Acid-Base Titration (Neutralization Method)

Practicum. Topic № 3

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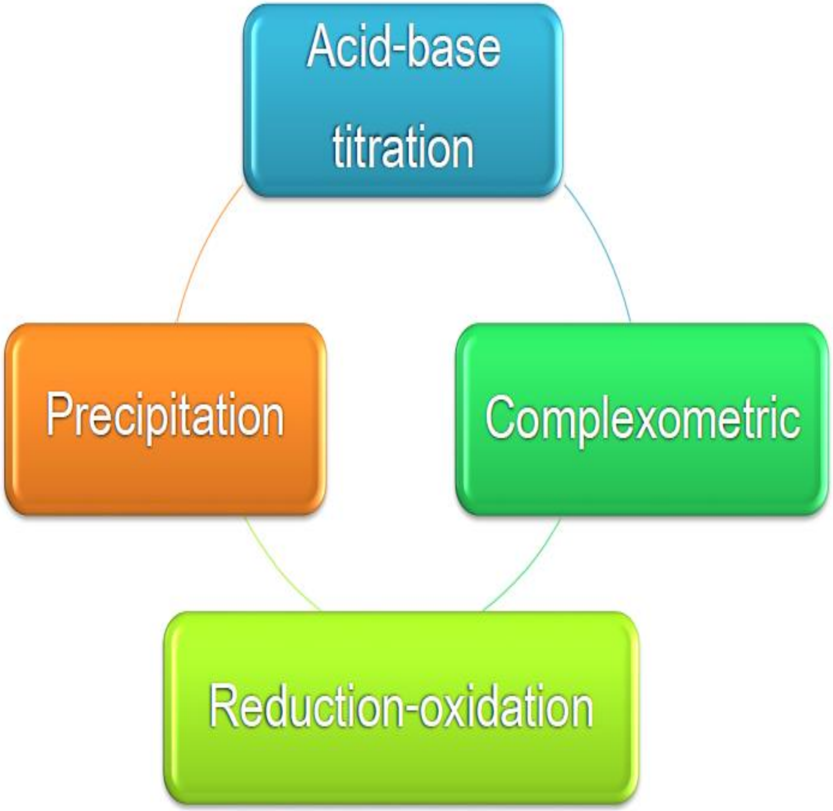
What will we study?

- Ways of expressing concentration and concentration relationship
- Law of equivalents
- Acid-Base Titration to determine the concentration of acids, bases, salt ions

Classification of reaction in titrimetric analysis

1. **Acid–base titrations**, in which an acidic or basic **titrant** reacts with an analyte that is a base or an acid
2. **Complexometric titrations** involving a metal–ligand complexation reaction
3. **Redox titrations**, where the titrant is an oxidizing or reducing agent
4. **Precipitation titrations**, in which the analyte and titrant react to form a precipitate.



Applications of Titrimetry in Pharmaceutical Analysis

- Provide standard pharmacopoeial methods for the assay of unformulated drugs and excipients and some formulated drugs, e.g. those that lack a strong chromophore.
- Used for standardisations of raw materials and intermediates used in drug synthesis in industry. Suppliers of raw materials may provide these materials at a specified purity which has been assayed titrimetrically to a pharmacopoeial standard.
- Certain specialist titrations, such as the Karl Fischer titration used to estimate water content, are widely used in the pharmaceutical industry..

Neutralization Method

- The neutralization method (acid-base titration) is mainly used for the quantitative determination of acids and alkalis. In clinical practice, the neutralization method is used to determine the acidity of gastric juice, blood buffer capacity, spinal fluid, urine, and other biological fluids. In sanitary laboratories, acid-base titration is used to determine the quality of food products. This method is also widely used in pharmaceutical chemistry for the analysis of medicinal substances of both inorganic and organic nature.

Neutralization Method

- In the technical execution of the method, the solution of a strong component (acid or base) is poured into the burette and is a titrant.

- The main reaction of the method correct to write:

$$\boxed{AH + \ddot{B} \rightleftarrows A^- + HB^+}$$

- **As a result of the acid-base interaction**, H^+ is transferred from the acid (AH) to the base (B). A new acid and a new base are formed, coupled with the original one. It is clear that the pH at the equivalence point will differ from the original one.\

Acid-Base Titration

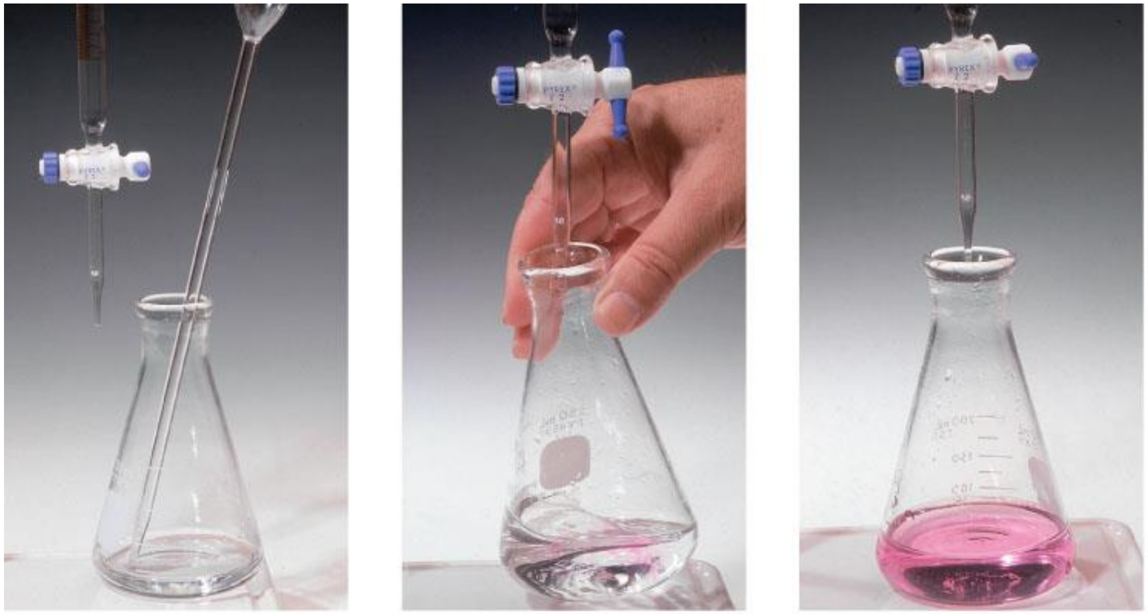
- Titration is the process of adding a *titrant* (titration solution) drop by drop to the *equivalence point* (end of the reaction).
- The equivalence point is the moment of the reaction when the substances have reacted to each other in equivalent quantities. Only in this case, the parameters of the substance being determined (mass, concentration or volume) can be calculated on the *law of equivalents*.
- Titrants (titration solutions) are a solutions the concentration of which is established using *standard solutions*.
- Standard solutions are solutions of known concentration.
- The working solutions in the neutralization method are strong acids or strong bases, which are used as titrants, as well as standard solutions of salts, which determine the exact concentration of titrants.

