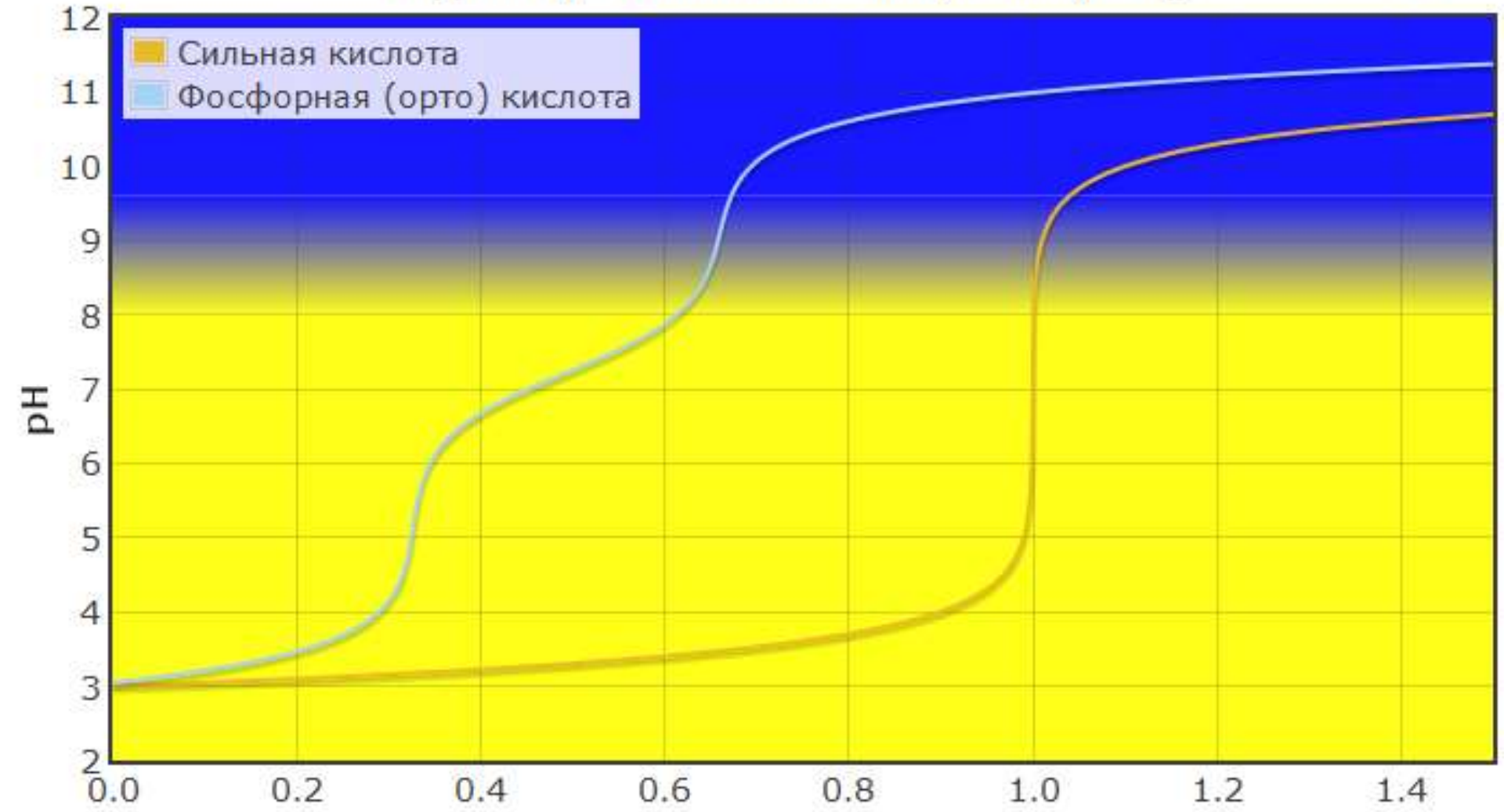
Щавелевая кислота –

Индикатор «Тимоловый синий; 2-й переход» 8 – 9.6



Фосфорная (орто) кислота –

Индикатор «Тимоловый синий; 2-й переход» 8 – 9.6

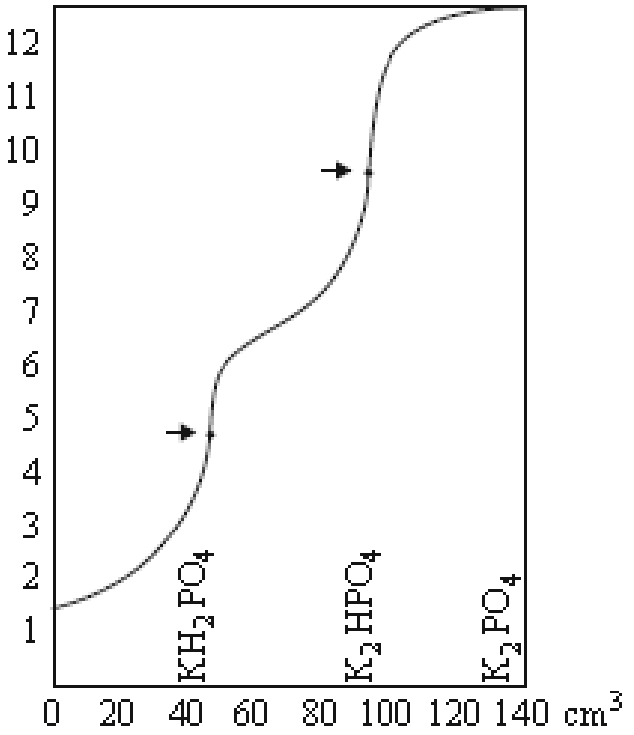


$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+ \qquad K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.11 \times 10^{-3}$$

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \qquad K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.32 \times 10^{-8}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+ \qquad K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.5 \times 10^{-13}$$

Titration of 50 ml of 0.10 mol/L phosphoric acid with 0.10 mol/L potassium hydroxide

