Ch(7): pH-metric titration of weak acids with strong bases and of weak bases with strong acids.

Objectives

- Write the equation of the reaction of weak acid with strong base.
- Plot the curve pH = f(V_b).
- Determine the equivalence point from the titration curve.
- Calculate the concentration C_a .
- Describe the curve pH =f(V_b) and indicate the remarquable points.

I-pH-metric titration of weak acids (HA) with strong bases (OH^-)

Consider a solution of weak acid (HA) having unknown concentration C_a =?

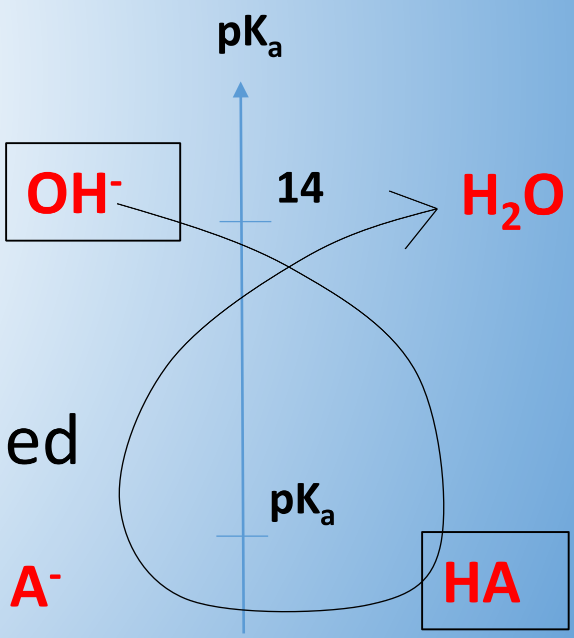
A volume $V_{a\ taken}$ = 10 mL form this solution is placed in a beaker and titrated with a solution of strong base (NaOH) of known concentration $C_b = 10^{-2}$ mol/L

The acid/base pair related to HA is : (HA/A^-) having a given pK_a

The pair related to strong base (NaOH) is : (H_2O/OH^-) : $pK_a = 14$

The equation of titration reaction is :

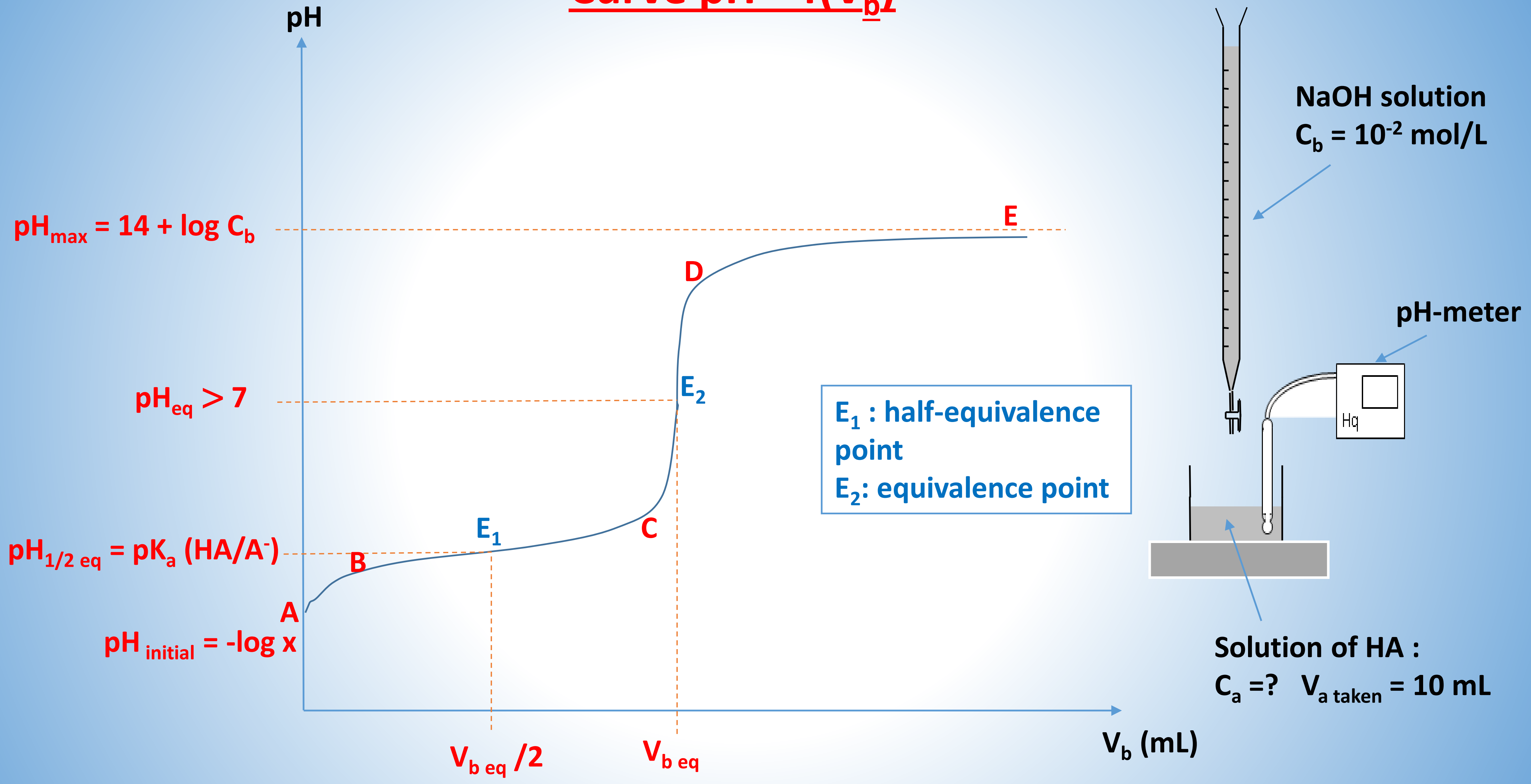
$$OH^- + HA \rightarrow A^- + H_2O \qquad K_R = 10^{(14-pKa)} > 10^4$$



