# Chapter 19
# General Principles of Calculations Involving the Activities of Ionic Species in Solution

**Abstract** The chapter describes some methodologies in order to obtain thermodynamic equilibrium constants, but in a manner less conventional and certainly more modern than previously.

The determination of equilibrium constants entails the knowledge of the "at equilibrium activities" of the species participating in it. There is a difficulty. It is the following one. If the determination of the activities of the uncharged substances is possible (but somewhat difficult and lengthy) it is impossible for the ions. As a rule, this impossibility leads to a problem which may appear as being impossible to solve.

The methodologies described in this chapter show how the thermodynamic equilibrium constants involving some ions may be approached by calculations using the Debye–Hückel relations. But, these calculations, in turn, also suffer as a rule from a difficulty which is briefly mentioned in this chapter. To use the "Debye–Hückel" relations, the ionic strength of the solution must be known and its knowledge involves that of the equilibrium constants, one of which, at least, by hypothesis is unknown! The principle and the followed methodology of these calculations are described in this chapter with the examples of the determinations of acidic constants.

**Keywords** Ion activity (experimental determination) ionic strength • Debye–Hückel relations use • Concentrations of the different species at equilibrium • Non-ideality corrections • Informatic calculations • Absorbance p*K*a determination

In this chapter, we are continuing to describe some methodologies in order to obtain thermodynamic equilibrium constants, but in a manner less conventional and certainly more modern than previously.

We have seen that the determination of equilibrium constants entails the knowledge of the "at equilibrium activities" of the species participating in it. Now, if the determination of the activities of the uncharged substances is possible but somewhat difficult and lengthy, we also know that it is impossible for the ions. As a rule, this impossibility leads to a problem fantastically difficult to solve.

The goal of this chapter is to show how the thermodynamic equilibrium constants involving some ions may be approached by calculations using the

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Debye–Hückel relations. But, these calculations, in turn, as a rule, also suffer from a difficulty that we first briefly mention. Then, we recall the conditions of ionic strengths for which corrections of nonideality must be done. Finally, we mention the principle and the methodology of these calculations.

## 19.1 Fundamental Difficulty

The fundamental difficulty concerning these calculations lies in the chain of the following facts:

- The ionic strength of the solution must be known in order to calculate the activity coefficients of the ions through the Debye–Hückel relations.
- The knowledge of the ionic strength entails that the extent of dissociation of the electrolytes (which are not obligatorily strong) must be known. The knowledge of this extent, in turn, entails the prior determination of the equilibrium constants . . . being searched for!

We shall see how this difficulty may be overcome.

## 19.2 Nonideality Corrections

For rough calculations, nonideality corrections can be neglected. In these conditions, the found values of the concentrations and those of the obtained equilibrium constants are only approached. Moreover, they vary with the ionic strength of the solution.

For ionic strengths of the solution less than $10^{-2}$ mol $L^{-1}$, the calculations are proved to be relatively simple. They are based on the Debye–Hückel limit equation. There is no reason to take into account the identity of the ions, i.e., to use the extended relation.

For ionic strengths ranging in the interval $10^{-2}$–$10^{-1}$ mol $L^{-1}$, it must be used. But, then, the nature of the ions must be taken into account by introducing the "ion-size parameter" $a$. This complicates the calculations.

Beyond ionic strength forces superior to $10^{-1}$ mol $L^{-1}$, Davies' relation (which gives reasonable results up to ionic strengths of the order of $5 \times 10^{-1}$ mol $L^{-1}$) may be used.

Roughly, it can be said that the theoretical prediction of the activity coefficients is very satisfactory up to ionic strengths of 0.1 mol $L^{-1}$. When only electrolytes 1–1 are involved, the activity coefficients may be then obtained with an accuracy of 3 p 100 by founding ourselves on the limit equation. When an adjustable parameter such as the so-called ion-size parameter $a$, is used, the accuracy may amount up to ±1 p 100. For the polycharged ions, an accuracy nearly as good as the preceding may be obtained, provided that all the equilibria existing in the solution are taken into account.

We shall see, immediately under, that the calculations of the activities are often necessary to perform at every step of the calculation of the equilibrium concentrations and of equilibrium constants, both types of calculations being, indeed, intimately linked.

## 19.3 Reasoning Allowing the Calculation of the Concentrations of the Different Species at Equilibrium

Before beginning the calculations (through the Debye–Hückel equations) of the activities and those of the equilibrium constants in which some ions intervene, it is judicious to give the strategy of the calculation of the different species concentrations at equilibrium.