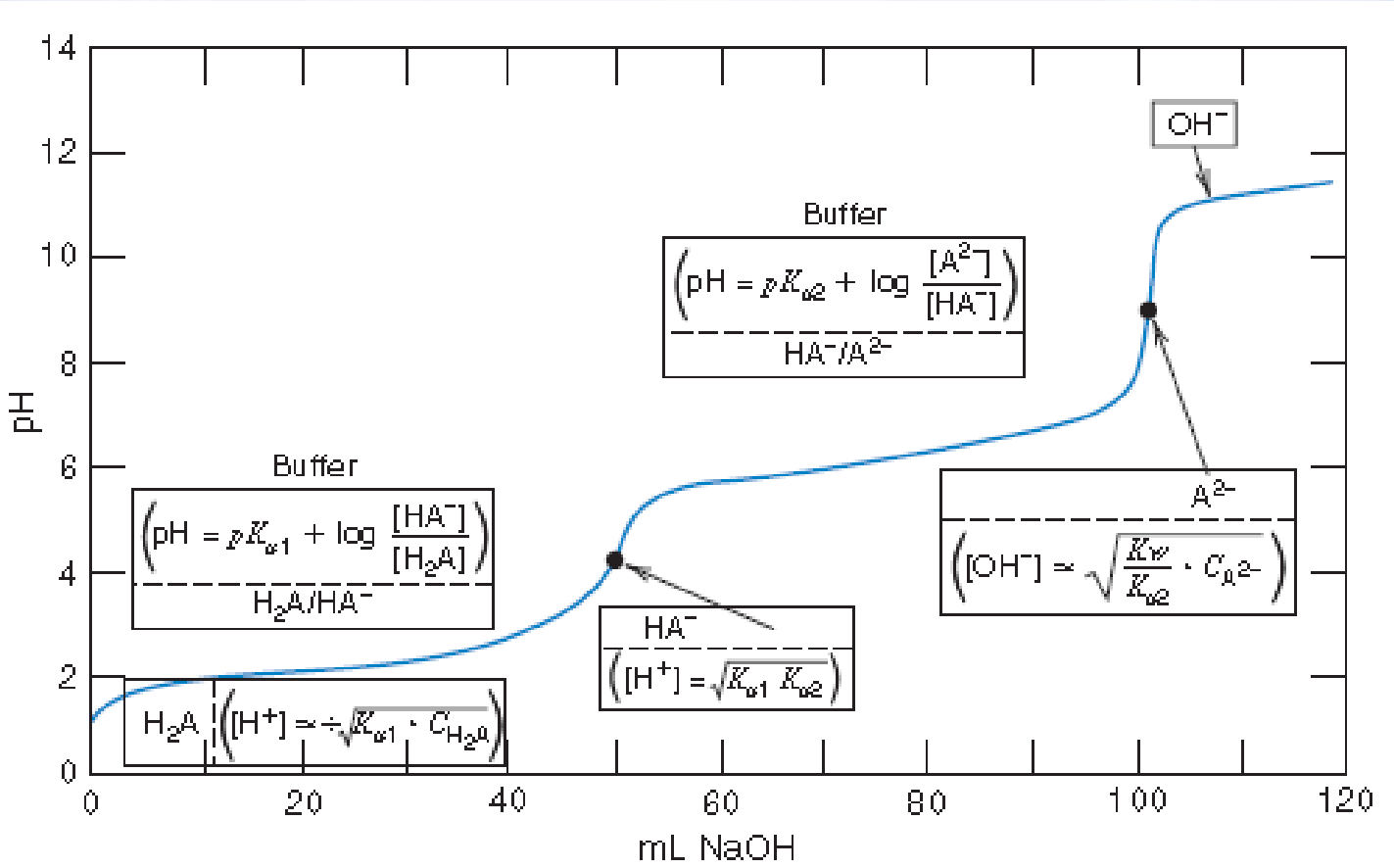


The differences between the *pK_a values permit us to detect clearly and successively* the ends of

- the neutralization of H_3PO_4,
- the neutralization of $H_2PO_4^-$,

at the first point (*V =0ml), the solution present in the* reaction vessel is that of a monoacid, with *pK_{a1}=2.23.* pH=1*.60.* before the first equivalence point the buffer $H_3PO_4/H_2PO_4^-$ appears. At the first equivalence point, present only species $H_2PO_4^-$, which is an ampholyte. pH=4*.7. Than* the couples $H_2PO_4^-/HPO_4^{2-}$ At the second equivalence point, the only species existing in the solution is the amphiprotic one: HPO_4^{2-}. pH=9*.8.*

Titration of Polyprotic Acids



$$H_2A \rightleftharpoons H^+ + HA^-$$

$$HA^- + H_2O \rightleftharpoons H_2A + OH^-$$