This reaction is spontaneous (gamma rule), complete and should be quantitative ($K_R > 10^4$) and unique.

The pH of the solution is measured after each mL of NaOH added from the buret by using the pH-meter and the titration curve obtained has the following shape :

Curve pH = f(V_b)


pH
pH_{max} = 14 + log C_b
$pH_{eq} > 7$
$pH_{1/2\ eq}$ = pK_a (HA/A^-)
$pH_{initial}$ = -log x
A
B
C
D
E
E_1
E_2
$V_{b\ eq}$ /2
$V_{b\ eq}$
V_b (mL)
E_1 : half-equivalence point
E_2: equivalence point
NaOH solution
$C_b = 10^{-2}$ mol/L
pH-meter
Hq
Solution of HA :
C_a =? $V_{a\ taken}$ = 10 mL

Calculation of concentration C_a

The volume $V_{b\ equivalence}$ is determined from the curve pH= f(V_b) by the two parallel tangents method.

At equivalence, acc. to.SR :

$$n(HA)_{taken} = n(NaOH)_{added\ at\ equivalence}$$

$$n(HA)_{taken} = n(OH^-)_{added\ at\ equivalence}$$

$$C_a \times V_{a\ taken} = C_b \times V_{b\ eq}$$

$$C_a = \frac{C_b \times V_{b\ eq}}{V_{a\ taken}}$$

Justification of the value of pH at equivalence point E_2

At equivalence, the two reactants (HA) and (OH^-) are reacted completely and transformed into products.

The species present in the titration beaker at equivalence are : **A^-, H_2O and Na^+** obtained from NaOH.

Na^+ : is spectator ion that has no effect on the pH.

H_2O: is neutral.

A^- : is a weak base that reacts with water in a reversible reaction to produce a **little amount of OH^-** ions that gives **a pH >7** according to the following reaction:

$$A^- + H_2O \leftrightarrow HA + OH^-$$

Justification of the value of pH at the half- equivalence point E_1

At the half equivalence : $V_{b\ added} = \frac{V_{beq}}{2}$

At this point, the half of concentration of the acid HA is reacted and the other half is transformed into A^- ,thus $[HA]_{remained} = [A^-]_{formed}$

Since the two species are present in the same solution, therefore the pH of the solution is determined by the Handerson relation :

$$pH = pK_a\ (HA/A^-) + \log\left(\frac{[A^-]}{[HA]}\right) = pK_a + \log(1) = pK_a$$

$$pH_{1/2\ eq} = pK_a\ (HA/A^-)$$

Description of the curve $pH = f(V_b)$

This curve is an ascending curve that consists of **4 parts** and **two inflection points** :

Part AB : The pH increases relatively rapidly.

