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## IONIC EQUILIBRIUM CALCULATIONS: A PROBLEM SOLVING APPROACH

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**ABSTRACT:** Students are not able to solve ionic equilibrium problems in a systematic way and using a series of rote-learned formulae is not the best didactic approach. The student has to ask himself or herself questions in order to decide what formula to use: *Is this a buffer solution? Are we at the equivalence point? Is the hydrolysis appreciable? Can the dissociation of this weak acid be considered negligible?* And so on. These questions bewilder the student (but not the expert chemist) who has to evaluate terms such as "negligible", "perceptible" or "significant". As instructors, we can agree that the difficulty faced by the students in solving such problems is the recognition of the chemical approach required in different situations. Here, a method is presented here that helps the student to develop metacognitive skills, such as planning and trying out of potential problem solutions in qualitative terms before making any calculations. Heuristics for checking the result such as "check the implications of your solution" or "are the units of measurements of the result correct?" are substituted by the more powerful numerical check of the mass balance equation, the electroneutrality condition and the control of unchanged quantity. [*Chem. Educ. Res. Pract. Eur.*: 2000, 1, 151-160]

**KEY WORDS:** *ionic equilibrium; problem solving; problem representation; numerical check; relative error*

### INTRODUCTION

Ionic equilibrium calculations constitute a homogeneous group of problems that are of substantial educational importance but students find cognitive difficulties in learning how to solve them. Ability in solving ionic equilibrium calculations is of importance not only in chemistry, biology, and geology, but also in environmental engineering because of the processes taking place in the environment, in natural waters and in the weathering of rocks. We need a solution procedure that can be used in these different didactic situations and that can suit very different reasoning styles. Because a rigorous mentality is needed to face all science courses, we can use this topic to improve the students' capacity of logical thinking in problem solving. Significant knowledge must be personally constructed. By promoting critical thinking skills we prompt our students to develop higher-order cognitive skills and conceptual learning.

Ionic equilibrium problems in general chemistry textbooks are solved using some formulas derived from the Butler 5% approximation rule (Butler, 1961). The drawback of using

memorized formulas to solve problems is that they are shortcuts and avoid a systematic reasoning. In practice, this approach leads the student to solve ionic equilibrium problems using some rote-learned formulas or an algorithm; they can solve problems without processing the information and referring to a correct chemical representation. The student has to ask himself or herself questions in order to decide what formula to use: is this a buffer solution? Are we at the equivalence point? Is the hydrolysis appreciable? Can the dissociation of this weak acid be considered negligible?

Sometimes, this approach leads to the application of a procedure that leads to imprecise results, because the student does not remember the hypothesis that makes the approximate formula work. This method fails because the student cannot estimate the result with the necessary precision. Often, this method leads to correct results, but the logical abilities and the critical thinking of the student are used at a very low level. On asking students to find the hydrogen ion concentration of a water solution of acetic acid ( $K_a = 1.753 \times 10^{-5}$  M)  $1.00 \times 10^{-7}$  M, much to my surprise, someone solved the problem in this way

$$[H^+] = (K_a C_a)^{1/2} = 1.32 \times 10^{-6} \text{ M}$$

where  $C_a$  is the total acid concentration. How is it possible that  $[H^+] = 13.2 \times C_a$  (Cardellini, 1996 a)? Referring to acid solutions, textbooks always work examples where  $[H^+] = C_a$  or  $[H^+] = (K_a C_a)^{1/2}$  and where  $C_a$  is the total acid concentration, without ever considering the water dissociation. In this way, students memorize a generalization of the hypothesis in the form "All p's are q"; this is a logical implication: p implies q. In our case p is "acid solution" and q is "there is no need to consider the water dissociation" (Cardellini, 1996 b). The same can be said about the Henderson-Hasselbach equation (Cardellini, 1997): all these approximate equations fail under some circumstances.