Properties of Titration

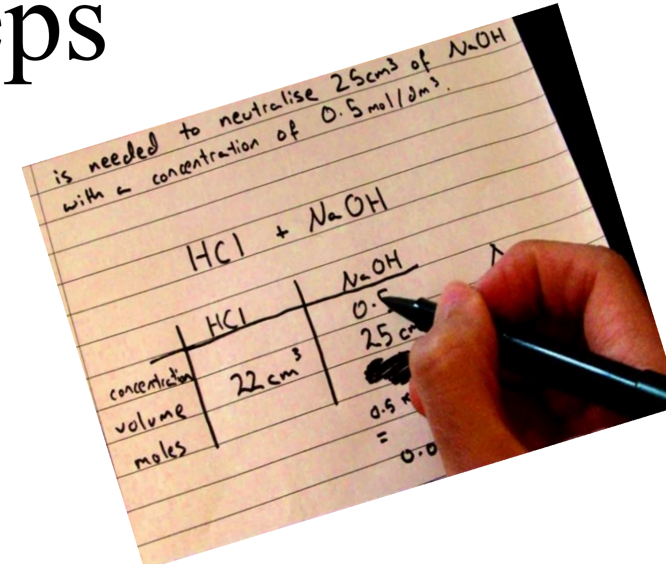
- **Advantages**
- Capable of a higher degree of precision and accuracy than instrumental methods of analysis.
- robust.
- Analyses can be automated.
- Cheap to perform and do not require specialised apparatus.
- They are absolute methods and are not dependent on the calibration of an instrument.

- **Limitations**
- Non-selective.
- Time-consuming if not automated and require a greater level of operator skill than routine instrumental methods.
- Require large amounts of sample and reagents.
- Reactions of standard solutions with the analyte should be rapid and complete.

Titration Steps



(a) (b) (c)



(d)

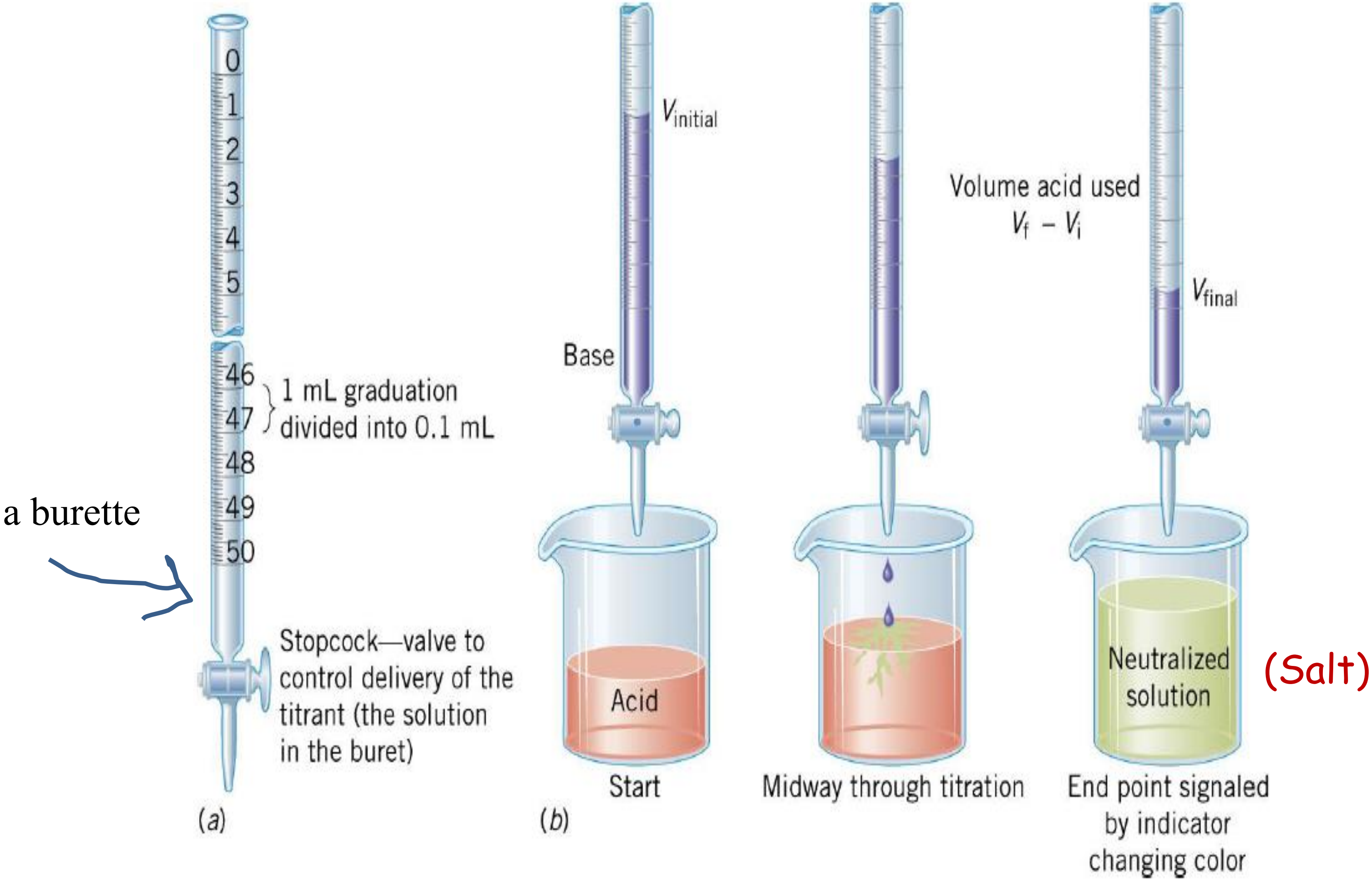
1/ A known volume of acid is measured into a flask.