Equations Governing Diprotic Acid (H_2A) Titration

Fraction f Titrated	Present	Equation
$f = 0$ (0%)	H_2A	$[H^+] \approx \sqrt{K_{a1} C_{H_2A}}$ (Example 7.7) (or Eq. 7.20; Ex. 7.17, quadratic, if ~strong acid)
$0 < f < 1$ (> 0 to < 100%)	H_2A/HA^-	$pH = pK_{a1} + \log \frac{C_{HA^-}}{C_{H_2A}}$ (Eq. 7.45) (or $C_{HA^-} + [H^+]$ and $C_{H_2A} - [H^+]$ if a strong acid)
$f = 1$ (100%) (1st eq. pt.)	HA^-	$[H^+] \approx \sqrt{K_{a1} K_{a2}}$ (Eq. 7.84) (or Eq. 7.83 if $H_2A \sim$ strong acid)
$1 < f < 2$ (> 100 to < 200%)	HA^-/A^{2-}	$pH = pK_{a2} + \log \frac{C_{A^{2-}}}{C_{HA^-}}$ (Eq. 7.45, Ex. 7.16, 7.24)
$f = 2$ (200%) (2nd eq. pt.)	A^{2-}	$[OH^-] \approx \sqrt{\frac{K_w}{K_{A2}} \cdot C_{A^{2-}}}$ (Eq. 7.32) (or Eq. 7.29, Ex. 7.20, quadratic if $A^{2-} \sim$ strong base)
$f > 2$ (> 200%)	OH^-/A^{2-}	$[OH^-] =$ [excess titrant]

