Practical Session n°15: How to determine the acidity constant K_A (and its corresponding pK_A) of an acid/base couple

1- Problem

Unfortunately, two stains deleted the formulas corresponding to two weak acids (**ethanoic acid** and **methanoic acid**) on a pK_A scale of a French chemist (see document 3).
In our lab, solutions of these two acids are available at a concentration C_A = 1.0 x 10^{-1} mol.L^{-1}.
You can also have two solutions of their conjugated bases (**sodium ethanoate** and **sodium methanoate**) with an identical concentration C_B = 1.0 x 10^{-1} mol.L^{-1}.
Using the documents, you have to design and carry out experiments to find the hidden names on the pK_A scale given in document 3. Note that only the pK_A values of the two acid/base couples are still legible: 3.8 and 4.8.

2- Documents at your disposal

Document 1: Equilibrium constant and pK_A

Some chemical reactions are total and when they are finished, the whole initial amount of limiting reactant is used up. But others don't.
Non-total reactions are said **reversible** because when products are formed they react together to re-produce the reactants. Therefore, the final state doesn't correspond to the total consumption of the limiting reactant. In such cases, when the chemical system reaches its final state, it reaches an **equilibrium state** in which both reactants and products are present. That's why the equations of reversible reactions are written with a double arrow $\rightleftharpoons$ reflecting the fact that the two reactions, the forward and the reverse ones, simultaneously occur in the system.

Let HA/A^- be an acid/base couple. The acid HA reacts with water:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons A^-_{(aq)} + H_3O^+_{(aq)}.$$

The **acidity constant K_A** at a given temperature is defined by the opposite relation.

$$K_A = \frac{[A^-]_{eq} \cdot [H_3O^+]_{eq}}{[HA]_{eq}}$$

And, by definition, $\mathbf{pK_A = -\log(K_A)}$. In other words, $\mathbf{K_A = 10^{-pK_A}}$.

Remarks: - K_A is a dimensionless physical quantity. It has no unit.
- In the opposite relation, the concentrations at the equilibrium state of each reactant and product should be expressed in mol/L.

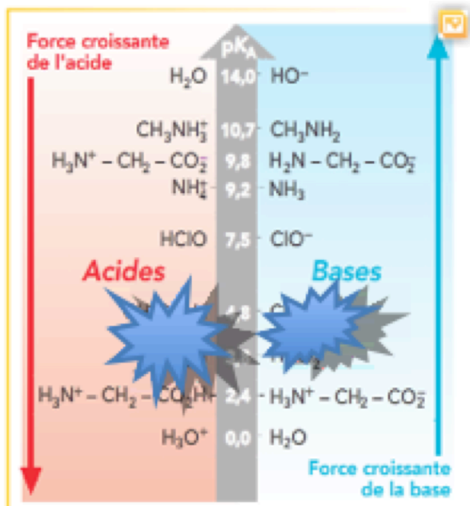
Therefore, a relation between pH and pK_A can be deduced (see the lesson).

$$pH = pK_A + \log\left(\frac{[A^-]_{eq}}{[HA]_{eq}}\right)$$

Document 2: pK_A scale in water

pK_A quantifies the ability of an acid to donate a proton (or the ability of a base to accept a proton).
The extreme values of the pK_A scale in water are the pK_A values of the two acid/base couples involving water.
In aqueous solution, the strongest acid is H_3O^+ and the strongest base is HO^-.

Document 3: a pK_A scale



3- Preliminary questions

- **a.** *Write the equation of ethanoic acid reacting with water.*
- **b.** *Write the equation of methanoic acid reacting with water.*
- **c.** *Express the K_A and the pK_A of each acid/base couple.*
- **d.** *Compare the pK_A of $HClO/ClO^-$ with the one of NH_4^+/NH_3.*
- **e.** *Compare the K_A of $HClO/ClO^-$ with the one of NH_4^+/NH_3.*
- **f.** *Compare the strength of HClO with the one of NH_4^+.*
- **g.** *Compare the pH of a solution of HClO of concentration C_A with the one of a solution of NH_4^+ at a same concentration.*
- **h.** *What should be done before measuring a pH?*

4- How to solve the problem easily

Suggest a simple method to complete the deleted part of the pK_A scale of document 3.
Carry out you method.

5- Solving the problem with an experimental determination of the pK$_A$ of each couple

5.1- Procedure

Let V_A be the volume of the solution containing the acid and V_B the volume of the solution containing the base.
All the solutions have the same concentration $C_A = C_B = 1.0 \times 10^{-1}$ mol.L^{-1}.

Take, with a graduated burette, an initial 25.0 mL volume of acid (or base) to which you will add the volumes of its conjugated base (or conjugated acid) indicated in the table below.
Place the mixture under magnetic stirring and measure its pH after having stopped stirring.
Take great care of the pH cell while stirring. The magnetic bar must never touch the glass part of the cell.
Reproduce and complete this table in an OpenOffice spreadsheet.
Then, record the results you get in this table.

V_A (mL)	V_B (mL)	$\frac{V_B}{V_A}$	$\log\left(\frac{V_B}{V_A}\right)$	pH
25.0	5.0			
25.0	8.0			
25.0	12.5			
25.0	20.0			
25.0	25.0			
5.0	25.0			
8.0	25.0			
12.5	25.0			
20.0	25.0			

5.2- Exploiting the results

- For the moment, let assume that $\frac{[A^-]_{eq}}{[HA]_{eq}} = \frac{V_B}{V_A}$ (the demonstration will be done later).

- Plot the graph of $pH = f\left(\log\left(\frac{V_B}{V_A}\right)\right)$

- Draw the shape of the curve and record its equation (obtained by building a model) on you report.
- Deduce from this equation the pKA of the acid/base couple you have studied. Justify your answer.

6- Conclusion

Assign to each values of pKA the correct acid/base couple.

Demonstrating the following relation : $\frac{[A^-]_{eq}}{[HA]_{eq}} = \frac{V_B}{V_A}$

During this lab session, we have artificially created equilibrium states by mixing various amounts of $AH_{(aq)}$ and $A^-_{(aq)}$. The reaction of these two species with water is very limited and we assume that the amounts of these two chemical species remain unchanged. Therefore, we consider that $[HA]_{eq} = [HA]_i$ and $[A^-]_{eq} = [A^-]_i$.

- Express the concentrations in acid $[HA]_{eq}$ and the one in base $[A-]_{eq}$ as a function of C_A, C_B, V_A and V_B.

- Deduce the following relation: $\frac{[A^-]_{eq}}{[HA]_{eq}} = \frac{V_B}{V_A}$.