Volumetry / Titrimetry

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Concept and general conditions

Volumetry *(titrimetry)* is a quantitative analytical method, during which the „equivalent" volume of a reagent *(titrant)* with the analyte is determined. Then, based on the known stoichiometry of the reaction, the unknown analyte concentration can be calculated, e.g.:

x *Analyte* + y *Reagent* → z *Product*

$$y \cdot n_{analyte} = x \cdot n_{reagent}$$

$$n_{reagent} = c_{reagent} \cdot V_{reagent}$$

$$\downarrow$$

$$n_{analyte} = (c_{reagent} \cdot V_{reagent}) / y$$

$$c_{analyte} = n_{analyte} / V_{analyte}$$

Concept and general conditions

There are basically four different types of titrimetry:

- acid/base (neutralization)
- precipitation
- complex
- redox

Some examples:

Analyte	**Titrant**
acid (e.g. HCl)	base (e.g. NaOH, KOH)
base (e.g. NH_4OH)	acid (e.g. HCl)
IO_3^- ions	precipitating agent (e.g. $AgNO_3$, $Hg_2(NO_3)_2$)
metal ions	complexing agent (e.g. NTA, EDTA, DCTA)

Concept and general conditions

There are conditions that have to be met before a reaction can be used for volumetric analysis:

1. The reaction is quantitive
2. There are no side reactions
3. Reaction speed is reasonably fast
4. Completion of the reaction is well detectable
5. The titrant can be produced in adequate purity and stability

Preparation of the titrant

The titrant solution provides the reagent neccessary for the titration reaction. For a given titration reaction and analyte, there are usually more than one ways to prepare the titrant.

For example, if a strongly basic titrant solution is needed for the titration of an acid, practically any strong bases can be used to prepare the titrant, as it is only the OH^- ions that take part in the neutralization reaction; so NaOH, KOH, LiOH, etc. would potentially equally do.

Based on this, it makes sense to speak about standards for titrant preparation…

Primary standards

The titrant is always prepared from a standard chemical compound.

Primary standards. If a primary standard is used, then the titrant can be simply prepared ***directly*** by accurately weighing out and dissolving the standard in the adequate solvent and dilute the solution up to the needed volume in a volumetric flask. Such a standard needs to have

- high purity
- high stability (low sensitivity to air, light, etc.)
- only a constant amount of hydrate water (non-hygroscopic)
- large molar mass
- reasonable solubility

Examples include: $K_2Cr_2O_7$, $KBrO_3$, etc.

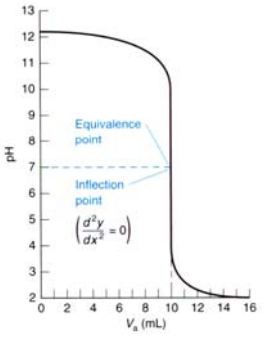
Secondary standards

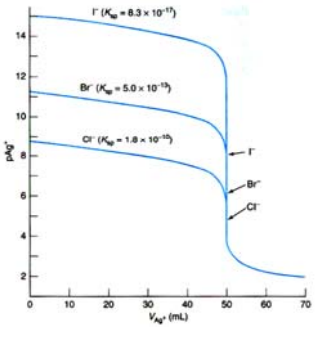
If no primary standards are available then a ***secondary standard*** has to be used. A secondary standard does not fulfill all requirements for a primary standard, but the exact concentration of its solution can be determined (***standardized***) to a solution of a primary standard by titration. Thus, it is an ***indirect*** preparation method.

Examples include: $KMnO_4$, $AgNO_3$, etc.

Titration curve

A titration curve by definition is one that shows the change of the concentration of either the analyte or the titrant as a function of the volume of titrant added. As the concentration changes over many orders of magnitude, it is customary to use the ***p-function*** of the concentration. Below are two examples:





Equivalence point and end-point

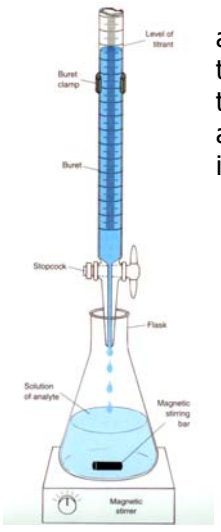
The ***equivalence point*** is where all analyte was consumed by the reaction and there is no excess of titrant. Mathematically, it can be usually expressed as the inflection point of the curve (zero crossing of the second derivative).

Classically, we stop the addition of the titrant at the ***end-point*** of the titration, which is where we estimate that we have reached the equivalence point. The ***end-point detection*** is performed using ***indicator dyes*** or ***instrumentally***.

Indicator dyes are select, colorful compounds that undergo a color change near the equivalence point, so the end-point can be visually detected by the analyst.

Instrumental end-point detection detects some changes in the physical or chemical properties of the analyte solution at the end-point (e.g. light absorption, electrical conductance).

Tools of the trade



Classical titration apparatus

Thus, a classical titration only takes a burette, a stirrer and an indicator dye. A modern titration is performed by recording the whole titration curve using a computer controlled automatic burette and a measuring instrument (e.g. pH meter, mV-meter).

Modern automatic titrator

Titration error

Titration error is the overall inaccuracy we have in the final result. The sources of this error can be various and depend on the titration tools. Here, we only name two important sources of the titration error:

• ***indicator error***. This occurs if an indicator dye is used for end-point detection. It originates either from that the indicator itself is consuming a relevant amount of titrant, or from that the indicator was not carefully selected and detects the equivalence point inaccurately.

• ***sampling error.*** This occurs if the titration data is collected using instruments, and the data array has inadequate resolution (derivative function).

Titrimetric approaches

Direct titration
The analyte is directly titrated with the titrant.

Back-titration
If the reaction is too slow between the analyte and the titrant, but the analyte reacts with an external reagent which also reacts with the titrant in a fast reaction, then one can add the reagent to the analyte in excess (and let it have enough time to react quantitatively). The excess of the reagent is then back-titrated with the titrant to obtain the analyte concentration.