The didactic approach of acid-base calculation must, as Freiser suggested years ago, avoid the Scylla of oversimplification to achieve "clarity" and the Charybdis of "cumbersome" rigorous equations (Freiser, 1970). The new method here proposed uses a logical-reasoning scheme that all students can apply and it needs some information from the theory. This method improves the ability level of all students and lets poor students become good students.

## PROCEDURE

The relative error, E, as a percentage is defined as the absolute value of

$$E = (1 - [H^+]_{\text{approx.}}/[H^+]) \times 100$$

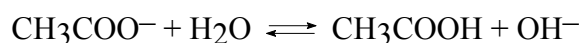
where  $[H^+]_{\text{approx.}}$  is the found result and  $[H^+]$  is the correct result. The correct result is the result obtained using a sounding solution procedure from a chemical point of view and which satisfies the verification, taking the significant figures into account. A good method of calculation, using three significant figures, is one that produces results with E no greater than 1%. The method here proposed uses a problem solving approach (Hayes, 1989):

- 1 - find the problem and categorize it;
- 2 - represent the problem and evaluate the result;

- 3 - make a plan for the solution;
- 4 - carry out the plan;
- 5 - verify the result.

The categorization of the problem (buffer solution, acid-base titration...) is useful because it can activate in the student's mind a useful scheme. So, categorization helps also in the representation step. The problem is represented using the information derived from the theory:

- 1 - Water is always ionized according to the equilibrium:  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$  and the ion product of water must always be verified:  $[\text{H}^+][\text{OH}^-] = K_w$ . Sometimes the  $\text{H}^+$  coming from water ionization must be taken into account.
- 2 - Acids and bases always react.
- 3 - Strong acids, bases and ionic salts are completely ionized.
- 4 - Weak acids and bases are partially ionized; conjugate species undergo hydrolysis:



Now, the student can evaluate the result: acidic, basic or neutral, using the D factor (difference between the acid-base balance equilibrium) and visualize the water equilibrium with diagrams, as suggested by Guenther (Guenther, 1991). When appropriate, at this point it is possible to redefine the problem and make a plan for the solution. The student then carries out the calculations and from the obtained  $[\text{H}^+]$  value can evaluate if  $[\text{H}^+]$  derived from the autoionisation of water must be taken into consideration.

At the end, the student must verify the correctness of the result by checking these equations:

- 1 - mass balance equation;
- 2 - electroneutrality condition;
- 3 - dissociation constant.

If the conditions are fulfilled, taking significant figures into account, students know that they have solved the problem in the correct way.

## SOME EXAMPLES

### Strong acids

Let us consider this problem: calculate the pH of a solution  $1.00 \times 10^{-7}$  M of hydrochloric acid. The following reactions take place:



This is the way the problem can be represented; the student can now evaluate the result: from the theory and from the information present in the text of the problem, he can establish that

an acid solution has to have a pH less than 7 (certainly, it cannot be 7, if the relation  $[H^+] = C_{HA}$  is used); so he must obtain:  $[H^+] > [OH^-]$ .



$$\begin{array}{l} b \quad 1.00 \times 10^{-7} \quad 0 \quad 0 \\ a \quad 0 \quad 1.00 \times 10^{-7} \quad 1.00 \times 10^{-7} \end{array}$$

where  $b$  means before (the reaction takes place) and  $a$  means after. So we have:

$$[H^+] = 1.00 \times 10^{-7} \text{ M} \quad [Cl^-] = 1.00 \times 10^{-7} \text{ M}$$

If  $r$  mol  $L^{-1}$  of  $H_2O$  ionizes at equilibrium,



$$\begin{array}{l} \text{Initial concentrations} \quad 1.00 \times 10^{-7} \quad 0 \\ \text{Equilibrium concentrations} \quad 1.00 \times 10^{-7+r} \quad r \end{array}$$

$r$  must be included in the interval  $0 < r < (K_w)^{1/2}$  M. Now, we can combine the various information:

$$K_w = 1.00 \times 10^{-14} \text{ M}^2 = (1.00 \times 10^{-7} \text{ M} + r \text{ M})(r \text{ M})$$