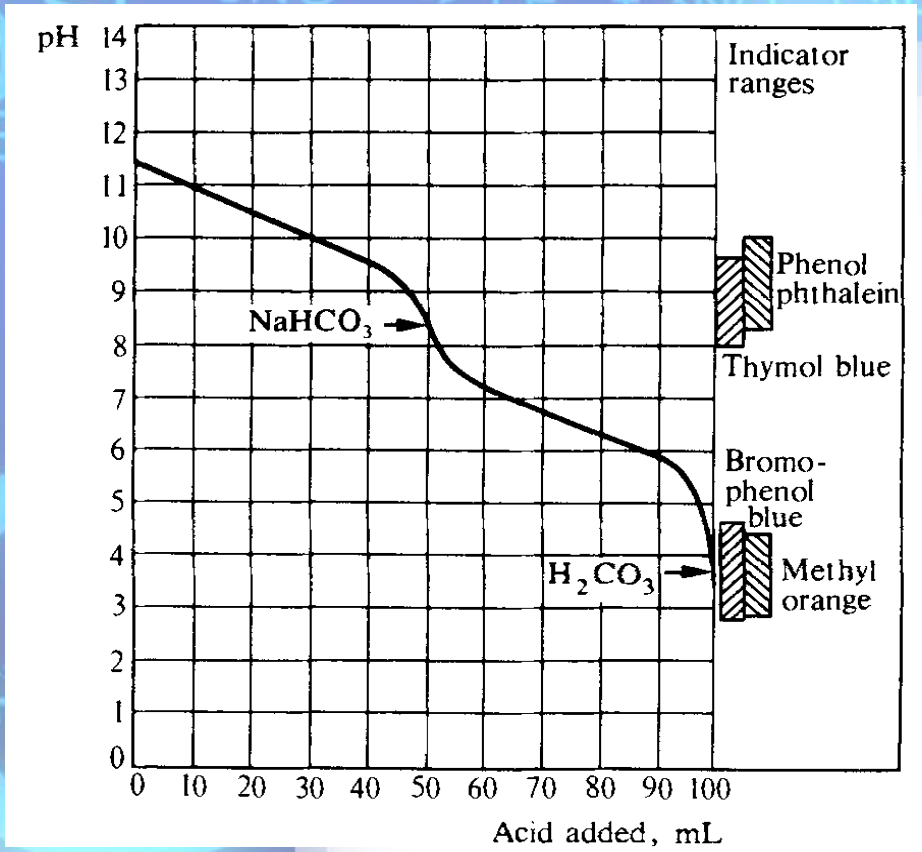
Titration of Sodium Carbonate—A Diprotic Base

Sodium carbonate is a Brönsted base that is used as a primary standard for the standardization of strong acids. It hydrolyzes in two steps:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \quad K_{H1} = K_{b1} = \frac{K_w}{K_{a2}} = 2.1 \times 10^{-4}$$

$$HCO_3^- + H_2O \rightleftharpoons CO_2 + H_2O + OH^- \quad K_{H2} = K_{b2} = \frac{K_w}{K_{a1}} = 2.3 \times 10^{-8}$$

where *Ka_1 and Ka_2 refer to the K_a values of H_2CO_3; HCO_3^- is the conjugate acid of* CO_3^{2-} and H_2CO_3 is the conjugate acid of HCO_3^-;



Titration curve for 50mL 0.1 *M* Na_2CO_3 *versus 0.1 M HCl. Dashed line represents a boiled solution with* CO_2 removed.

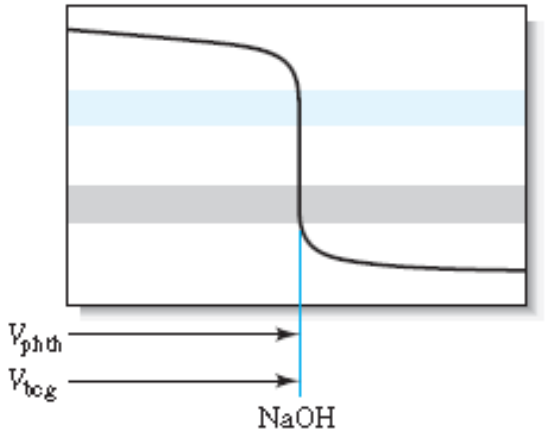
At the start of the titration, the pH is determined by the hydrolysis of the Brönsted base CO_3^{2-}. After the titration is begun, part of the CO_3^{2-} is converted to HCO_3^-, and a CO_3^{2-} */* HCO_3^- *buffer region is established. At the first equivalence point, there* remains a solution of HCO_3^-, and $[H^+] \approx \sqrt{K_{a1}K_{a2}}$. *Beyond the first equivalence* point, the HCO_3^- is partially converted to H_2CO_3*(*CO_2*) and a second buffer region* is established, the pH being established by $[HCO_3^-]/[CO_2]$. *The pH at the second* equivalence point is eternined by the concentration of the weak acid CO_2.