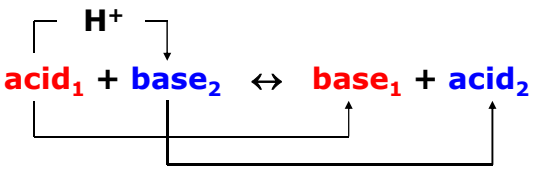
Reverse titration
In this approach, the sample solution is in the buret (e.g. the sample is sensitive to air)

Indirect titration
By using a reagent the analyte can be converted into something directly titratable.

Neutralization (acid/base) equilibria and titrations

Acids and bases: Brönsted-Lowry

Most typically, acids and bases are treated in analytical chemistry according to the Brönsted-Lowry theory. As it is well known, this theory is based on the concept that the acidic/basic character of a compound always shows in equlibrium processes and it's based on proton exchange. In these acid/base reactions, a proton donor reacts with a proton acceptor, and their ***conjugate pairs*** are formed:



Acids and bases

In aqueous solution, the „strength" of a Brönsted-Lowry type **HA acid** depends on the relative hydrogen affinity of the acid and water molecules. This can be characterized by the ***acid dissociation constant,*** K_a

$$\mathbf{HA + H_2O \leftrightarrow A^- + H_3O^+}$$

$$K_a = \frac{[A^-][H_3O^+]}{[HA][H_2O]} \approx \frac{[A^-][H_3O^+]}{[HA]} \qquad pK_a = -\lg(K_a)$$

Acids and bases

Similarly, for an **A^- base**, the ***base dissociation constant,*** K_b can be written as :

$$\mathbf{A^- + H_2O \leftrightarrow HA + OH^-}$$

$$K_b = \frac{[HA][OH^-]}{[A^-][H_2O]} \approx \frac{[HA][OH^-]}{[A^-]} \qquad pK_b = -\lg(K_b)$$

Autoprotolysis of water

The water molecule is capable of both releasing and accepting a proton, hence it undergoes an autoprotolysis (self-dissociation):

$$\mathbf{H_2O + H_2O \leftrightarrow OH^- + H_3O^+}$$

$$K_w = \frac{[OH^-][H_3O^+]}{[H_2O]^2} \approx [OH^-][H_3O^+]$$

As it is known, $K_w = 10^{-14}\ M^2$ at 25 °C, so $pK_w = 14$.

pH= -lg[H_3O^+] **pOH= -lg[OH^-]**

Therefore, in aqueous solutions: **pH + pOH = 14**

Conjugate acid-base pairs in water

$$K_a \cdot K_b = \frac{[A^-][H_3O^+]}{[HA]} \cdot \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w$$

pK_a + pK_b = pK_w = 14

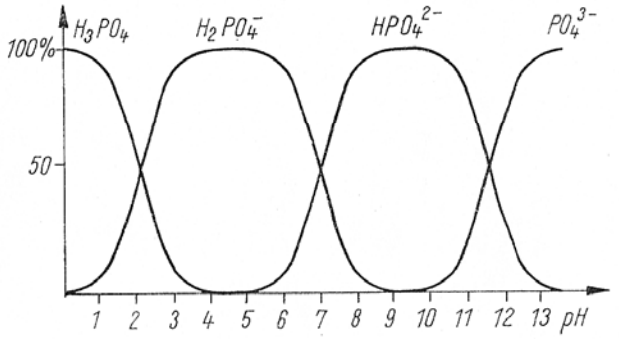
This means that the conjugate base for a weak acid is strong (high K_b) and vice versa.

Polyprotic acids – phosphoric acid

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \qquad pK_1 = 1{,}96,$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad pK_2 = 6{,}70,$$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \qquad pK_3 = 12{,}44.$$



pH calculation of strong acids/bases

If K_a or K_b is larger than ca. 10^{-4} then we call the acid or base „strong". These compounds can be considered to fully dissociate in water, thus they produce $[H_3O^+]$ and $[OH^-]$ approximately equivalent to c_{acid} and c_{base} :

$$\mathrm{pH} = -\lg[H_3O^+] \approx -\lg(c_{acid})$$

$$\mathrm{pOH} = -\lg[OH^-] \approx -\lg(c_{base}) \quad \rightarrow \quad pH = 14 - pOH$$

pH calculation of weak acids/bases

Here, the dissociation equilibrium has to be considered. A practically important case is when the acid/base is still much stronger than water and the concentration is significant (at least 0.01 M). In this case, the $[H_3O^+]$ and $[OH^-]$ produced by the acid/base is much larger than ca. 10^{-7} M, the amount from the autoprotolysis of water. Then, ***for an acid***, we can estimate:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \approx \frac{[H_3O^+]^2}{c_{acid}}$$

$$pH = -\lg(\sqrt{K_a \cdot c_{acid}}) = \frac{1}{2} \cdot pK_a - \frac{1}{2} \cdot \lg(c_{acid})$$

pH calculation of weak acids/bases

Analogously, for a weak base:

$$K_b = \frac{[HA][OH^-]}{[A^-]} \approx \frac{[OH^-]^2}{c_{base}}$$

$$pOH = -\lg(\sqrt{K_b \cdot c_{base}}) \quad \rightarrow \quad pH = 14 - \frac{1}{2} \cdot pK_b + \frac{1}{2} \cdot \lg(c_{base})$$

pH calculation of polyprotic acids/bases

The exact treatment of this scenario is more complicated, but again, there are reasonable estimations.

One case is when all consequtive dissociation constants are larger than 10^{-4}. Then $[H_3O^+]$ and $[OH^-]$ concentrations can be considered to be multiples of c_{acid} and c_{base} (strong acid/base).