2/ Standard base of known concentration is added from a burette.

3/ The **endpoint (equivalence point)** is indicated by a color change.

4/ The volume of base is recorded.

Acid Base Titration



Titration of an acid solution of unknown concentration with a base solution of known concentration

Acid-base equivalent point

- **Equivalence point of acid-base titration**: The point at which moles of H^+ ion from the acid equals moles of $OH^–$ ion from the base. An abrupt change in pH occurs at the equivalence point.

- The solution itself **at the end-point** may be:
  - **Basic,** if the reaction involves a strong base and a weak acid.
  - **Neutral,** if the reaction involves a strong acid and a strong base.
  - **Acidic,** if the reaction involves a strong acid and a weak base.

- **Method for finding the end point in acid-base titration**

1- With a Visual Indicator.

2- By Monitoring pH

3- By Monitoring Temperature

But the solutions of acids and alkaline are colorless.
How we can fix the end of reaction (i.e. equivalence point)?

The equivalence point is set using indicators

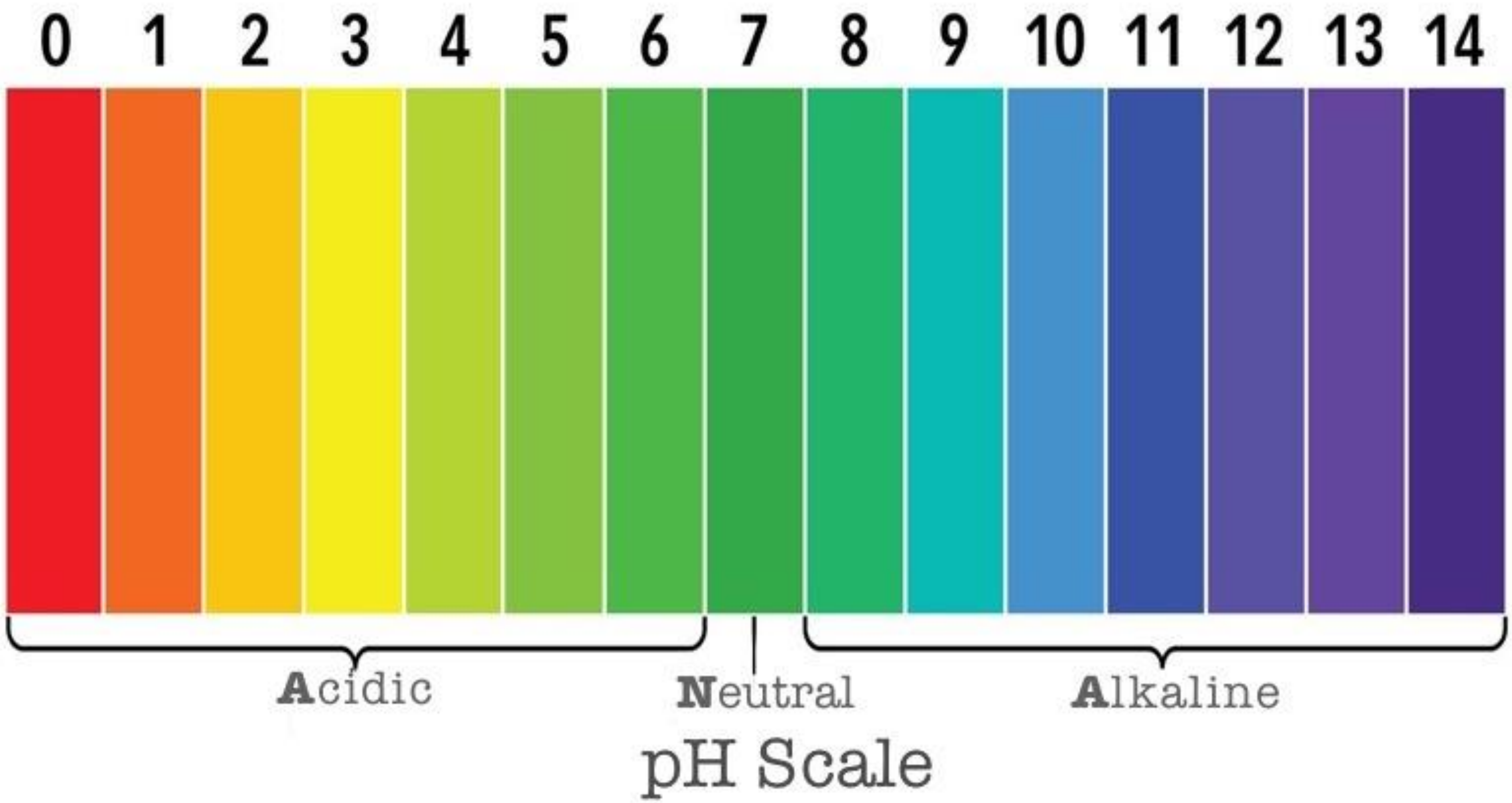
Indicators

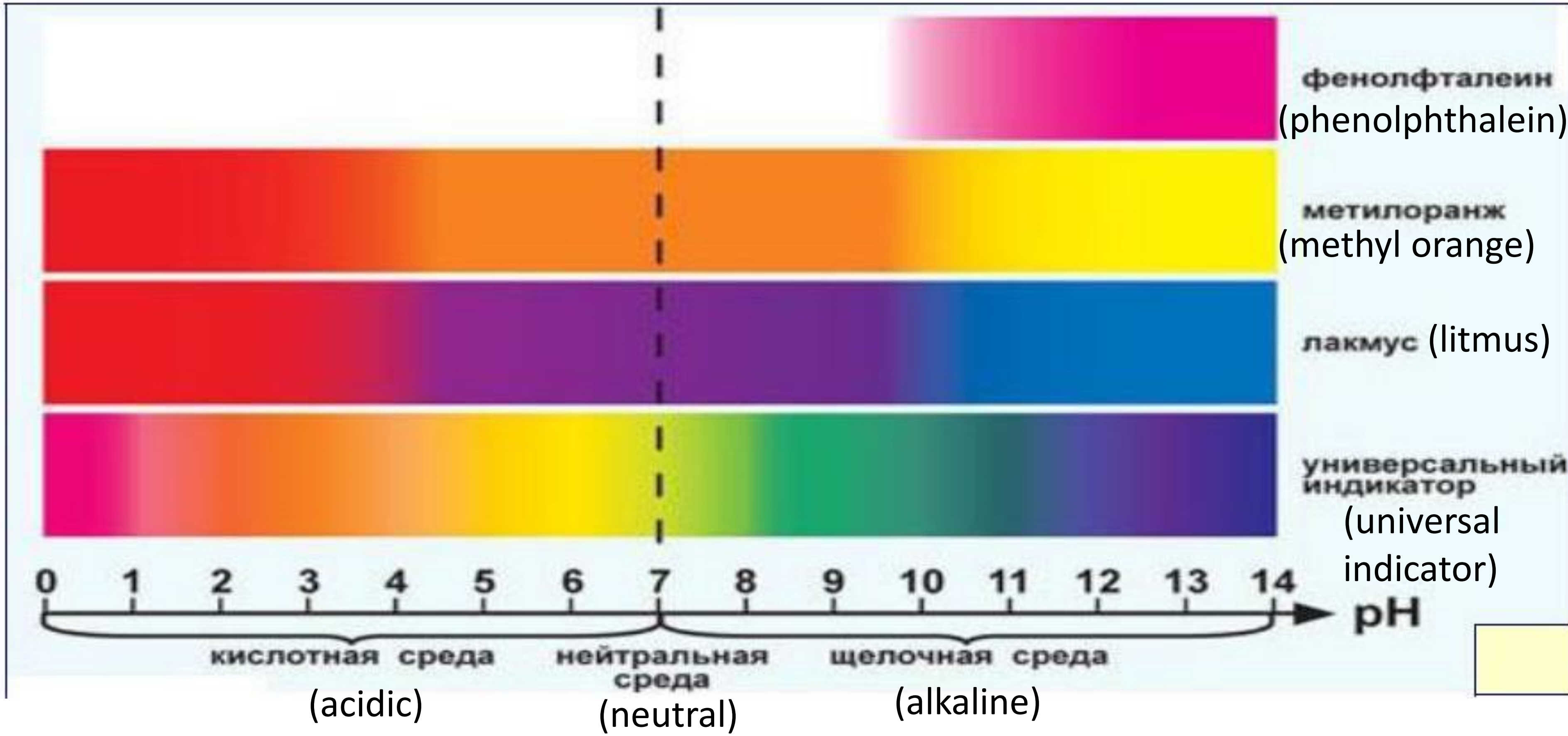
$$HInd \rightleftarrows H^+ + Ind^-$$

color I **color II**