Students can try to evaluate an approximate solution of this equation: they can make the hypothesis  $1.00 \times 10^{-7} \text{ M} + r \text{ M} = 1.00 \times 10^{-7} \text{ M}$ . The approximate solution is  $r = (1.00 \times 10^{-14} \text{ M}^2) / (1.00 \times 10^{-7} \text{ M}) = 1.00 \times 10^{-7} \text{ M}$ . So they know that the approximation is not acceptable.

$$r = 6.18 \times 10^{-8} \text{ M} \quad [OH^-] = r = 6.18 \times 10^{-8} \text{ M}$$

$$[H^+] = 1.00 \times 10^{-7} \text{ M} + 6.18 \times 10^{-8} \text{ M} = 1.618 \times 10^{-7} \text{ M} \quad \text{pH} = 6.791$$

Verification. It is necessary to verify if the solution is acceptable:

$$1. \text{ Electroneutrality condition: } [OH^-] + [Cl^-] = 1.62 \times 10^{-7} \text{ M}$$

$$2. \text{ Dissociation constant: } [H^+][OH^-] = 1.00 \times 10^{-14} \text{ M}^2$$

The conditions are fulfilled taking significant figures into account. Thus, students know that they have solved the problem in the correct way.

### Weak acids

With this method, the initial problem can be solved, obtaining  $[H^+] = 1.61 \times 10^{-7} \text{ M}$  (Cardellini, 1996 a); an identical result for the same problem is found by using Guenther's

method (Guenther, 1991, p. 37). Let us now consider this problem: find the hydrogen ion concentration of a water solution that contains acetic acid  $1.00 \times 10^{-3}$  M and citric acid ( $\text{H}_3\text{Ci}$ ;  $K_1 = 7.41 \times 10^{-4}$  M;  $K_2 = 1.74 \times 10^{-5}$  M;  $K_3 = 3.98 \times 10^{-7}$  M; )  $1.00 \times 10^{-3}$  M.

The students can solve the problem in this way: because  $[\text{H}_3\text{Ci}]_i K_1 > [\text{CH}_3\text{COOH}]_i K_a$ , it is better to start with the ionisation of citric acid.  $[\text{H}_3\text{Ci}]_i$  is the initial concentration; if  $r_1$  mol  $\text{L}^{-1}$  of  $\text{H}_3\text{Ci}$  ionizes, we have:



Initial concentrations	$1.00 \times 10^{-3}$	0	0
Equilibrium concentrations	$1.00 \times 10^{-3} - r_1$	$r_1$	$r_1$

$r_1$  must be included in the interval  $0 < r_1 < 1.00 \times 10^{-3}$  M. We have:

$$K_1 \times (1.00 \times 10^{-3} \text{ M} - r_1 \text{ M}) = (r_1 \text{ M})^2$$

$$r_1 = 5.67 \times 10^{-4} \text{ M.}$$

Analogously, we have:

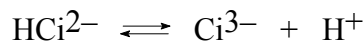


Initial concentrations	$5.67 \times 10^{-4}$	0	$5.67 \times 10^{-4}$
Equilibrium concentrations	$5.67 \times 10^{-4} - r_2$	$r_2$	$5.67 \times 10^{-4} + r_2$

$r_2$  must be included in the interval  $0 < r_2 < 5.67 \times 10^{-4}$  M. We obtain:

$$K_2 \times (5.67 \times 10^{-4} \text{ M} - r_2 \text{ M}) = (5.67 \times 10^{-4} \text{ M} + r_2 \text{ M}) \times (r_2 \text{ M})$$

$$r_2 = 1.64 \times 10^{-5} \text{ M} \quad [\text{H}^+] = r_1 \text{ M} + r_2 \text{ M} = 5.83 \times 10^{-4} \text{ M.}$$