For example, in the case of oxalic acid, $K_{a1}= 5{,}6\cdot10^{-2}$; $K_{a2}= 5{,}4\cdot10^{-4}$, thus both protons can be considered to dissociate in a single step:

$$HOOC\text{-}COOH + 2\ H_2O \leftrightarrow {}^{-}OOC\text{-}COO^{-} + 2\ H_3O^+$$

$$pH = -\lg[H_3O^+] \approx -\lg(2 \cdot c_{acid})$$

Another example is H_2SO_4 ($K_{a1}= 10^3$; $K_{a2}= 1{,}2\cdot10^{-2}$)

pH calculation of polyprotic acids/bases

In a more general case, there is a several orders of magnitude difference between the dissociation constants for the step. If, by the first step, the acid/base is strong, then we can safely ignore the rest of the steps and treat the acid/base as a monoprotic one. One example is phosphoric acid:

$$\begin{aligned} H_3PO_4 &\rightleftharpoons H_2PO_4^- + H^+ & pK_1 &= 1{,}96, \\ H_2PO_4^- &\rightleftharpoons HPO_4^{2-} + H^+ & pK_2 &= 6{,}70, \\ HPO_4^{2-} &\rightleftharpoons PO_4^{3-} + H^+ & pK_3 &= 12{,}44. \end{aligned}$$

$$pH \approx -\lg(c_{\text{phosphoric acid}})$$

Hydrolysis of salts

Salts are strong electrolytes, therefore dissociate fully in water. On the other hand, salts are results of neutralization reactions. Example:

$$\mathbf{NaOH} + \mathbf{HCl} \rightarrow \mathbf{NaCl} + H_2O$$

As a rule of thumb, the acidic/basic character of a salt solution is determined by the relative strength of the acid and base which reacted with each other to produce the given salt. In the above example, NaCl can be safely said to produce a pH neutral solution upon dissolution.

Hydrolysis of salts

In the case of NaCN, out of the „parenting" compounds, NaOH is a strong base, while HCN is a weak acid ($K_a=4\cdot10^{-10}$). When dissolving NaCN in water, CN^- forms which is the conjugate base of HCN. This is a strong base, hence:

$$CN^- + H_2O \leftrightarrow HCN + OH^-$$

$$K_w = K_{a,HCN} \cdot K_{b,\ CN^-}$$

The result is a basic pH; NaCN is „hydrolysing" and behaves like a strong base:

$$pOH = -\lg[OH^-] \approx -\lg(c_{NaCN})$$

Hydrolysis of salts

A similar example is NH_4Cl. Here, NH_4OH is a weak base, whereas HCl is a strong acid, Thus their product is expected to be acidic. Indeed, after full dissociation, NH_4^+ ion reacts with water:

$$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$$

$$K_w = K_{a,NH_4^+} \cdot K_{b,\,NH_3}$$

So the result is an acidic solution. One has to consider that the ammonium ion is a weak acid, thus the pH is:

$$pH = -\lg\left(\sqrt{K_{a,NH_4^+} \cdot c_{NH_4Cl}}\right)$$

pH calculation of buffer solutions

Buffers are solutions that contain either

a) a weak acid and its salt formed with a strong base (e.g. CH_3COOH és CH_3COONa)

or

b) a weak base and its salt formed with a strong acid (e.g. NH_3 és NH_4Cl)

at comparable concentrations. Note, that this means a solution containing an acid (base) and its conjugate pair.

pH calculation of buffer solutions

The nature of buffer solutions is such that they hinder the pH changing effect of any acid or base added to the solution – thus keeping the pH more or less „constant” (buffered).

For example in an acetate buffer, extra protons will be taken care of by acetate ions:

$$CH_3COO^- + H^+ \leftrightarrow CH_3COOH$$

whereas extra hydroxide ions will be consumed by acetic acid:

$$CH_3COOH + OH^- \leftrightarrow CH_3COO^- + H_2O$$

pH calculation of buffer solutions

The pH of buffers can be approximated by only considering the reaction of the weak component with water. In case of the acetate buffer:

$$CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$$

$$K_{a,CH_3COOH} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \approx \frac{c_{CH_3COONa} \cdot [H_3O^+]}{c_{CH_3COOH}}$$

$$pH = -\lg\left(\frac{K_{a,CH_3COOH} \cdot c_{CH_3COOH}}{c_{CH_3COONa}}\right) = pK_{a,CH_3COOH} + \lg\frac{c_{CH_3COONa}}{c_{CH_3COOH}}$$

in general, according to the Henderson-Hasselbalch equation

$$pH \approx pK_{acid} + \lg\frac{c_{salt}}{c_{acid}}$$

pH calculation of buffer solutions

Similarly, for an opposite buffer composition, e.g. NH_3 and NH_4Cl:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

$$K_{b,NH_3} = \frac{[NH_4^+][OH^-]}{[NH_3]} \approx \frac{c_{NH_4Cl} \cdot [OH^-]}{c_{NH_3}}$$

$$pOH = -\lg\left(\frac{K_{b,NH_3} \cdot c_{NH_3}}{c_{NH_4Cl}}\right) = pK_{b,NH_3} + \lg\frac{c_{NH_4Cl}}{c_{NH_3}}$$

in general, according to the Henderson-Hasselbalch equation

$$pOH \approx pK_b + \lg\frac{c_{salt}}{c_{base}}$$

Acids and bases in non-aquoeus media

In the Brönsted-Lowry concept, solvents have a strong effect on the strength of acids and bases. Consequently, changing the solvent from water to something else can be employed in neutralization titrations. The following classes of solvents are usually defined:

indifferent solvents do not take part in proton exchange reactions (e.g. benzene, CCl_4, $CHCl_3$)

amphoteric solvents are capable of autoprotolysis (e.g. water, CH_3COOH, pyridine, NH_3)

protogenic (proton releasing) solvents (e.g. HF, H_2SO_4)

protophilic (proton accepting) solvents (e.g. NH_3, amines)

Acids and bases in non-aqueous media

There are at least two ways of exploiting non-aqueous media in neutralization titrations:

1. An analyte with poor solubility in water can be dissolved in amphoteric or indifferent solvents

2. The strength of acids and bases can be enhanced by using a solvent with opposite character (protophilic or protogenic) for the dissolution of the analyte

Now let's do neutralization titration!