Let us assume, at this moment, that activities are equal to concentrations. The strategy is based on the fact that the species concentrations at equilibrium must, obligatorily, obey some mathematical relations. They are, of course, the reflection of intangible physical laws. It happens that, from an absolute standpoint, they are systematically in a sufficient number in order that the resultant mathematical system is systematically determined. These relations are the following:

- The mass balance of the solution
- Its charge balance
- The equilibrium state

Let us take the example intentionally simple of the dissolution of $C_0$ moles of acetic acid in water to form 1 L of solution. The matter is to calculate the concentrations of the different species stemming from the ionization of acetic acid, once the equilibria are reached. The two chemical equilibria are the following:

- The revelation of the acid character of acetic acid:

$$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{CH_3COO^-} + \mathrm{H^+}$$

- The ionic product of water:

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-}$$

The corresponding mathematical equations, which must be obligatorily satisfied, are the expressions of the equilibria, which we write temporarily (the species concentrations are figured in square brackets):

$$|CH_3COO^-||H^+|/|CH_3COOH| = K_a \tag{19.1}$$

$$|H^+||OH^-| = K_w \tag{19.2}$$

- The mass law:

$$[CH_3COO^-] + [CH_3COOH] = C_0 \tag{19.3}$$

(There is no reason to take into account the water balance because the theory is only valid in dilute aqueous solutions. Since the "concentration" of water is expressed in molar fractions—viz. Chap. 17—it can be considered as being constant and equal to unity.) (Here, the equilibria are written according to the Arrhenius theory, equivalent, in the occurrence, to that of Brönsted.)

- The charge balance:

$$[H^+] = [OH^-] + [CH_3COO^-] \tag{19.4}$$

Hence, for this example, there exist four equations for four unknowns $[H^+]$, $[OH^-]$, $[CH_3COOH]$, and $[CH_3COO^-]$. The system is mathematically determined. It is reduced easily into one equation with only one unknown. It is (19.5) of the third order in $|H^+|$ which must be, finally, solved:

$$[H^+]^3 + K_a[H^+]^2 - (K_w + K_aC_0)[H^+] - K_aK_w = 0 \tag{19.5}$$

Of course, (19.5) depends on the parameters $K_a$, $K_w$, and $C_0$ which govern the system. Once the root $[H^+]$ is found, all the other concentrations are immediately accessible through the handling of the initial relations which are obligatorily satisfied at equilibrium.

## 19.4 Taking into Account the Activities

The taking into account of the activities is performed by using the Debye–Hückel equations since some ions intervene in the equilibrium. Concerning, now, the uncharged species, one assigns the value unity to their activity coefficients since the solutions are sufficiently dilute in order that this is legitimate.

Let us recall that the problem we face with is that we must know the ionic strength of the solution in order to use Debye–Hückel equations, and consequently we must know the true species concentrations which are, actually, searched for.

Before entering into the problem of the unknown ionic strength, the fact that some relations are expressed in terms of activities and other ones expressed in terms of concentrations must be handled simultaneously. For example, in the above case of acetic acid, (19.1) and (19.2) are expressed, in principle, in activities, that is to say according to (the terms located in round brackets are the activities)

$$(H^+)(CH_3COO^-)/(CH_3COOH) = K_a{}^\circ \quad \text{and} \quad (H^+)(OH^-) = K_w{}^\circ$$

whereas (19.3) and (19.4) are expressed in concentrations. Let us also recall that the conditional constants $K_a{}'$ and $K_w{}'$ are given by the expressions

$$[H^+][CH_3COO^-]/[CH_3COOH] = K_a{}' \quad \text{and} \quad [H^+][OH^-] = K_w{}'$$

and that thermodynamic and conditional constants are linked together by the relations

$$K_a{}^\circ = K_a{}'\left(\gamma_{CH3COOH}/\gamma_{H+}\gamma_{CH3COO-}\right) \quad \text{and} \quad K_w{}^\circ = K_w{}'/\gamma_{H+}\gamma_{OH-}$$

According to the retained scale of “concentrations” (molarities or molalities), the constants should, of course, be symbolized by $K_{a\ c}{}'$ or $K_{a\ m}{}'$ (viz. Chap. 11).

## 19.5 Calculations

The calculations of concentrations and of activities of the species are performed in an iterative way.