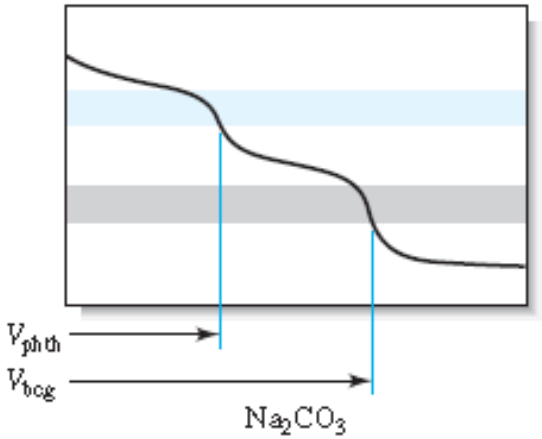
$$CO_3^{2-} + H^+ = HCO_3^-$$

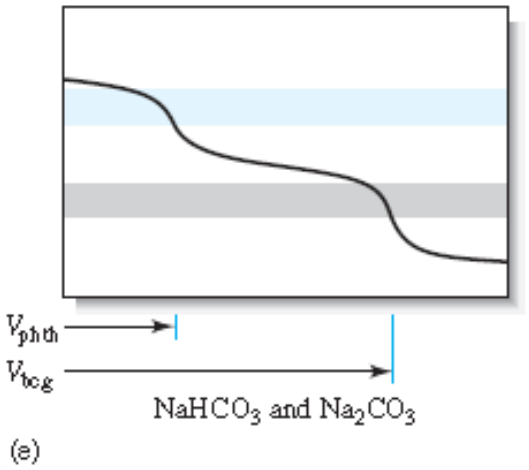
$$HCO_3^- + H^+ = H_2CO_3$$

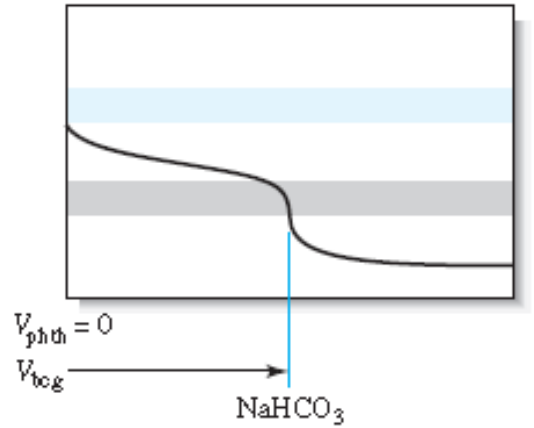
$$CO_3^{2-} + 2H^+ = H_2CO_3$$

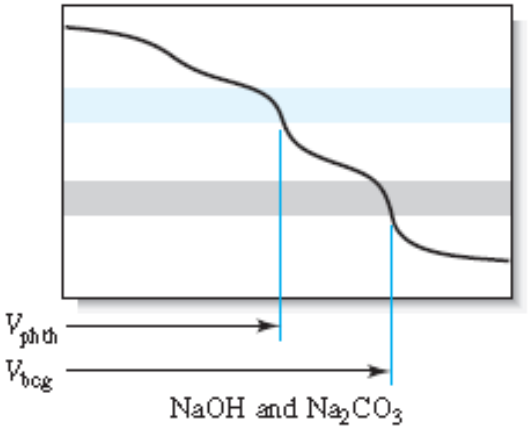
Phenolphthalein is used to detect the first end point, and methyl orange is used to detect the second one.