Obviously, volumetric (titrimetric) analysis is possible based on acid/base reactions. Neutralization titrations occur in numerous variants, including:

- strong acid with a strong base (or vice versa)
- strong acid with a weak base (or vice versa)
- weak acid with a weak base (or vice versa)
- polyprotic acids with a strong base (or vice versa)
- acid mixtures with a strong base (or vice versa)

and more. We are going to discuss the above cases in aqueous solutions by calculating the theoretical points of their titration curve.

Logically, in neutralization titration curves, the pH (or pOH) is plotted against the volume of titrant added.

Titration of strong acid with strong base

Let's consider the case of

20 mL 0.1 M HCl (analyte) and 0.1 M NaOH (titrant)

$HCl + NaOH \rightarrow NaCl + H_2O$

Three regions will have to be considered in the calculations:

1.Before the equivalence point:
the pH will be determined by the remaining acid (analyte)

2.At the equivalence point:
the pH will be determined by the „hydrolysis" of the product of the reaction, that is now NaCl

3.After the equivalence point:
The pH will be determined by the excess of base (titrant)

Titration of strong acid with strong base

Region 1: Before the equivalence point

0 mL titrant added (0%):

$pH = - \lg c_{HCl} = - \lg 0.1 = 1.00$

5 mL titrant added (25%):

$pH = - \lg c_{HCl,\ remaining}$

$c_{HCl,\ remaining} = ((c_{HCl,\ total} \cdot V_{HCl}) - (c_{NaOH} \cdot V_{NaOH,\ added})) / V_{total}$

$pH = - \lg (((0.1\ M \cdot 20\ mL) - (0.1\ M \cdot 5\ mL)) / 25\ mL) = 1.22$

10 mL titrant added (50%):

$pH = - \lg (((0.1\ M \cdot 20\ mL) - (0.1\ M \cdot 10\ mL)) / 30\ mL) = 1.47$

Titration of strong acid with strong base

Region 2: At the equivalence point

20 mL titrant added (100%):

pH= 7.00 as the product of reaction (H_2O) is neutral

Titration of strong acid with strong base

Region 3: After the equivalence point

25 mL titrant added (125%):

$pOH = - \lg c_{NaOH,\ extra}$

$c_{NaOH,\ extra} = ((c_{NaOH} \cdot V_{NaOH,\ added}) - (c_{HCl,\ total} \cdot V_{HCl})) / V_{total}$

$pOH = - \lg (((0.1\ M \cdot 25\ mL) - (0.1\ M \cdot 20\ mL)) / 45\ mL) = 1.95$

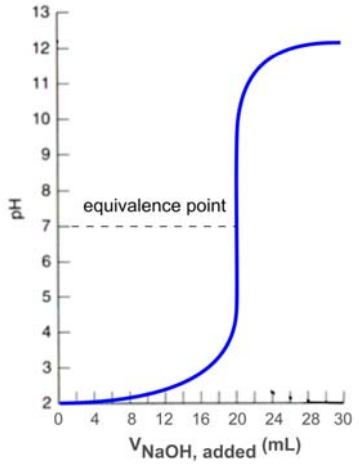
$pH = 14 - pOH = 12.05$

30 mL titrant added (150%):

$pOH = - \lg (((0.1\ M \cdot 30\ mL) - (0.1\ M \cdot 20\ mL)) / 50\ mL) = 1.70$

$pH = 14 - pOH = 12.30$

Titration curve of a strong acid with a strong base



Titration of weak acid with strong base

Let's consider the case of HA weak acid (pK_a= 5.20)

20 mL 0.1 M HA (analyte) and 0.1 M NaOH (titrant)

$HA + NaOH \rightarrow NaA + H_2O$

Four regions will have to be considered in the calculations:

1. ***At the start of titration:***
   the weak acid is present
2. ***Before the equivalence point:***
   a buffer is present (weak acid and its salt with NaOH)
3. ***At the equivalence point:***
   the pH will be determined by the „hydrolysis" of NaA
4. ***After the equivalence point:***
   hydrolysing salt plus extra NaOH is present

Titration of weak acid with strong base

Region 1: At the start of titration

0 mL titrant added (0%):

$$pH = -\lg(\sqrt{K_a \cdot c_{acid}}) = \frac{1}{2} \cdot (pK_a - \lg c_{acid}) = 0.5 \cdot (5.20 - \lg 0.1) = 3.10$$

Titration of weak acid with strong base

Region 2: Before the equivalence point

5 mL titrant added (25%):

$$pH \approx pK_a + \lg \frac{c_{salt}}{c_{acid}}$$

$c_{salt} = (c_{NaOH} \cdot V_{NaOH,\ added}) / V_{total} = (0.1M \cdot 5\ mL) / 25\ mL$

$c_{acid,\ remaining} = ((c_{acid,\ total} \cdot V_{acid}) - (c_{NaOH} \cdot V_{NaOH,\ added})) / V_{total} = 0.06\ M$

$pH = 4.72$

10 mL titrant added (50%):

same as above, but because at 50%, $c_{salt} = c_{acid}$

$pH = pK_a = 5.20$

Titration of weak acid with strong base

Region 3: At the equivalence point

20 mL titrant added (100%):

$c_{salt} = (c_{NaOH} \cdot V_{NaOH,\ added}) / V_{total} = (0.1\text{M} \cdot 20\ \text{mL}) / 40\ \text{mL}$

the pH is governed by A^-, the conjugate base of HA, which is released into the solution due to the full dissociation of NaA. For this conjugate base, K_b is

$K_b = 10^{-14} / 10^{-5.20} = 1.58 \cdot 10^{-9}$

consequently, this a weak base. To calculate the pH, we use the appropriate formula:

$$pOH = -\lg(\sqrt{K_{b,A^-} \cdot c_{A^-}}) = -\lg(\sqrt{1.58 \cdot 10^{-9} \cdot c_{salt}}) = 5.05$$