The indicator is a weak acid or weak base of organic nature, the molecular and ionic form of which differs in color. According to the protolytic theory of Brønsted, the indicator is a conjugate acid-base pair, the components of which differ in color.

The colors of universal indicator in pH scale





Litmus in a different solutions

Acid base equilibrium

For the reaction of a strong base (e.g NaOH) with a strong acid (e.g HCl) the only equilibrium reaction of importance is

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

The first task in constructing the titration curve is to calculate the volume of base (NaOH) needed to reach the equivalence point.

<u>At the equivalence point</u> :

Moles of acid = moles of base $\boldsymbol{n}_a = \boldsymbol{n}_b$

or

$C_{M1}*V_1 = C_{M2}*V_2$ $\boldsymbol{C}_{\boldsymbol{M}a}\boldsymbol{V}_a = \boldsymbol{C}_{\boldsymbol{M}b}\boldsymbol{V}_b$

Where $\boldsymbol{C_M}$ *refers to the molarity,* ***V*** *refers to the volume , the subscript* ***'a'*** *indicates the acid, and the subscript* ***'b'*** *indicates the base*

Example…

- A 43.0 mL of sodium hydroxide (NaOH) was titrated against 32.0 mL of 0.100 M hydrochloric acid(HCl). What is the molarity (M) of sodium hydroxide solution?