Part BC : The pH increases slightly forming a plateau. This part consist of inflection point E_1 which represents the half equivalence.

Part CD : The pH increases rapidly and the curve shows a jump of pH. This part consists of the inflection point E_2 which represents the equivalence point.

Part DE : The pH increases slightly again and the curve tends to reach a limit of pH.

II-Titration of weak base (B^-) with strong acid (H_3O^+)

The solution of **weak base (B^-)** of unknown concentration C_b is placed in the beaker and titrated by a **strong acid (HCl or HNO_3)** of known concentration C_a.

The volume of the base taken is **$V_{b\ taken}$ = 10 mL** is placed in the beaker and the pH-meter measures the pH after each mL of the acid added from the buret.

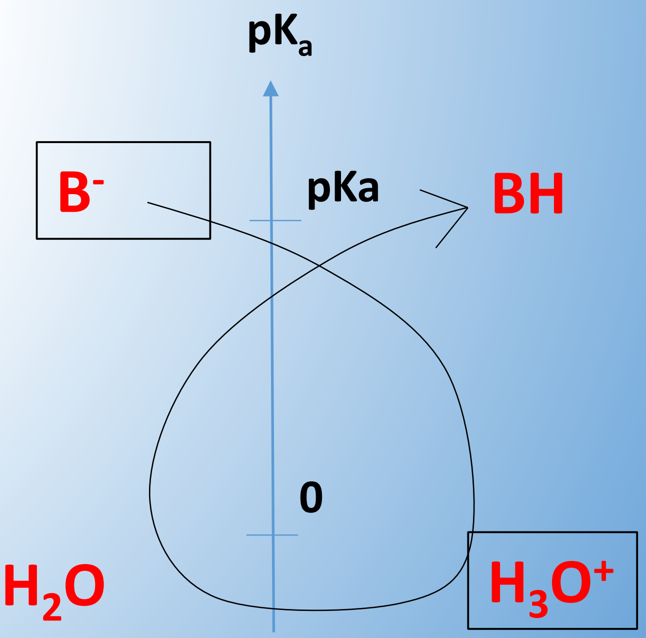
The acid/ base pair related to B^- is: **(BH/B^-)** having a given pK_a.

The pair related to the strong acid (HCl or HNO_3) is: **(H_3O^+/H_2O)** having a $pK_a = 0$

The equation of titration reaction is :