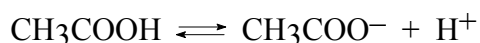
Initial concentrations	$1.64 \times 10^{-5}$	0	$5.83 \times 10^{-4}$
Equilibrium concentrations	$1.64 \times 10^{-5} - r_3$	$r_3$	$5.83 \times 10^{-4} + r_3$

$r_3$  must be included in the interval  $0 < r_3 < 1.64 \times 10^{-5}$  M. We have:

$$K_3 \times (1.64 \times 10^{-5} \text{ M} - r_3 \text{ M}) = (5.83 \times 10^{-4} \text{ M} + r_3 \text{ M}) \times (r_3 \text{ M})$$

$$r_3 = 1.12 \times 10^{-8} \text{ M} \quad [\text{H}^+] = r_1 \text{ M} + r_2 \text{ M} + r_3 \text{ M} = 5.83 \times 10^{-4} \text{ M.}$$

Now we consider the ionisation of acetic acid:



Initial concentrations	$1.00 \times 10^{-3}$	0	$5.83 \times 10^{-4}$
Equilibrium concentrations	$1.00 \times 10^{-3} - r$	$r$	$5.83 \times 10^{-4} + r$

$r$  must be contained in the interval  $0 < r < 1.00 \times 10^{-3}$  M. We have:

$$K_a \times (1.00 \times 10^{-3} \text{ M} - r \text{ M}) = (5.83 \times 10^{-4} \text{ M} + r \text{ M}) \times (r \text{ M})$$

$$r = 2.79 \times 10^{-5} \text{ M} \quad [\text{H}^+] = 5.83 \times 10^{-4} \text{ M} + r \text{ M} = 6.11 \times 10^{-4} \text{ M},$$

but the verification conditions are not fulfilled.

Now we consider how the ionisation of acetic acid influences the ionisation of citric acid:

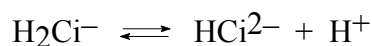


Initial concentrations	$1.00 \times 10^{-3}$	0	$2.79 \times 10^{-5}$
Equilibrium concentrations	$1.00 \times 10^{-3} - r_1$	$r_1$	$2.79 \times 10^{-5} + r_1$

again,  $r_1$  must be included in the interval  $0 < r_1 < 1.00 \times 10^{-3}$  M. We have:

$$K_1 \times (1.00 \times 10^{-3} \text{ M} - r_1 \text{ M}) = (2.79 \times 10^{-5} \text{ M} + r_1) \times (r_1 \text{ M})$$

$$r_1 = 5.58 \times 10^{-4} \text{ M} \quad [\text{H}^+] = 5.86 \times 10^{-4} \text{ M}.$$

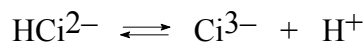


Initial concentrations	$5.58 \times 10^{-4}$	0	$5.86 \times 10^{-4}$
Equilibrium concentrations	$5.58 \times 10^{-4} - r_2$	$r_2$	$5.86 \times 10^{-4} + r_2$

$r_2$  must be contained in the interval  $0 < r_2 < 5.58 \times 10^{-4}$  M. We have:

$$K_2 \times (5.58 \times 10^{-4} \text{ M} - r_2 \text{ M}) = (5.86 \times 10^{-4} \text{ M} + r_2 \text{ M}) \times (r_2 \text{ M})$$

$$r_2 = 1.59 \times 10^{-5} \text{ M} \quad [\text{H}^+] = r \text{ M} + r_1 \text{ M} + r_2 \text{ M} = 6.02 \times 10^{-4} \text{ M}.$$



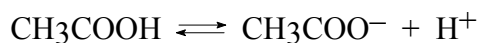
Initial concentrations	$1.59 \times 10^{-5}$	0	$6.02 \times 10^{-4}$
Equilibrium concentrations	$1.59 \times 10^{-5} - r_3$	$r_3$	$6.02 \times 10^{-4} + r_3$

$r_3$  must be included in the interval  $0 < r_3 < 1.59 \times 10^{-5}$  M. We have:

$$K_3 \times (1.59 \times 10^{-5} \text{ M} - r_3 \text{ M}) = (6.02 \times 10^{-4} \text{ M} + r_3 \text{ M}) \times (r_3 \text{ M}) \quad r_3 = 1.05 \times 10^{-8} \text{ M}.$$

Now we find how the ionisation of citric acid influences the ionisation of acetic acid.