Answer…

$$\boldsymbol{C_{M}}_{\mathrm{a}} * V_{\mathrm{a}} = \boldsymbol{C_{M}}_{\mathrm{b}} * V_{\mathrm{b}}$$

$$\boldsymbol{C_{M}}_{\mathrm{HCl}} * V_{\mathrm{HCl}} = \boldsymbol{C_{M}}_{\mathrm{NaOH}} * V_{\mathrm{NaOH}}$$

$$M_{\mathrm{NaOH}} = \frac{32\mathrm{mL} * 0.1\mathrm{M}}{43\ \mathrm{mL}}$$

Ans: $C_{M\ \mathrm{NaOH}}$ = 0.0744 M

Ways of expressing concentration

Concentration	Formula	Definition
Mass fraction of solute (percentage) C (%)	$\omega = \frac{m_{\text{в-ва}}}{m_{\text{р-ра}}} \cdot 100\%$	**C (%)** is the ratio of the mass of the solute to the total mass of the solution. The mass fraction of a solute shows what mass of a substance is dissolved in 100 g of a solution
Molar concentration C (mol/l)	$C = \frac{n_{\text{в-ва}}}{V_{\text{р-ра}}} = \frac{m_{\text{в-ва}}}{V_{\text{р-ра}} M_{\text{в-ва}}}$	**C (mol/L)** is the ratio of the amount of solute to the volume of the solution. Molar concentration indicates the number of moles of a solute contained in 1 liter of solution
Molar equivalent concentration (normal concentration) C (1/z) (mol/l)	$C(1/z) = \frac{n(1/z)}{V} = \frac{m}{M(1/z)V}$	**C (1/z) (mol/l)** is the ratio of the amount of substance equivalents to the volume of the solution. The molar equivalent concentration indicates the number of mole equivalents of a solute contained in 1 liter of solution
Molal concentration Cm (mol/kg)	$C_m = \frac{n_{\text{в-ва}}}{m_{\text{р-ля}}}$	**Cm (mol/kg)** is the ratio of the amount of solute to the mass of the solvent. Molal concentration indicates the number of moles of a solute in 1000 g of solvent
Titer T (g/ml)	$T = \frac{m}{V_{(\text{мл})}}$	**T (g/ml)** is the ratio of the mass of the solute to the volume of the solution, expressed in milliliters. The titer shows what mass of the substance is contained in 1 ml of solution

Ways of expressing concentration

$$C_{\%}(x) = \frac{m(x)\cdot 100}{m(\text{раствора})} = \frac{m(x)\cdot 100}{\rho \cdot V_{\text{мл}}(\text{р-ра})}, \quad \%$$

$$C_{\text{м}}(x) = \frac{n(x)}{V_{\text{л}}(\text{р-ра})}, \quad \text{моль/л}$$

$$C_{\text{э}}(x) = \frac{n(\frac{1}{z}x)}{V_{\text{л}}(\text{р-ра})}, \quad \text{моль/л}$$

$$\boxed{C_{\text{э}}(x) = C_{\text{м}}(x) \cdot Z}$$

$$\text{T}(x) = \frac{m(x)}{V_{\text{мл}}(x)}, \quad \text{г/мл}$$

$$\text{T}(x/y) = \frac{m(y)}{V_{\text{мл}}(x)}, \quad \text{г/мл}$$

Concentration relationship

- $C_M * M$
- $C_{(1/z)} * M_{(1/z)}$
- $C\% * 10\rho$
- $T * 1000$

For example, if you know a molar concentration (C_M), but you need a titer (T) we have this equation:

$$C_M * M = T * 1000$$

$$T = C_M * M / 1000$$

Example…

- The molarity of a solution containing 750 mL of 4.47 g of HCl is …

Answer…

$$C_M = \frac{n_{s-sa}}{V_{p-pa}} = \frac{m_{s-sa}}{V_{p-pa} M_{s-sa}}$$

C_M = 4.47 / 0.75 * (1+35.5) = **0.16 M***(mol/l)*

Example…

- Titer of H_2SO_4 solution is 0.004933 g /ml. Calculate the C_M of H2SO4

Answer…

Краткое изложение задачи:

$T(H_2SO_4) = 0{,}004933$ г/мл

$C_м(H_2SO_4) - ?$

$M(H_2SO_4) = 98$ г/моль

Решение: $C_M * M = T * 1000$

$$C_м(H_2SO_4) = \frac{T(H_2SO_4) \cdot 1000}{M(H_2SO_4)} =$$

$$= \frac{0{,}004933 \cdot 1000}{98} = 0{,}05 \text{ моль/л}$$

Example…

- There are 200 ml of NaOH solution with a concentration of 1 E. It is required to obtain from this solution a new one with a concentration of 0.05 E. How much water should be poured to the initial solution to obtain a solution with a given concentration?

Answer…

Write down a case summary (see below) and solve the case in general, interrupting for the search for an unknown parameter (finite volume NaOH - V). Insert the found parameter (4000 ml) into the required formula (first line) and write the final answer: it is necessary to pour 3.8 liters of water

Краткое изложение задачи:

$\Delta V(H_2O)$ - ?

$V^0(NaOH)$=200 мл
$C^0_э(NaOH)$=1 моль/л
$C_э(NaOH)$=0,05 моль/л

Ответ: надо прилить 3,8 л воды

Решение:

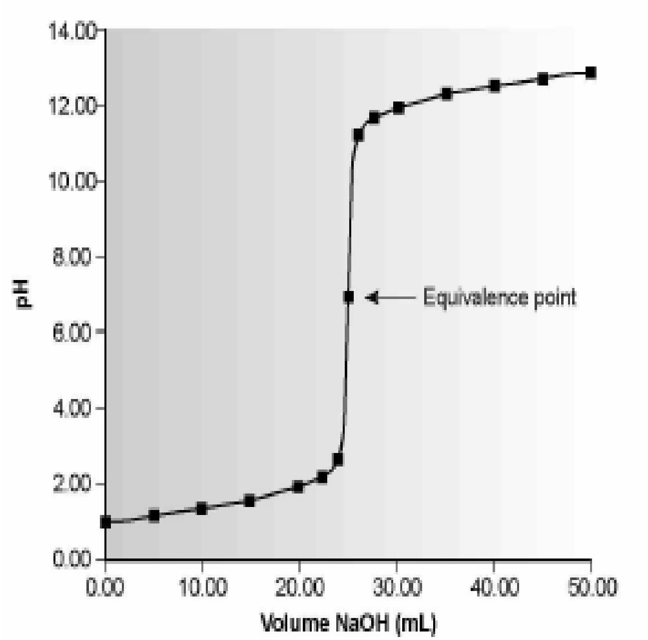
$\Delta V(H_2O) = V(NaOH) - V^0(NaOH)$ =:=

= 4000 – 200=3800 мл=3,8 л

$V(NaOH) = \frac{C^0_э \cdot V^0}{} = \frac{1 \cdot 200\ мл}{} = 4000$ мл

Acid Base Titration

To find the end point we monitor some property of the titration reaction that has a well defined at the equivalence point. For example, the equivalence point for a titration of HCl with NaOH occurs at a pH of 7.0. We can find the end point, therefore, by monitoring the pH with a pH electrode or by adding an indicator that changes color at a pH of 7.0.