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

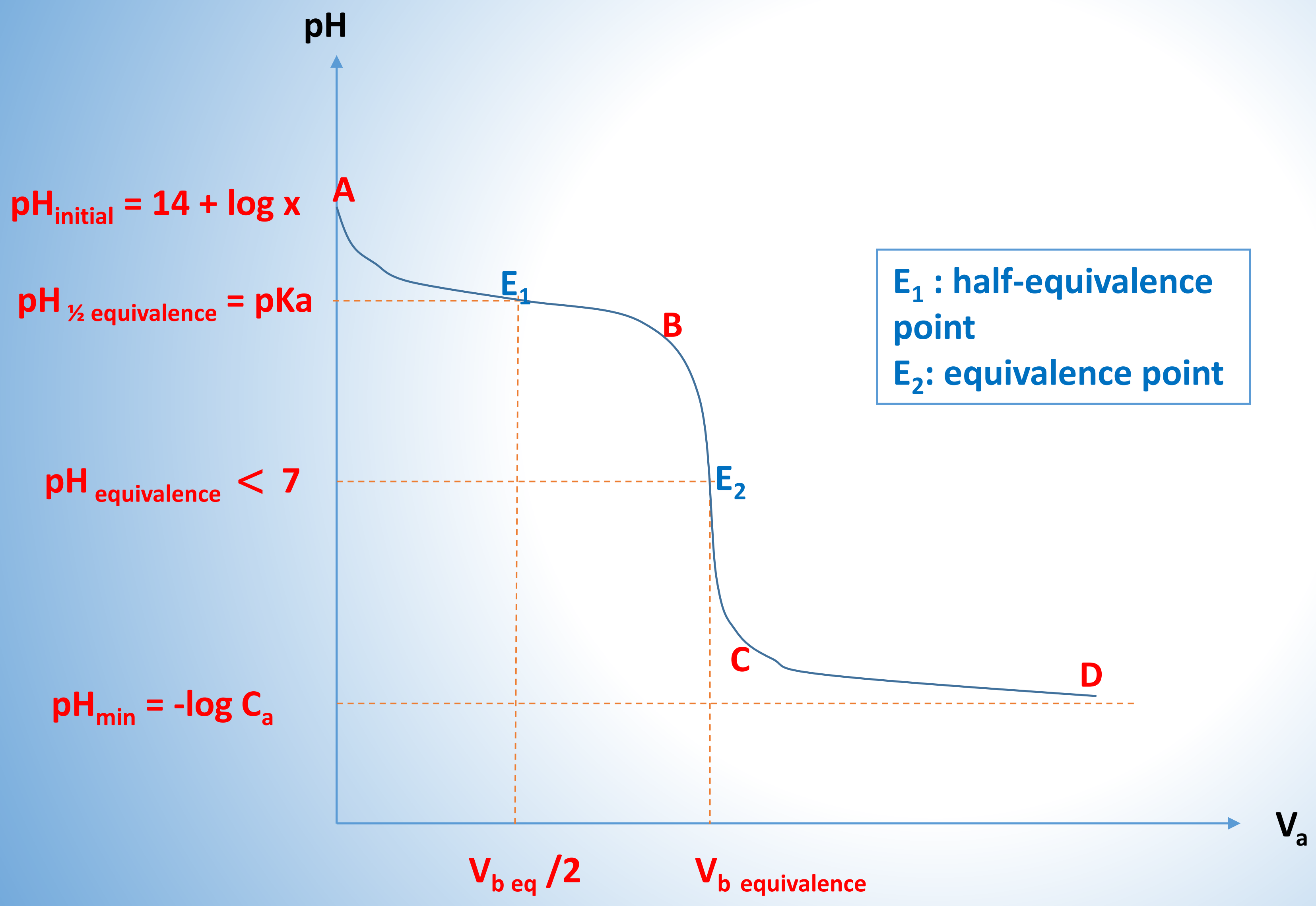
$$K_R = 10^{(pKa-0)} = 10^{pKa} > 10^4$$

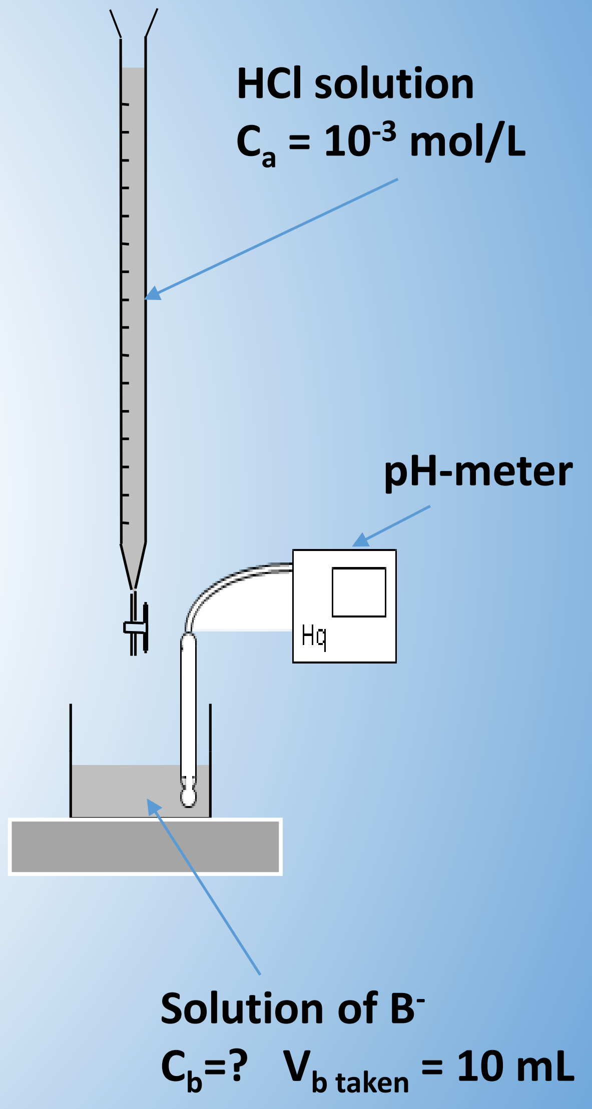


This reaction is spontaneous (gamma rule), complete and should be quantitative ($K_R > 10^4$) and unique.