From citric acid,  $[\text{H}^+] = r_1 \text{ M} + r_2 \text{ M} + r_3 \text{ M} = 5.78 \times 10^{-4} \text{ M}$ ,



Initial concentrations	$1.00 \times 10^{-3}$	0	$5.78 \times 10^{-4}$
Equilibrium concentrations	$1.00 \times 10^{-3} - r$	r	$5.78 \times 10^{-4} + r$

r must be contained in the interval  $0 < r < 1.00 \times 10^{-3}$  M.

$$K_a \times (1.00 \times 10^{-3} \text{ M} - r \text{ M}) = (5.78 \times 10^{-4} \text{ M} + r \text{ M}) \times (r \text{ M})$$

$$r = 2.81 \times 10^{-5} \text{ M.}$$

The relative difference of this value with the precedent r is  $(2/281) \times 100$ , which is less than 1%.  
Now we check the results:

$$[\text{H}^+] = 5.78 \times 10^{-4} \text{ M} + 2.81 \times 10^{-5} \text{ M} = 6.06 \times 10^{-4} \text{ M}$$

Because  $[\text{H}^+] > 1.00 \times 10^{-6}$  M (Gordus, 1991), we can neglect the water ionisation:

$$[\text{OH}^-] = K_w / [\text{H}^+] = 1.65 \times 10^{-11} \text{ M} \quad [\text{CH}_3\text{COOH}] = 1.00 \times 10^{-3} \text{ M} - r \text{ M} = 9.72 \times 10^{-4} \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = 2.81 \times 10^{-5} \text{ M} \quad [\text{C}_i^{3-}] = 1.05 \times 10^{-8} \text{ M} \quad [\text{HC}_i^{2-}] = 1.59 \times 10^{-5} \text{ M}$$

$$[\text{H}_2\text{C}_i^-] = 5.42 \times 10^{-4} \text{ M} \quad [\text{H}_3\text{C}_i] = 4.42 \times 10^{-4} \text{ M}$$

Verification:

### 1. Mass balance equation

$$[\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-] = 1.00 \times 10^{-3} \text{ M}$$

$$[\text{C}_i^{3-}] + [\text{HC}_i^{2-}] + [\text{H}_2\text{C}_i^-] + [\text{H}_3\text{C}_i] = 1.00 \times 10^{-3} \text{ M}$$

### 2. Electroneutrality condition

$$[\text{OH}^-] + [\text{CH}_3\text{COO}^-] + [\text{H}_2\text{C}_i^-] + 2[\text{HC}_i^{2-}] + 3[\text{C}_i^{3-}] = 6.02 \times 10^{-4} \text{ M}$$

### 3. Dissociation constants

$$[\text{H}^+][\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}] = 1.75 \times 10^{-5} \text{ M} \quad [\text{H}^+][\text{C}_i^{3-}]/[\text{HC}_i^{2-}] = 4.00 \times 10^{-7} \text{ M}$$

$$[\text{H}^+][\text{HC}_i^{2-}]/[\text{H}_2\text{C}_i^-] = 1.78 \times 10^{-5} \text{ M} \quad [\text{H}^+][\text{H}_2\text{C}_i^-]/[\text{H}_3\text{C}_i] = 7.43 \times 10^{-4} \text{ M}$$

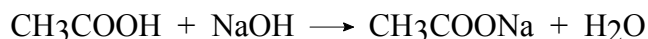
The conditions are fulfilled taking significant figures into account. We can note that if we stop at the first iteration, the electroneutrality condition is not verified. For the solution of this problem students cannot find ready-to-use formulas.