Acid-base titration curve for 25.0 mL of 0.100 M HCl with 0.100 M NaOH.

Acid-Base Titration Curves

- Acid base titration curve: a graph of pH of a solution as titrant is added

- For an acid-base titration, the equivalence point is characterized by a **pH** level that is a function of the acid-base strengths and concentrations of the analyte and titrant.
- However, the pH at the end point may or may not correspond to the pH at the equivalence point. To understand the relationship between end points and equivalence points we must know how the pH changes during a titration. In this section we will earn how to construct titration curves for several important types of acid-base titrations.

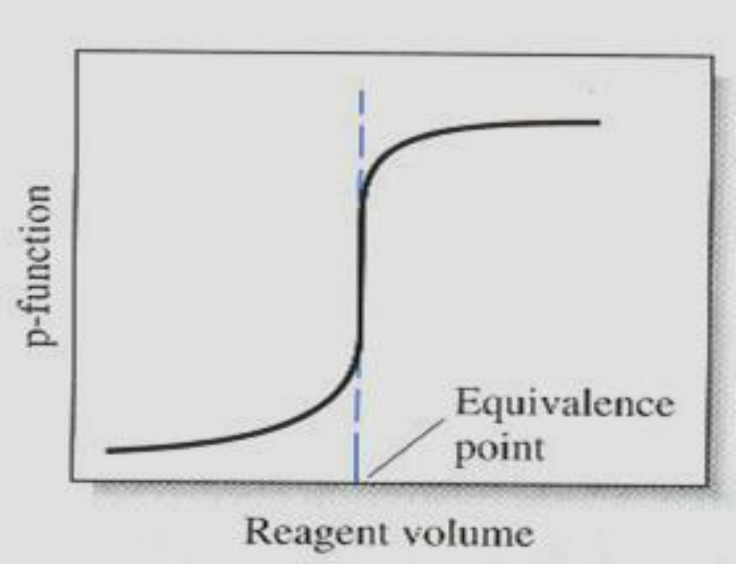
Titration Curves

Titration Curves are plots of a concentration-related variables as a function of reagent volume

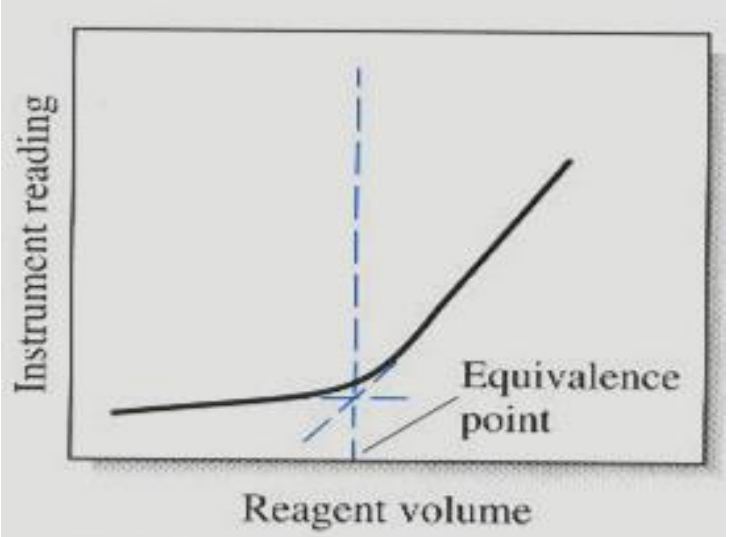
Two types of titration curves:

1. **Sigmoidal curve:** p-function of analyte (or sometimes the reagent) is plotted as a function of reagent volume.
2. **Linear segment curve:** measurement are made on both sides of but well away from the equivalence point. (advantageous for reaction that are complete only in the presence of a considerable excess of the reagent or analyte)