The titration curve obtained has the following shape :

Curve : pH = f(V_a)


pH
$pH_{initial}$ = 14 + log x
A
$pH_{½ \ equivalence}$ = pKa
E_1
B
$pH_{equivalence}$ < 7
E_2
C
D
pH_{min} = -log C_a
V_a
$V_{b \ eq}$ /2
$V_{b \ equivalence}$
E_1 : half-equivalence point
E_2: equivalence point


HCl solution
$C_a = 10^{-3}$ mol/L
pH-meter
Solution of B^-
C_b=? $V_{b \ taken}$ = 10 mL

Calculation of concentration C_b

The volume $V_{a\ equivalence}$ is determined from the curve pH = f(V_a) by using the two parallel tangents method.

$$n(B^-)_{taken} = n(HCl)_{added\ at\ equivalence}$$

$$n(B^-)_{taken} = n(H_3O^+)_{added}$$

$$C_b \times V_{b\ taken} = C_a \times V_{a\ equivalence}$$

$$C_b = \frac{C_a \times V_{a\ eq}}{V_{b\ taken}}$$

Justification of the value of pH at the equivalence point E_2

At equivalence, the two reactants (B^-) and (H_3O^+) are reacted completely and transformed into products.

The species present in the titration beaker at equivalence are : **BH, H_2O and Cl^-** obtained from HCl.

Cl^- : is a spectator ion that has no effect on the pH.

H_2O: is neutral.

BH : is a weak acid that reacts with water in a reversible reaction to produce a **little amount of H_3O^+** ions that gives **a pH <7** according to the following reaction:

$$BH + H_2O \leftrightarrow B^- + H_3O^+$$

Justification of the value of pH at the half equivalence point E_1

At the half equivalence : $V_{a\ added} = \frac{V_{a\ eq}}{2}$

At this point, the half of concentration of the base B^- is reacted and the other half is transformed into BH ,thus $[B^-]_{remained} = [BH]_{formed}$

Since the two species are present in the same solution, therefore the pH of the solution is determined by the Handerson relation :

$$pH = pK_a\ (BH/B^-) + \log\left(\frac{[B^-]}{[BH]}\right) = pK_a + \log(1) = pK_a$$

$$pH_{1/2\ eq} = pK_a\ (BH/B^-)$$

Description of the curve pH = f(V_a)

This curve is an descending curve that consists of **4 parts** and **two inflection points** :

Part AB : The pH decreases relatively rapidly.

Part BC : The pH decreases slightly forming a plateau. This part consist of inflection point E_1 which represents the half equivalence.

Part CD : The pH decreases rapidly and the curve shows a jump of pH. This part consists of the inflection point E_2 which represents the equivalence point.

Part DE : The pH decreases slightly again and the curve tends to reach a limit of pH.

III- Acid/base indicators

An acid base indicator is an **acid/ base pair (HA/A^-)** having a **given pKa** where the conjugate **acid HA** has a color different than that of its conjugate **base A^-.**

For example : **HA** has a **yellow color** and **A^-** has a **blue color**.

Three cases are possible :

First case

If the indicator is placed in a solution having a **$pH < pKa-1$**, thus **HA predominates** in the solution and the color of the solution **becomes yellow**.

Second case

If the indicator is placed in a solution having a **$pH > pKa + 1$**, thus **A^- predominates** in the solution and the color of the solution **becomes blue.**

Third case

If the indicator is placed in a solution having a pH that ranges between pKa-1 and pKa+1 (**$pKa-1 < pH < pKa+1$**), thus **$[HA] \approx [A^-]$** and the color of solution is a mixture of yellow and blue **(green).**

Examples of acid/base indicators

Indicators	pKa	Color of the acid species (HA)	pH change range	Color of the base species (A^-)
Methyl orange	3.6	**Red**	3.1 – 4.4 **Orange**	**Yellow**
Methyl red	5.1	**Red**	4.2 – 6.2 **Orange**	**Yellow**
Bromothymol blue	6.8	**Yellow**	6 – 7.6 **Green**	**Blue**
Phenolphtalein	9	**Colorless**	8.2 – 10 **Pink**	**Purple**