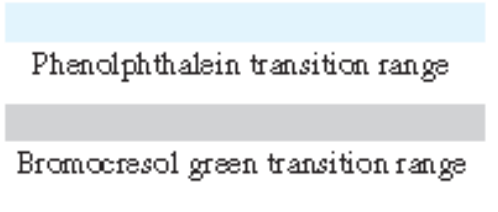












Volume Relationships in the Analysis of Mixures Containing Hydroxide, Carbonate, and Hydrogen Carbonate Ions

Constituents in Sample	Relationship between V_{phth} and V_{bcg} in the Titration of an Equal Volume of Sample*
NaOH	$V_{phth} = V_{bcg}$
Na_2CO_3	$V_{phth} = \frac{1}{2} V_{bcg}$
$NaHCO_3$	$V_{phth} = 0$; $V_{bcg} > 0$
NaOH, Na_2CO_3	$V_{phth} > \frac{1}{2} V_{bcg}$
Na_2CO_3, $NaHCO_3$	$V_{phth} < \frac{1}{2} V_{bcg}$

*V_{phth} = volume of acid needed for a phenolphthalein end point; V_{bcg} = volume of acid needed for a bromocresol green end point

the **Winkler method for the analysis of** carbonate/hydroxide mixtures, both components are titrated with a standard acid to the end point with an acid-range indicator, such as bromocresol green. An unmeasured excess of neutral barium chloride is then added to a second aliquot of the sample solution to precipitate the carbonate ion, following which the hydroxide ion is titrated to a phenolphthalein end point.

Titration Errors with Acid/Base Indicators

1. Determinate error that occurs when the pH at which the indicator changes color differs from the pH at the equivalence point. This type of error can usually be minimized by choosing the indicator carefully or by making a blank correction.

2. indeterminate error that originates from the limited ability of the human eye to distinguish reproducibly the intermediate color of the indicator. The magnitude of this error depends on the change in pH per milliliter of reagent at the equivalence point, on the concentration of the indicator, and on the sensitivity of the eye to the two indicator colors. On average, the visual uncertainty with an acid/base indicator is in the range of ±0.5 to ± 1 pH unit. This uncertainty can often be decreased to as little as 60.1 pH unit by matching the color of the solution being titrated with that of a reference standard containing a similar amount of indicator at the appropriate pH.

Titration Errors Associated with Choice of Indicator

Demands to indicators choice:

1) is necessary to have a sharp colour distinction of indicator in acidic and alkaline environment;

2) colour transition interval of indicator must lie near equilibrium point;

3) an indicator must be sensible uses 1-2 drops. If to add richly up indicator, the titrant expends on titration of indicator itself;

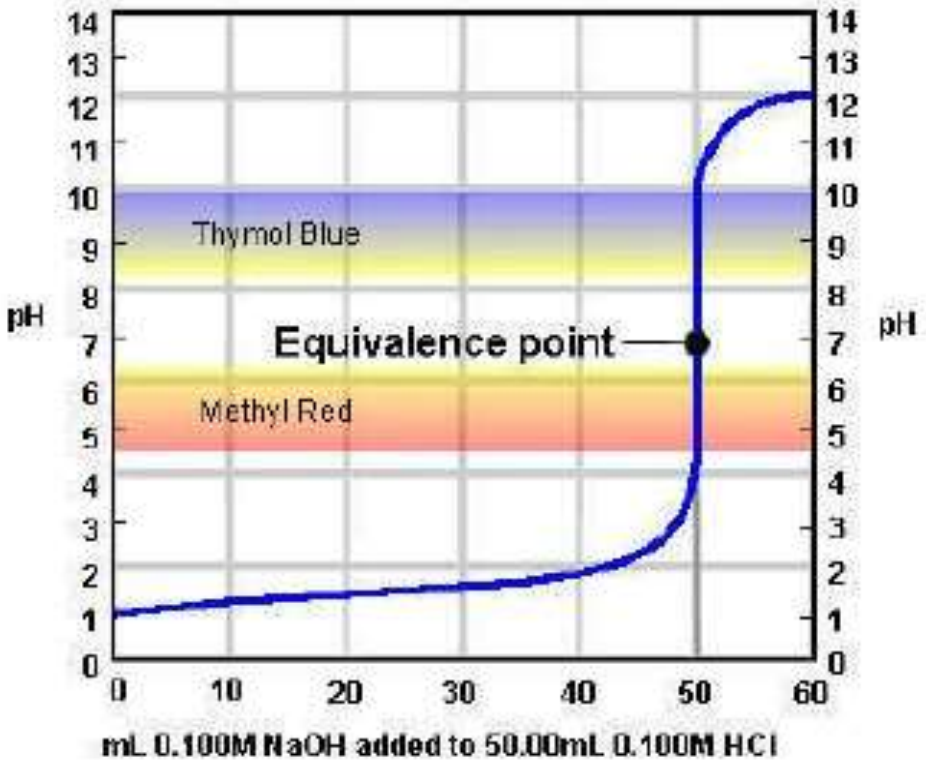
4) always necessary titrate to appearance of one hue of solution, making the same volumes of titrated solution;

5) get such indicator, that pT is coincided with titration interval.