Types of Titration Curves



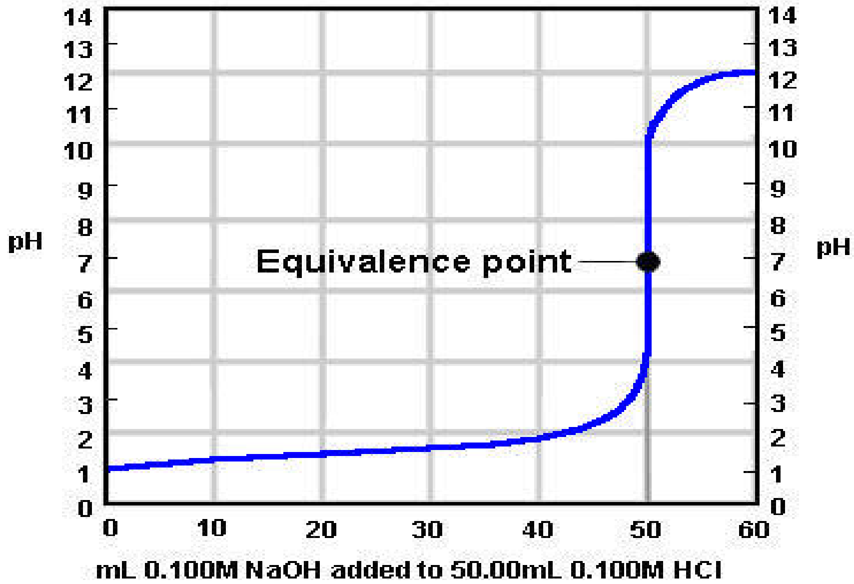
(a) Sigmoidal curve



(b) Linear-segment curve

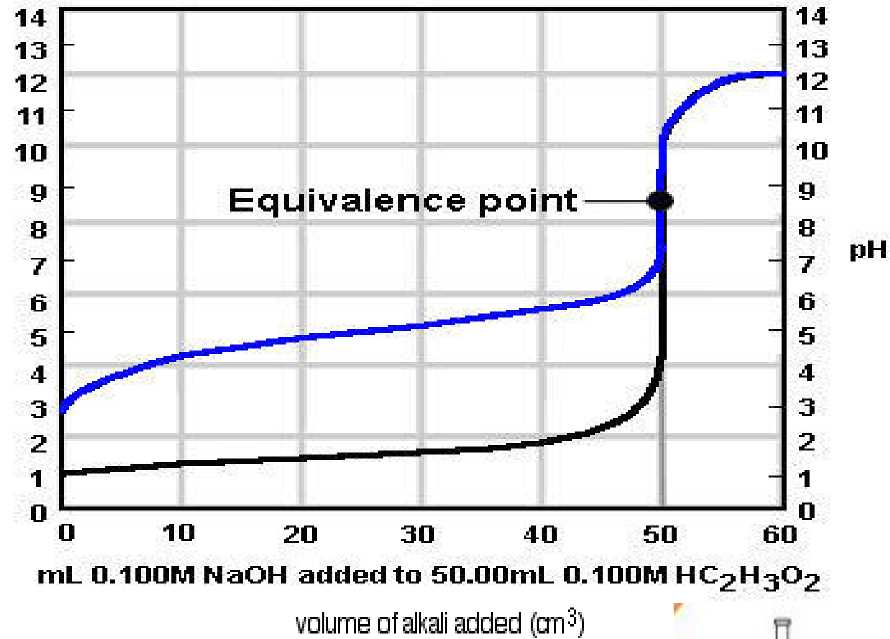
Titration Curves

1-Strong Acid-Strong Base Titrations

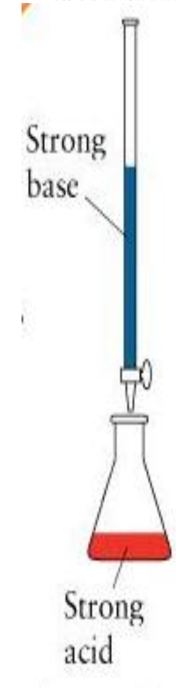


The **equivalence point** of the titration is the point at which exactly enough titrant has been added to react with all of the substance being titrated with no titrant left over. In other words, at the equivalence point, the number of moles of titrant added so far corresponds exactly to the number of moles of substance being titrated according to the reaction stoichiometry.

Titrations of a Weak Acid and Strong Base



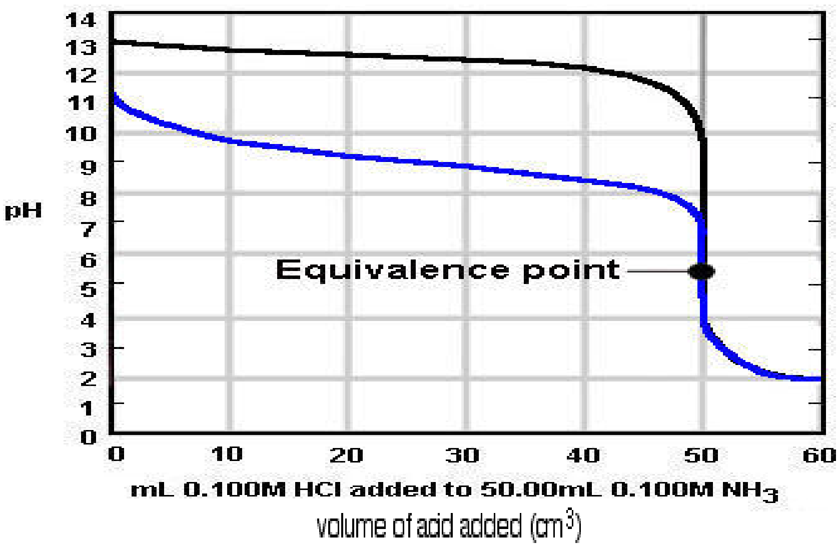
- There are three major differences between this curve (in blue) and the one we saw before (in black):
- 1. The weak-acid solution has a higher initial pH.
- 2. The pH rises more rapidly at the start, but less rapidly near the equivalence point.
- 3. The pH at the equivalence point does not equal 7.00.



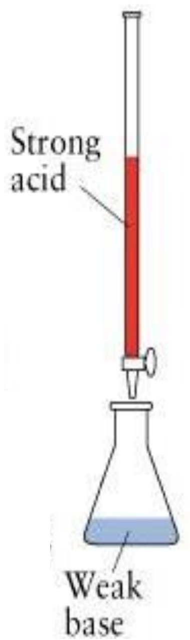
The equivalence point for a weak acid-strong base titration has a pH > 7.00.

Salt produced at equivalent point is **basic**

Titrations of a Weak Acid and Strong Base



1. The weak-base solution has a lower initial pH (blue curve)
2. The pH drops more rapidly at the start, but less rapidly near the equivalence point.
3. The pH at the equivalence point does not equal 7.00.