$pH = 14 - pOH = 8.95$

Titration of weak acid with strong base

Region 4: After the equivalence point

25 mL titrant added (125%):

There is the hydrolysing salt (weak base) and the extra NaOH, (strong base). When calculating the $[OH^-]$, the effect of the salt can be safely neglected. Only the excess NaOH is considered:

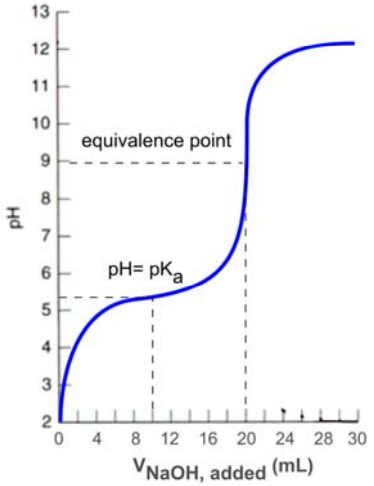
$pOH \approx -\lg c_{NaOH,\ extra}$

$c_{NaOH,\ extra} = ((c_{NaOH} \cdot V_{NaOH,\ added}) - (c_{HA,\ total} \cdot V_{HA})) / V_{total}$

$pOH = -\lg (((0.1\ \text{M} \cdot 25\ \text{mL}) - (0.1\ \text{M} \cdot 20\ \text{mL})) / 45\ \text{mL}) = 1.95$

$pH = 14 - pOH = 12.05$

Titration curve of a weak acid with a strong base



Titration curve of a diprotic weak base (or base mixture) with a strong acid

Rule of thumb: if there is at least a 1000 times difference in the dissociation constants, then each proton can be separately titrated, unless they are „too weak".

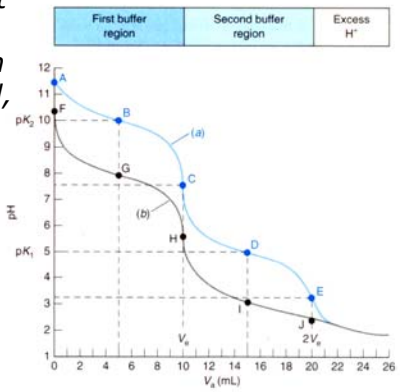
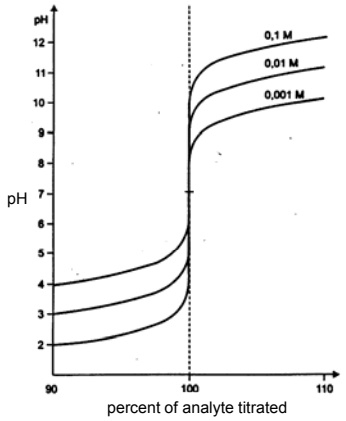


Figure 11-4 (*a*) Titration of 10.0 mL of 0.100 M base (pK_{b1} = 4.00, pK_{b2} = 9.00) with 0.100 M HCl. The two equivalence points are C and E. Points B and D are the half-neutralization points, whose pH values equal pK_{b2} and pK_{b1}, respectively. (*b*) Titration of 10.0 mL of 0.100 M nicotine (pK_{b1} = 6.15, pK_{b2} = 10.85) with 0.100 M HCl. There is no sharp break at the second equivalence point, J, because the pH is too low.

The effect of concentration on the shape of titration curves

Generally: the larger is the concentration, the sharper is the „jump" at the equivalence point.

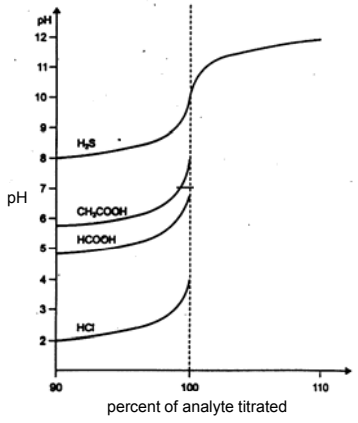
If the concentrations of the analyte and titrant change the same way then the curve remains more or less symmetrical and the position of the equivalence point does not change significantly.



The effect of dissociation constant on the shape of titration curves

Generally: the larger is the dissociation constant, the sharper is the „jump" at the equivalence point.

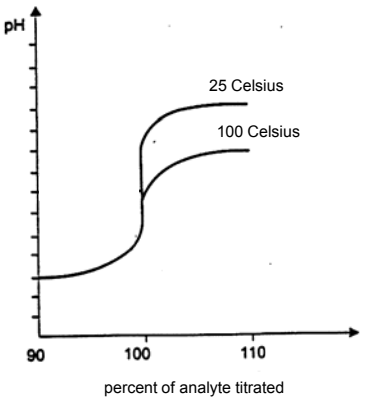
Note: the position of the equivalence point also does change significantly.



The effect of temperature on the shape of titration curves

The effect of temperature on the titration curve is a complex one. Dissociation constants usually increase with the temperature, but so does that of the solvent (water)…

The curve on the right shows the case of acetic acid/NaOH titration.



End point indication by indicator dyes

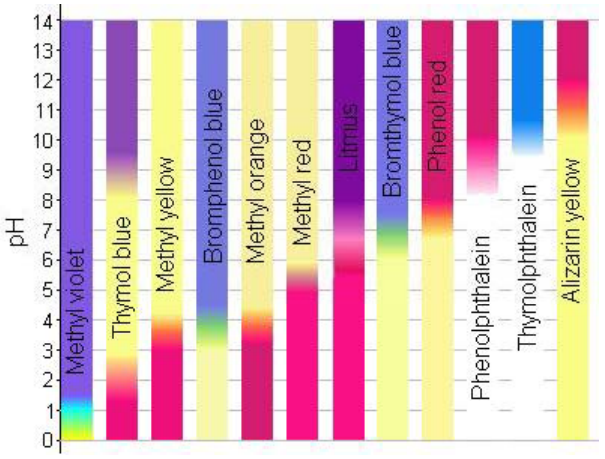
Acid/base indicators are organic dyes, which typically have weak acidic/basic characteristics themselves. Most of them are two-color indicators where the acidic and basic forms have contrasting colors (or one of them is colorless).