As a rule, the end point do not coincided with equivalence point. Because of analysed solution is over or short titrated. Or, another words, the analysed solution have any surplus of acid or base.

If **pT** value is less then pH in equivalence point, titration error is caused H^+ ions surplus and called **hydrogen error.**

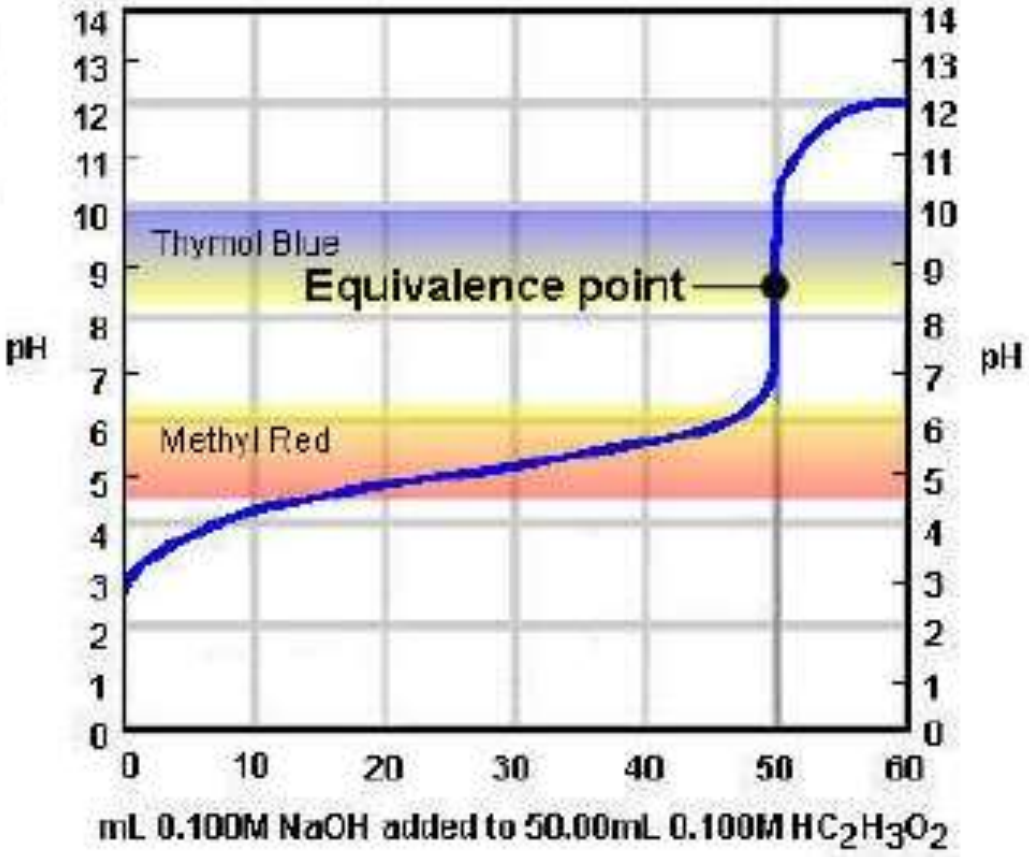
If pT value is more then pH in equivalence point, titration error is caused OH^- ions surplus and arise **hydroxyl error**.



$$[H^+]\ \text{error} = \frac{10^{-pT} \cdot V_2}{N \cdot V_1} \cdot 100\%$$

$$[OH^-]\ \text{error} = \frac{10^{-(14-pT)} \cdot V_2}{N \cdot V_1} \cdot 100\%$$

N – normality of titrant;
V_1 – volume of used titrant, ml;
V_2 – volume of sample after titration, ml.



When is titrated weak acids or weak bases, in solution present unionised electrolytes. In these cases arise **acidic error** or **alkaline error.**

$$\text{alkaline error} = 10^{pM+pT-14}$$

$$pK_b = -\log K_b$$

$$\text{acidic error} = 10^{pK_a-pT}$$

$$pK_a = -\log K_a$$