

Practical Work No. 1:

pH-metric dosage (Dosage of a weak acid with a strong base)

1- Reminder:

- The self-containment of water and pH: It results in the following equilibrium:



- The law of mass action: $K_c(T) = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$

$[\text{H}_3\text{O}^+][\text{OH}^-] = K_c [\text{H}_2\text{O}]^2 = K_e / K_e$: The ionic product of water.

At 25°C: $[\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14} \text{ mol.l}^{-1}$

- The medium is acidic: $[\text{H}_3\text{O}^+] > 10^{-7} \text{ mol.l}^{-1}$
- The medium is neutral: $[\text{H}_3\text{O}^+] = 10^{-7} \text{ mol.l}^{-1}$
- The medium is basic: $[\text{H}_3\text{O}^+] < 10^{-7} \text{ mol.l}^{-1}$

The concentration limit between an acidic medium and a basic medium is an extremely small number $[\text{H}_3\text{O}^+] = 10^{-7} = 0.0000001 \text{ mol.l}^{-1}$

Generally speaking, $[\text{H}_3\text{O}^+]$ is expressed by negative powers of 10, such numbers are not convenient & handle. They should be transformed using a mathematical operation that simplifies writing. Each concentration is characterized by its negative decimal logarithm (cologarithm = 1/log).

We pose: $\text{pH} = \text{colog} [\text{H}_3\text{O}^+] = -\log [\text{H}_3\text{O}^+]$
 $\text{pOH} = \text{colog} [\text{OH}^-] = -\log [\text{OH}^-]$
 $\text{pK} = \text{colog} K = -\log K$

Example: $[\text{H}_3\text{O}^+] = 10^{-x} \text{ mol.l}^{-1} \Rightarrow \log [\text{H}_3\text{O}^+] = \log 10^{-x} = 10^{-\text{pH}} \Rightarrow \text{pH} = x (x > 0)$

pH of a strong monoacid:

A concentration C_a of strong acid HA is introduced into the water.

The dissociation is total: $\text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{A}^-$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = \log C_a$$

pH of a weak monoacid:

This time the dissociation reactions are equilibrium: $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$

Three equations will allow us to calculate the pH:

• **Law of mass action:** $K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}] [\text{H}_2\text{O}]} \Rightarrow K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \dots\dots\dots(1)$

• **Electrical neutrality of the solution:** In dissociation forms as many positive charges as charges negative. Neglecting the self-ionization of water, we have $[\text{H}_3\text{O}^+] = [\text{A}^-] \dots\dots\dots(2)$

• **Conservation of A during the dissociation:** $C_a = [\text{HA}] + [\text{A}^-] \dots\dots\dots(3)$

Equation (3) simplifies. In fact, the weak acid is very little dissociated. We neglect $[\text{A}^-]$ in front of $[\text{HA}]$.

We obtain the equation: $C_a = [\text{HA}] \dots\dots\dots(4)$

We enter into equation (1) the results (2) and (4)

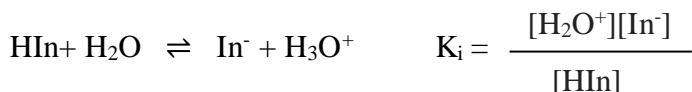
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{C_a} \Rightarrow [\text{H}_3\text{O}^+] = (K_a C_a)^{1/2} \Rightarrow -\log [\text{H}_3\text{O}^+] = \frac{1}{2} (-\log K_a - \log C_a)$$

And

$$\text{pH} = 1/2(\text{pK}_a - \log C_a)$$

- **Colored indicators:** A colored indicator is an acid-base pair whose acid form and basic form have different colors

Let K_i be the mass action constant of the equilibrium between the two forms:



- The first color is observed when: $[\text{H}_3\text{O}^+] \geq 10K_i$ either: $\text{pH} \leq \text{pK}_i - 1$
- The second color is observed when: $[\text{H}_3\text{O}^+] \leq K_i / 10$ either: $\text{pH} \geq \text{pK}_i + 1$

Example: Helianthin ($\text{pK}_i = 3.4$)

- First color:red when $\text{pH} \leq \text{pK}_i - 1 \Rightarrow \text{pH} \leq 2.4$
- Second color:yellow when $\text{pH} \geq \text{pK}_i + 1 \Rightarrow \text{pH} \geq 4.4$

2- Objectives:

- How to do the calibration?
- Determination of the concentration of ethanolic acid (CH_3COOH) by pH-metric assay.

3- Materials:

- pH-metric + electrode, stirrer, magnetic rod, graduated cylinder (150 ml), beaker (250 ml), graduated burette, funnel, volumetric pipette (10 ml).

4- Products:

- Buffer solutions ($\text{pH} = 7$, $\text{pH} = 4$ or $\text{pH} = 10$), Ethanol acid solution (CH_3COOH), Sodium hydroxide solution (NaOH) 0.1 mol/l. colored indicator and distilled water.

5- Operating Mode:

- Prepare the pH meter (calibration) using the buffer solutions.
- Refill the burette with the basic solution (NaOH).
- Using a pipette, take 10ml of CH_3COOH then add it to the graduated cylinder.
- Make up with distilled water to 150ml.
- Pour this volume into a beaker (250ml).
- Immerse the electrode and the magnetic bar in the acid solution then start stirring.
- Note the pH_0 value (initial pH).
- Add 2 to 3 drops of the colored indicator.
- Add 1ml each time and note the pH
 - ✓ **Note:** In the toning area (pour the basic solution drop by drop).
 - ✓ **Data:** Table of some colored indicators,

Indicator	turning area	First color (color in acidic environment) (HA)	Second color (color in the basic environment) (A ⁻)
Helianthin (Methyl's orange)	2.4 – 4.4	Red	Yellow
Methyl red	4,1 – 6.1	Red	Yellow
Bromothymol blue	6.6 – 7.6	Yellow	Red
Phenolphthalein	8.2 – 10.2	colorless	Red