Let us suppose that we are interested in the “concentrations” and the activities of the different species at equilibrium and that we have at our disposal the thermodynamic equilibrium constants (in the example of acetic acid $K_a{}^\circ$ and $K_w{}^\circ$). Equations (19.1)–(19.4) are not homogeneous. The first two are expressed in activities, and the latter two in concentrations. Solving the system as it has been done above, that is to say by not taking into account this inhomogeneity, induces the problem of the physical significance of the calculated quantities: Are they activities or concentrations? The answer and the whole problem are overcome by adopting the following iterative process:

- In the first step of iterations, one operates by mixing activities and concentrations, i.e., one supposes that the equations are homogeneous, i.e., one mixes activities and concentrations. The system of the initial equations is reduced to a single one, the unknown of which is $|H^+|$ (it is (19.5) in the case of acetic acid). It is solved. One obtains a first value $|H^+|_1$ which has neither the meaning of an activity nor that of a concentration, since it is obtained from initial equations involving both kinds of quantities. Nevertheless, from this first value, one calculates the other “pseudo-concentrations or activities” $\left|CH_3COO^-\right|_1$, $\left|CH_3COOH\right|_1$, and $\left|OH^-\right|_1$. Thus, one calculates a first pseudo-ionic strength $I_1$. (Notice the used symbols with vertical lines—and not round or square brackets—which mean that the quantities are a kind of mixture of activity and of concentration.) Once obtained, the value $I_1$ is introduced into the judicious equation Debye–Hückel equation (that applies for the found $I_1$). It permits to calculate a first set of pseudo-activity coefficients $\gamma_{H+1}$, $\gamma_{CH3COO-\ 1}$, $\gamma_{OH-\ 1}$. The latter ones, in turn, permit to obtain a first set of the values of the conditional constants $K_a{}'_1$ and $K_w{}'_1$ by using the following relations (and by setting up $\gamma_{CH3COOH-} = 1$. This is justified—viz. Chap. 15)—

$$K_{a1}' = K_a{}^\circ/\gamma_{CH3COO-}\gamma_{H+} \quad \text{and} \quad K_{w1}' = K_w{}^\circ/\gamma_{H+}\gamma_{OH-}$$

The first iteration is finished. It is important to notice that the constants $K_a{}'_1$ and $K_w{}'_1$ do not have, yet, the meaning of pure formal constants. But, however, they approach them and, hence, their meaning begins to deviate from that of thermodynamic constants, given the manner which has permitted to obtain them.

- The second iteration is then initiated. It is strictly performed just like the first one, but in the calculations intervene the pseudo-constants $K_a{}'_1$ and $K_w{}'_1$ stemming from the preceding iteration. At the end of the second iteration, we obtain a new set of pseudo-concentrations $|H^+|_2$, . . ., a new pseudo-ionic strength $I_2$, new pseudo-activity coefficients $\gamma_{H+2}$, and new formal equilibrium pseudo-constants. After this second iteration, constants $K_a{}'_2$ and $K_w{}'_2$ do possess the meaning of formal constants more than did $K_a{}'_1$ and $K_w{}'_1$ obtained at the end of the previous iteration. It is the same thing concerning the activity coefficients of ionic species which tend more and more to the coefficients such as they are defined, that is to say, in such a manner that they transform pure concentrations into pure activities.
- The further iterations evolve strictly in an analogous manner. The process is stopped when the pseudo-ionic strength $I_n$ is equal to the preceding one $I_{n-1}$. Then, the constants $K_a{}'_n$ and $K_w{}'_n$ are the *true conditional or formal constants*. The equation system is then homogeneous. They are all expressed in terms of *concentrations*. At the end of this *n*nd and definitive loop of iteration, the concentrations of all the species are found. They are no longer a cross of concentrations and activities. The problem is solved.

At this point of the operations, one can immediately calculate the activities of the different species since their concentrations are known and because of the "true ionic strength" also. It suffices to calculate the activity coefficients through the Debye–Hückel equations and to multiply them by their concentrations. Besides, the activity coefficients are known through the calculations performed during the last iteration.

Generally, the convergence of the whole process is fast. The number of iterations is weak, of the order of 3 or 4.[1]

This process is general. The difficulty often lies at the level of the obtention of the suitable root of the single equation stemming from the reduction of the system of initial equations which must be satisfied. Equations of the fourth order are not rare in this realm. Abel's theorem stipulates that there is no general solution to the

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[1] These calculations can be performed on some pocket calculators.

equations with one unknown of order superior to four. However, several informatic routines permitting to obtain the root, with the required precision, exist in the literature.