Indicators will change their color (have ***transition color***) at the pH where their acidic and basic forms are present in equal concentrations.

$$K_{Hind} = \frac{[H^+] \cdot [Ind^-]}{[HInd]}$$

it easily follows that at this pH, pH= pK_{HInd}. This value is typical of any indicator dye and is called the ***indicator exponent***.

End point indication by indicator dyes



End point indication by indicator dyes

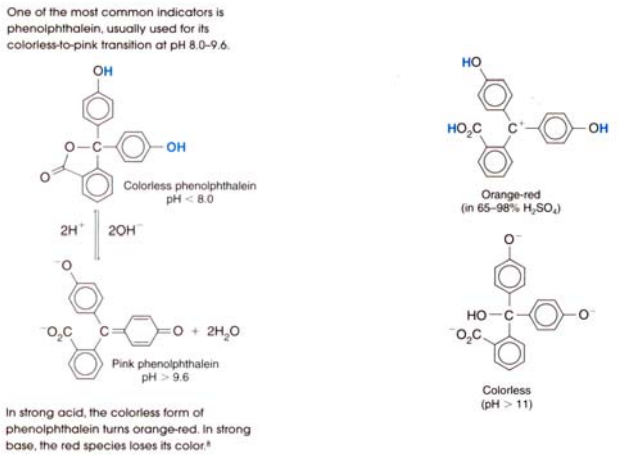
When the pH shifts from the above value, the color will also shift towards the appropriate acidic/basic color. However, for practical reasons, we can only observe the clear acidic/basic color of a dye if one of these forms is present at least in a 10 times higher concentration than the other, so:

$$\frac{1}{10} \leq \frac{[Ind^-]}{[HInd]} \quad \text{or} \quad \frac{10}{1} \leq \frac{[Ind^-]}{[HInd]}$$

thus a transition color can be seen when

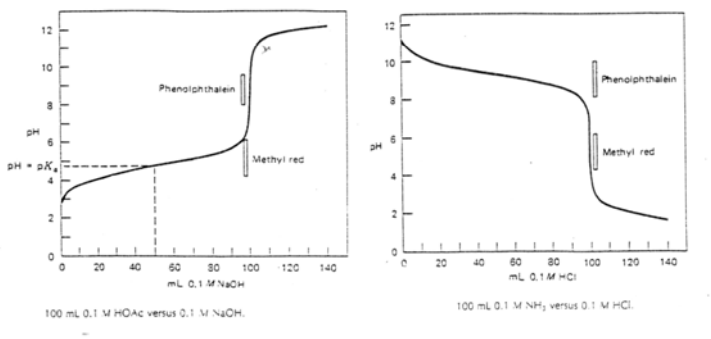
$$pK_{HInd} - 1 < pH < pK_{HInd} + 1$$

End point indication by indicator dyes



It is easy to see why it is important to use only the minimum neccessary amount of indicator („type 1" indicator error)

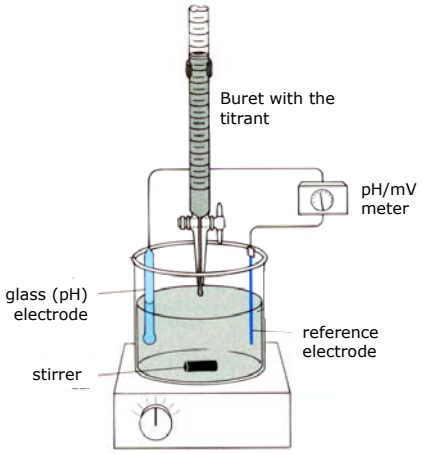
End point indication by indicator dyes



correct selection of the indicator

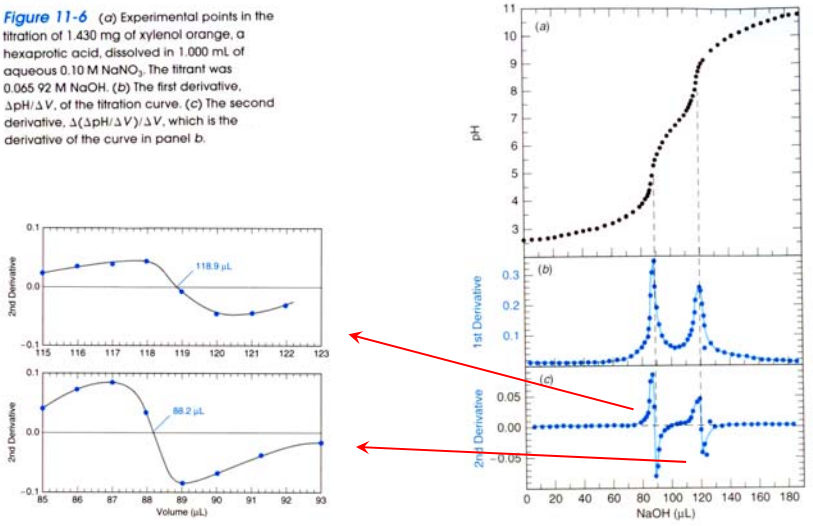
Again, it is easy to see why it is important to choose an indicator with the proper exponent („type 2" indicator error)

End point indication by instruments



End point indication by instruments

Figure 11-6 (*a*) Experimental points in the titration of 1.430 mg of xylenol orange, a hexaprotic acid, dissolved in 1.000 mL of aqueous 0.10 M $NaNO_3$. The titrant was 0.065 92 M NaOH. (*b*) The first derivative, $\Delta pH/\Delta V$, of the titration curve. (*c*) The second derivative, $\Delta(\Delta pH/\Delta V)/\Delta V$, which is the derivative of the curve in panel *b*.



Hence, the use of 2nd derivative curve is recommended to minimize sampling error.