**Acid-base titration**

To 25.00 mL of  $1.000 \times 10^{-2}$  M  $\text{CH}_3\text{COOH}$  are added  $2.500 \times 10^{-1}$  mL of  $1.000 \times 10^{-2}$  M  $\text{NaOH}$ . Calculate the pH of the resulting solution. A reaction takes place; we have:

$$(25.00 \text{ mL}) \times (1.000 \times 10^{-2} \text{ mol CH}_3\text{COOH/L}) \times (10^{-3} \text{ L/mL}) = 2.500 \times 10^{-4} \text{ mol CH}_3\text{COOH}$$

$$(2.500 \times 10^{-1} \text{ mL}) \times (1.000 \times 10^{-2} \text{ mol NaOH/L}) \times (10^{-3} \text{ L/mL}) = 2.500 \times 10^{-6} \text{ mol NaOH}$$



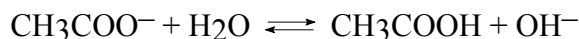
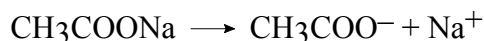
<i>b</i>	$2.500 \times 10^{-4}$	$2.500 \times 10^{-6}$	0	0
<i>a</i>	$2.475 \times 10^{-4}$	0	$2.500 \times 10^{-6}$	$2.500 \times 10^{-6}$

where *b* means before (the reaction takes place) and *a* means after. If we train our students to use formulas, the result is:  $\text{pH} = \text{pK}_a + \log (C_s/C_a) = 2.761$ . If we train our students to use a reasoning procedure based on chemistry processes, it is possible to obtain a better result. After the addition of  $\text{NaOH}$ , we have:  $V = 25.00 \text{ mL} + 2.500 \times 10^{-1} \text{ mL} = 25.25 \text{ mL}$ ;

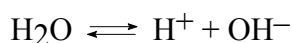
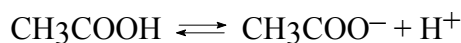
$$[\text{CH}_3\text{COOH}] = (2.475 \times 10^{-4} \text{ mol CH}_3\text{COOH}) / (25.25 \times 10^{-3} \text{ L}) = 9.80 \times 10^{-3} \text{ M};$$

$$[\text{CH}_3\text{COONa}] = (2.500 \times 10^{-6} \text{ mol CH}_3\text{COONa}) / (25.25 \times 10^{-3} \text{ L}) = 9.90 \times 10^{-5} \text{ M}.$$

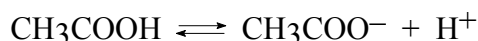
At this point the problem can be redefined: calculate the pH of a solution that is  $9.80 \times 10^{-3}$  M in  $\text{CH}_3\text{COOH}$  and  $9.90 \times 10^{-5}$  M in  $\text{CH}_3\text{COONa}$ . Therefore the student can develop this solution by referring to an analogous problem. Some reactions take place:



$$K_b(\text{CH}_3\text{COO}^-) = K_w/K_a = 5.70 \times 10^{-10} \text{ M}.$$



Because  $K_a \gg K_b$ , and  $[\text{CH}_3\text{COOH}] > [\text{CH}_3\text{COO}^-]$ , it is wise to consider this equilibrium:



Initial concentrations	$9.80 \times 10^{-3}$	$9.90 \times 10^{-5}$	0
Equilibrium concentrations	$9.80 \times 10^{-3} - r_1$	$9.90 \times 10^{-5} + r_1$	$r_1$



$r_1$  must be included in the interval  $0 < r < 9.80 \times 10^{-3}$  M. We have:

$$K_a \times (9.80 \times 10^{-3} \text{ M} - r_1 \text{ M}) = (9.90 \times 10^{-5} \text{ M} + r_1 \text{ M}) \times (r_1 \text{ M})$$