## 19.6 Simultaneous Determination of Concentrations, Activities, and Equilibrium Constants Using Computers

We finish this chapter by showing, with the help of an example, that the use of computers may greatly facilitate the handling of activities and the obtaining of equilibrium constants. The chosen example is that of the determination of the successive acidity constants $K_{a1}$ and $K_{a2}$ of the diacid $H_2A$:

$$\begin{aligned} H_2A &\rightleftharpoons HA^- + H^+ \quad K_{a1} \quad \Rightarrow \\ HA^- &\rightleftharpoons A^{2-} + H^+ \quad K_{a2} \quad \Rightarrow \end{aligned}$$

The analytical instrumental method used is the UV-visible spectrophotometry since, usually, the diacid $H_2A$ and the dibasic $A^{2-}$ forms exhibit spectra clearly distinct from each other. In this case, of course, the use of the spectrophotometry is convenient.

### *19.6.1 Determination for a Monoacid*

In introduction, we recall the principle of the determination of the $pK_a$ of the monoacid HA by spectrophotometry UV-visible. It is founded on the relation

$$pK_a = pH + \log[HA]/[A^-] \tag{19.6}$$

where [HA] and $[A^-]$ are the concentrations of the conjugate forms at a given pH value. The principle of the method consists in fixing the pH of the solution with the help of a buffer and to measure both concentrations by spectrophotometry. Then, relation (19.6) permits to calculate $pK_a$. Let us already remark, however, that relation (19.6) is not homogeneous since pH is defined as being rather a measurement of the *activity of the proton* whereas [HA] and $[A^-]$ are concentrations, since the UV-visible spectrophotometry responds to the concentrations.

In order to obtain [HA] and $[A^-]$, one uses the Beer-Lambert law which, at a given fixed wavelength, relates the absorbance $A$ of the solution to the concentration(s) of the species. For example, at very acid pH, provided that the $pK_a$ value is not too low,

$$A = \varepsilon_{\mathrm{HA}}\mathrm{C}.\,1.\,[\mathrm{HA}] \qquad \text{(acid pH)}$$

where $\varepsilon_{\mathrm{HA}}$ is the molar extinction coefficient of the form HA, [HA] is its concentration (for example in mol $\mathrm{L}^{-1}$) and l the length of the measurement cell. $\varepsilon_{\mathrm{HA}}$ is a constant for a given temperature, wavelength, and solvent. Likewise, in a very basic medium, provided that the p$K_a$ value is not too large,

$$A = \varepsilon_{\mathrm{A}}\mathrm{C}.\,1.\,[\mathrm{A}^-] \qquad \text{(basic pH)}$$

At intermediary pH, that is to say in the pH interval where both forms are present, the total absorbance $A$ of the solution is the sum of the absorbances of both forms since the two are present and also because of the properties of Beer-Lambert's law:

$$A = \varepsilon_{\mathrm{HA}}\mathrm{C}.\,1.\,[\mathrm{HA}] + \varepsilon_{\mathrm{A}}\mathrm{C}.\,1.\,[\mathrm{A}^-] \quad \text{(intermediary pH)}$$

From another side of reasoning, since in the solution

$$[\mathrm{HA}] + [\mathrm{A}^-] = C$$

and

$$K_a = |\mathrm{A}^-||\mathrm{H}^+|/|\mathrm{HA}|$$

by assimilating activities (terms in which the p$K_a$ is expressed) and concentrations, we obtain the two relations:

$$|\mathrm{HA}| = |\mathrm{H}^+|/[|\mathrm{H}^+| + K_a] \quad \text{and} \quad |\mathrm{A}^-| = |\mathrm{A}^-|/[|\mathrm{H}^+| + K_a] \tag{19.7}$$

And by handling the relations (19.6) and (19.7), we obtain

$$\mathrm{p}K_a = \mathrm{pH} + \log(A - \varepsilon_{\mathrm{A}}\mathrm{C}.1)/(\varepsilon_{\mathrm{HA}}\mathrm{C}.1 - A) \tag{19.8}$$

$\varepsilon_{\mathrm{A}}$C.1 and $\varepsilon_{\mathrm{HA}}$C.1 are the absorbances of the sole basic and acid forms at the total concentration $C$ of the whole species. These values are easily determined. It is sufficient to "work" at the judicious pH. The measurement of the absorbance $A$ at an intermediary pH immediately gives the p$K_a$ value. The problem of the activities is studied under. In principle, only one measurement is sufficient for the determination, but several ones are indicated in order to take into account a maximum of experimental information and, thus, to obtain an optimal precision. In order to perform the determination, the working wavelength (the "analytical wavelength") must be chosen in such a way that the spectra of the pure acid and basic forms differ as much as possible from each other. This is the "analytical wavelength."