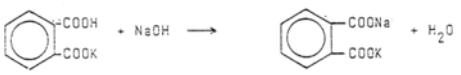
Preparation and standardization of titrants in neutralization titrations

A solution of a strong base of known concentration is needed for the determination of acids by acid/base titration. Strong bases are hygroscopic and are usually partially carbonated

$$2\ NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

so they are not primary standards. Therefore, they have to be standardized with a solution of an acid of known concentration. The following primary standards (pure, solid acids) are mainly used for their standardization:

KH-phtalate



Oxalic acid

$$(COOH)_2 + 2\ NaOH \rightarrow Na_2(COO)_2 + 2\ H_2O$$

Preparation and standardization of titrants in neutralization titrations

A solution of a strong acid of known concentration is needed for the determination of bases by acid/base titration. For this purpose, mainly HCl is used, which is also not a primary standard (vaporizes easily).

For the standardization of a HCl titrant, the following primary standards (pure, solid bases) are typically used:

$KHCO_3$

$$KHCO_3 + HCl \rightarrow KCl + H_2O + CO_2$$

Borax ($Na_2B_4O_7 \cdot 10\ H_2O$)

$$Na_2B_4O_7 + 5\ H_2O + 2\ HCl \rightarrow 2\ NaCl + 4\ B(OH)_3$$

Applications of acid-base titrations

Beside the obvious, the following applications are worth particular attention:

- ✓ titration of carbonates by a strong acid
- ✓ Kjeldahl nitrogen determination
- ✓ boric acid determination (enhancement)
- ✓ titration in acetic acid
- ✓ determination of organic acids/bases

Titration of carbonates

Carbonates are important industrial materials

$CaCO_3$	limestone
Na_2CO_3	washing soda, baking soda

which are used in many chemical processes. Carbonic acid is formed when CO_2 from the atmosphere is dissolved in water:

$$CO_2(g) \overset{H_2O}{\rightleftarrows} CO_2(aq) \leftrightarrow H_2CO_3(aq)$$

Carbonic acid itself is a weak diprotic acid:

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \quad K_{a1} = 10^{-6.34}$$
$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-} \quad K_{a2} = 10^{-10.36}$$

which implies that carbonates are fairly strong bases:

$$K_b = \frac{K_w}{K_{a,HCO_3^-}} = \frac{10^{-14}}{10^{-10.36}} = 10^{-3.64}$$

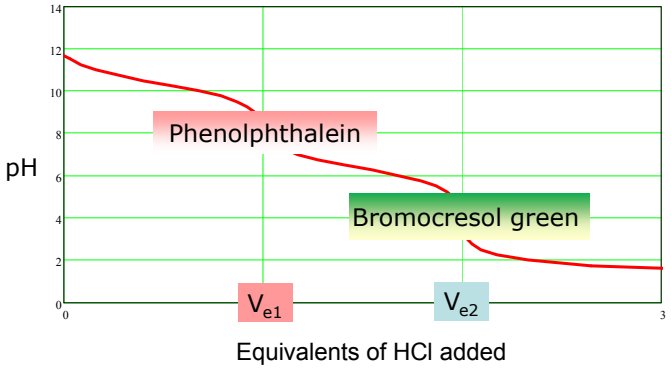
K_{a2} for H_2CO_3

Titration of carbonates

Step 1: $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

Step 2: $NaHCO_3 + HCl \rightarrow H_2CO_3 + NaCl$

Overall: $Na_2CO_3 + 2HCl \rightarrow H_2CO_3 + 2NaCl$



Thus, both equivalence points can be detected and used for the determination.

Titration of carbonates

But, absorbed CO_2 from air reacts with a carbonate sample

$$CO_{2\,(g)} + H_2O_{\,(l)} + CO_3^{2-}{}_{(aq)} \rightarrow 2\ HCO_3^{-}{}_{(aq)}$$

which affects the volume of HCl required to reach phenolphthalein endpoint (decreases it), because the amount of carbonate ions decreases.

However, the BCG endpoint is not affected. This is so because, for example, for 1 mmol CO_3^{2-}, the titration until BCG endpoint would need 2 mmol HCl. If this CO_3^{2-} is consumed by reaction with the absorbed CO_2, the reaction produces just 2 mmol HCO_3^-, which still requires 2 mmol HCl ultil the BCG endpoint.

So it is recommended to use the BCG endpoint for carbonate determination. The endpoint detection can be facilitated by boiling off CO_2 (from H_2CO_3).

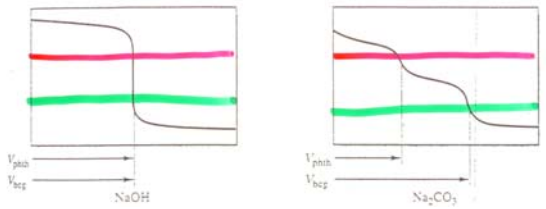
Titration of carbonates

Another related case is when a partially carbonated hydroxide solution is to be titrated… in this case, practically OH^-, HCO_3^-, CO_3^{2-} are all present. To assess the situation, the following curves and data can be of assistance:

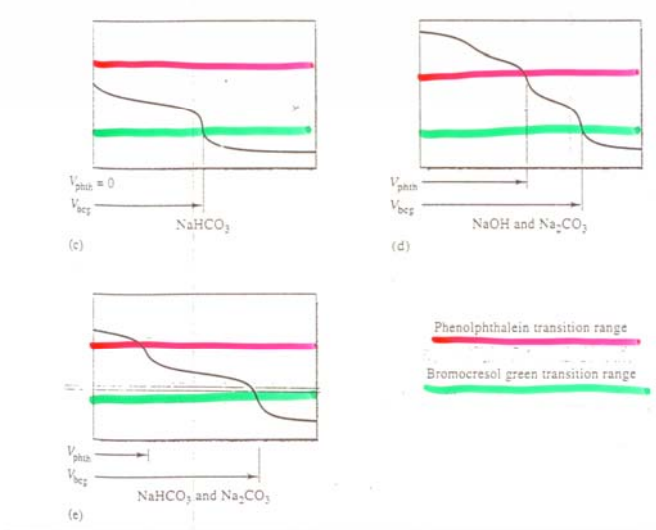
TABLE 16-2
Volume Relationships in the Analysis of Mixtures Containing Hydroxide, Carbonate, and Hydrogen Carbonate Ions

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

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



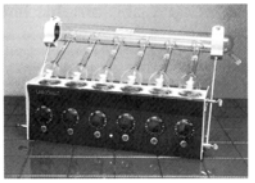
Titration of carbonates



Kjeldahl titration

This titrimetric method is a highly accurate and widely used method for the nitrogen determinaton in organic materials (such as food).