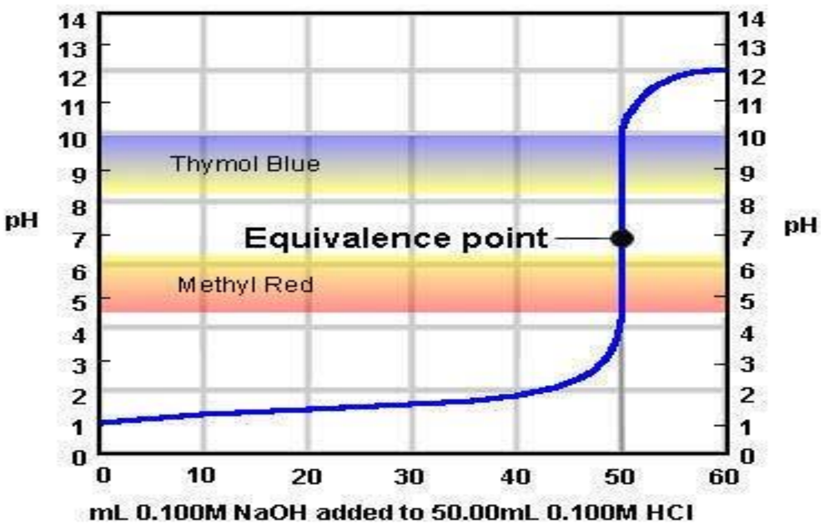
The equivalence point for a weak base-strong acid titration has a pH < 7.00

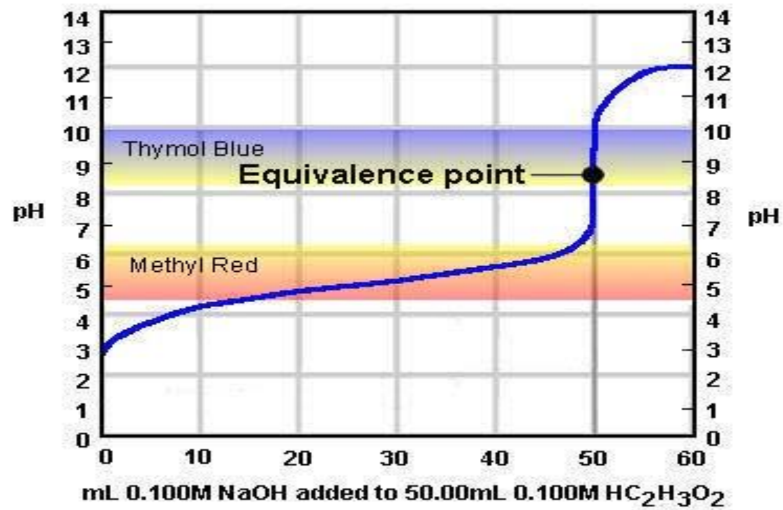
Salt formed at the equivalent point is **acidic**

When selecting an indicator, follow the rule:

- the pH value at the equivalence point (pHe) must fall within the transition zone of the indicator color, i.e. $\boxed{pH = pT \pm 1}$ *(please, see the next slide and read the Instructional guidelines, Theme No 1)*.

Choosing an indicator





In the strong acid titration, both indicators begin to change colour at the equivalence point (50 mL of base) so both work equally well. In the weak acid titration, thymol blue changes colour at the equivalence point, but methyl red begins to change colour after only 15mL of base are added, which is far from the equivalence point, illustrating the importance of choosing an appropriate indicator.

Таблица 1. Индикаторы

Индикатор	Окраска		$pK_a(pT_{Ind})$	pH-диапазонов изменения окраски
	в форме кислоты	в форме основания		
Тимоловый синий (первое изменение)	Красная	Желтая	1,5	1,2 – 2,8
Метиловый оранжевый	«	Желтая	3,7	3,2 – 4,4
Бромкрезоловый зеленый	Желтая	Синяя	4,7	3,8 – 5,4
Метиловый красный	Красная	Желтая	5,1	4,2 – 6,2
Лакмус (азолитмин)	«	Синяя		5,0 – 8,0
Бромтимоловый синий	Желтая	Синяя	7,0	6,0 – 7,6
Феноловый красный	«	Красная	7,9	6,8 – 8,4
Тимоловый синий (второе изменение)	«	Синяя	8,9	8,0 – 9,6
Фенолфталеин	Бесцветная	Малиновая	9,4	8,2 – 10,0
Тимолфталеин	«	Синяя		9,3 – 10,5

Task 1: choose one correct answer at this test (5 questions)

1/ TO DETERMINE THE EQUIVALENCE POINT IN THE METHOD OF NEUTRALIZATION IS/ARE USED:

a) starch

b) reactions with precipitate's formation

c) reactions with complex substances' formation

d) acid-base indicators

Task 1: choose one correct answer at this test (5 questions)

2/ THE MOLAR CONCENTRATION OF 20% HCL SOLUTION (P=1.1 G/ML) IS:

a) 5,1 mol/l

b) 6,03 mol/l

c) 4,75 mol/l

d) 2,35 mol/l

Task 1: choose one correct answer at this test (5 questions)

3/ THE MASS OF HNO_3 CONTAINED IN 200 ML OF 0.1 M OF ITS SOLUTION IS:

a) 1,41 g

b) 2,54 g

c) 1,26 g

d) 3,22 g

Task 1: choose one correct answer at this test (5 questions)

4/ THE VOLUME OF WATER THAT MUST BE ADDED TO 1.2 L OF 0.24 M HCL SOLUTION TO PREPARE 0.2 M HCL IS:

a) 240 ml

b) 100 ml

c) 150 ml

d) 200 ml

Task 1: choose one correct answer at this test (5 questions)

5/ THE INDICATORS IN THE METHOD OF NEUTRALIZATION ARE:

a) complexing agents

b) weak organic acids or bases

c) the solutions acting as indicators

d) eriochrome black

Task 2: prepare a short report (0.5 - 1.5 pages)

- What is gastric juice? What substances does it consist of?
- What are associated acidity, free acidity and total acidity? What are their normal values?
- How is the neutralization method used to determine the acidity of gastric juice?