Students can evaluate an approximate result:  $r_1 = K_a \times (9.80 \times 10^{-3} \text{ M}) / (9.90 \times 10^{-5} \text{ M}) = 1.74 \times 10^{-3} \text{ M}$ . Hence, they realize that they cannot accept the approximations:  $9.80 \times 10^{-3} \text{ M} - r_1 \text{ M} \cong 9.80 \times 10^{-3} \text{ M}$  and  $9.90 \times 10^{-5} \text{ M} + r_1 \text{ M} \cong 9.90 \times 10^{-5} \text{ M}$ . We obtain:

$$r_1 = 3.60 \times 10^{-4} \text{ M} \quad [\text{H}^+] = 3.60 \times 10^{-4} \text{ M}$$

Now it is possible to evaluate the  $[\text{H}^+]$  coming from the water dissociation. If  $r_2 \text{ mol L}^{-1}$  of  $\text{H}_2\text{O}$  ionize at equilibrium,



Initial concentrations	$3.60 \times 10^{-4}$	0
Equilibrium concentrations	$3.60 \times 10^{-4} + r_2$	$r_2$

$$1.00 \times 10^{-14} \text{ M}^2 = (3.60 \times 10^{-4} \text{ M} + r_2 \text{ M}) \times (r_2 \text{ M})$$

If  $3.60 \times 10^{-4} \text{ M} + r_2 \text{ M} = 3.60 \times 10^{-4} \text{ M}$  (numeric approximation), we have:

$$r_2 = (1.00 \times 10^{-14} \text{ M}^2) / (3.60 \times 10^{-4} \text{ M}) = 2.78 \times 10^{-11} \text{ M}$$

we check that the numeric approximation is acceptable:  $3.60 \times 10^{-4} \text{ M} + 2.78 \times 10^{-11} \text{ M} = 3.60 \times 10^{-4} \text{ M}$ . We obtain:

$$[\text{CH}_3\text{COOH}] = 9.80 \times 10^{-3} \text{ M} - r_1 \text{ M} = 9.44 \times 10^{-3} \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = 9.90 \times 10^{-5} \text{ M} + r_1 \text{ M} = 4.59 \times 10^{-4} \text{ M} \quad [\text{H}^+] = 3.60 \times 10^{-4} \text{ M}$$

$$[\text{OH}^-] = r_2 = 2.78 \times 10^{-11} \text{ M} \quad [\text{Na}^+] = 9.90 \times 10^{-5} \text{ M} \quad \text{pH} = 3.444$$

Now, it is necessary to verify if the solution is acceptable:

### 1. Mass balance equation

$$\text{mol CH}_3\text{COOH} + \text{mol CH}_3\text{COO}^- = 2.384 \times 10^{-4} \text{ mol} + 1.159 \times 10^{-5} \text{ mol} = 2.50 \times 10^{-4} \text{ mol}$$

### 2. Electroneutrality condition

$$[\text{H}^+] + [\text{Na}^+] = 4.59 \times 10^{-4} \text{ M} \quad [\text{OH}^-] + [\text{CH}_3\text{COO}^-] = 4.59 \times 10^{-4} \text{ M}$$

### 3. Dissociation constants

$$[\text{H}^+][\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}] = 1.75 \times 10^{-5} \text{ M}$$

and, of course:  $[H^+][OH^-] = 1.00 \times 10^{-14} M^2$

The conditions are fulfilled taking significant figures into account. The students know that they have solved the problem in the correct way from a numeric point of view and they have used the right chemical representation.

All ionic equilibrium problems can be solved with this method. The Sienko problem (Sienko, 1964) was solved for the first time and this method can be applied to more difficult problems (Cardellini, 1987).

## CONCLUSIONS AND IMPLICATIONS FOR INSTRUCTION

This method is useful in high school and at university because it makes the students reason and uses the information and the knowledge at disposal of every student. The mathematical difficulties are minimum; it works for all concentrations and for polyprotic weak acids (or bases) and applies independently from the ratio  $K_i/K_{i+1}$ . Furthermore, this method produces correct results as the same as solving a polynomial equation with a computer program (Malinowsky, 1990) and the student can verify them: the relative error of the result obtained using the Henderson-Hasselbach equation in the above problem is 380.6%.

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