The method is named after the Danish chemist Johan Kjeldahl, who developed the method in 1883 while working in the Carlsberg Laboratories on a method to determine the amount of protein in the grains used in the malt production.



Kjeldahl titration – step 1 of 4

Prereduction

Nascent hydrogen produced by the reaction between an acid and a metal (or alloy, such as Devarda's: 50% Cu, 45% Al, 5% Zn) reduces nitrogen containing inorganic or organic compounds (e.g. nitrates, nitro or azo compounds) to ammonia or amino compounds.

$$NO_3^- \rightarrow NH_3$$

$$R\text{-}NO_2 \rightarrow R\text{-}NH_2$$

$$R\text{-}N{=}N\text{-}R \rightarrow R\text{-}NH_2$$

Kjeldahl titration – step 2 of 4

Digestion

The sample is decomposed by digestion with hot, concentrated sulfuric acid (a very strong oxidant). Amines and ammonia is converted to ammonium hydrogen sulphate, organic matter is oxidized to water and carbon dioxide.

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_4 + H_2O + CO_2$$

$$R\text{-}NH_2 + H_2SO_4 \rightarrow NH_4HSO_4 + H_2O + CO_2$$

in its modern realization, this digestion step is often catalysed by Hg, Cu or Se.

Kjeldahl titration – step 3 of 4

Distillation

NaOH is added to the solution, which expells NH_3 (a weaker base) from the solution. Heating facilitates this process. The ammonia distillate is taken up in a receiver flask containing a known amount of standard HCl solution.

$$2\ NaOH + NH_4HSO_4 \rightarrow NH_{3\,(g)} + 2\ H_2O + Na_2SO_4$$

$$NH_{3\,(g)} + H_2O \rightarrow NH_4OH$$

$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$$

Kjeldahl titration – step 4 of 4

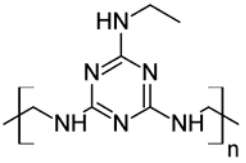
Back-titration

The excess HCl is finally ***back-titrated*** using NaOH:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

The drawback of the accurate and widespread Kjeldahl method is that it actually measures *all nitrogen sources*, not only proteins, for which it was conceived. An alternative method is the *Dumas* method.

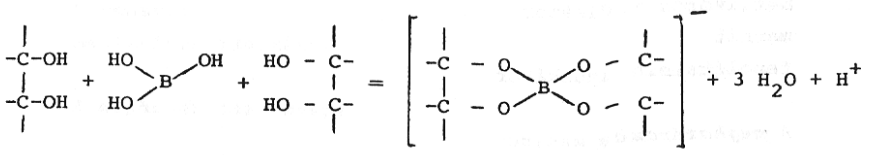
This problem surfaced e.g. in the *2007 pet food and 2008 milk powder scandals* related to China, where melamine (a formaldehyde resin) was added to milk products to make them appear to have higher protein content.



Boric acid determination

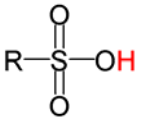
Orthoboric acid (H_3BO_3) is a very weak organic acid – which also reflects in its alternative formula $B(OH)_3$ – and therefore can not be directly titrated. However, it can be titrated ***indirectly***.

The method takes advantage of its reaction with vicinal diols (such as mannite, glycerine, etc.) which produces a stable complex and a strongly acidic solution. The released proton can be then titrated using NaOH and phenolphtalein.

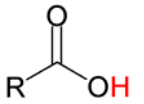


Determination of organic acids/bases

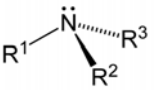
Sulfonic acids are generally strong enough for direct titration using a strong base.



Most **carboxylic acids** can also be directly titrated, but their solubility in water may hamper the titration. In this case, the acid can be dissolved in an excess of a strong base followed by back-tritration.

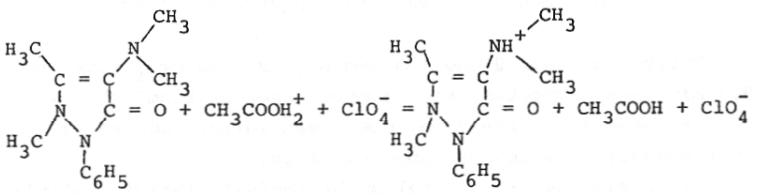


Amines are usually too weak for direct titration in water, but they readily dissolve in anhydrous acetic acid, which enhances their basicity and allows the titration.



Titration of an amine in anhydrous acetic acid

Amidazophenum (also called aminophenazone or 1-phenil-2,3-dimetil-4-dimetil-amino-pirazol -5-on) is an analgesic, anti-inflammatory compound with so weak basicity that it can not be directly titrated in water. In anhydrous acetic solvent however, it can be titrated using perchloric acid as titrant and tropeoline 00 as indicator.



Perchloric acid is often used in titrations in non-aqueous media for it mixes readily with organic solvents and it is the strongest acid in anhydrous acetic acid. Its standardization has to be done using KH-phtalate.

Checklist for neutralization titrations

Remember:

- the discussed formulas for pH calculations in acidic/basic solutions, mixtures, buffers and titration curves
- effect of concentration and K on the titration curve (titrant is always a strong acid or base!)
- methods of standardization for the titrants
- end-point detection possibilities (instrumental/indicator dyes)
- important applications
- potential sources of titration errors