When neither of both forms HA and $\mathrm{A}^-$ absorb in the UV-visible domain, of course, the determination is not possible. However, let us notice that when only one form does absorb, the determination remains possible.

### 19.6.2 Case of the Diacid $H_2A$

The preceding considerations can be generalized, but a supplementary difficulty may often happen. Both acidities $K_{\mathrm{a1}}$ and $K_{\mathrm{a2}}$ may, indeed, overlap. Then, it is impossible to experimentally determine the molar absorption $\varepsilon_{\mathrm{HA}}$ since the intermediary form $HA^-$ cannot exist, alone, contrary to the forms $H_2A$ and $A^{2-}$. $HA^-$ is always accompanied by one of the two other forms $H_2A$ or $A^{2-}$, and even by both. This is due to the overlapping of the two constants $K_{\mathrm{a1}}$ and $K_{\mathrm{a2}}$. Its spectrum in the pure state is, therefore, inaccessible by an experimental way. However, at the extreme pH values, $H_2A$ and $A^{2-}$ exist, alone, whence the possible registering of their spectra in the "pure" state remains possible.

The absorbance at a given $\mathrm{pH_i}$ is the sum of the absorbances of the three present forms:

$$A = \varepsilon_{\mathrm{H2A}}[\mathrm{H_2A}]_{\mathrm{i}}.1 + \varepsilon_{\mathrm{HA}}[\mathrm{HA^-}]_{\mathrm{i}}.1 + \left[\mathrm{A^{2-}}\right]_{\mathrm{i}}.1 \tag{19.9}$$

The handling of the equations which are obligatorily satisfied

$$K_{\mathrm{a1}} = \left|\mathrm{H^+}\right|_{\mathrm{i}}\left|\mathrm{HA^-}\right|_{\mathrm{i}}/\left|\mathrm{H_2A}\right|_{\mathrm{i}} \quad \text{and} \quad K_{\mathrm{a2}} = \left|\mathrm{H^+}\right|_{\mathrm{i}}\left|\mathrm{A^{2-}}\right|_{\mathrm{i}}/\left|\mathrm{HA^-}\right|_{\mathrm{i}}$$

and

$$C = [\mathrm{H_2A}]_{\mathrm{i}} + [\mathrm{HA^-}]_{\mathrm{i}} + \left[\mathrm{A^{2-}}\right]_{\mathrm{i}}$$

leads to the following expressions:

$$[\mathrm{H_2A}]_{\mathrm{i}} = 1\left\{[\mathrm{H^+}]_{\mathrm{i}}^{\,2}C/D; \quad [\mathrm{HA^-}]_{\mathrm{i}} = K_{\mathrm{a1}}[\mathrm{H^+}]_i C/\,D; \quad \left[\mathrm{A^{2-}}\right]_{\mathrm{i}} = K_{\mathrm{a1}}K_{\mathrm{a2}}/D\right\} \tag{19.10}$$

with

$$D = [\mathrm{H^+}]_{\mathrm{i}}^{\,2} + K_{\mathrm{a1}}[\mathrm{H^+}]_{\mathrm{i}} + K_{\mathrm{a1}}K_{\mathrm{a2}} \tag{19.11}$$

The examination of (19.9)–(19.11) shows that the absorbance at a given pH depends on the three molar extinction coefficients, on the constants $K_{\mathrm{a1}}$ and $K_{\mathrm{a2}}$, on $C$, and on $|H^+|$, that is to say on the pH.

### 19.6.3 Determination of Constants $\mathrm{K}_{a1}$ and $\mathrm{K}_{a2}$ Without Taking into Account the Activities

The two unknowns to determine are both constants $K_{\mathrm{a1}}$ and $K_{\mathrm{a2}}$. Their determination entails that the molar extinction coefficient $\varepsilon_{\mathrm{HA}}$ of the intermediary pure form, which is directly inaccessible by an experimental means, must be known. Therefore, it is the third unknown. On the other hand, the pH is known and, also, the coefficients $\varepsilon_{\mathrm{H2A}}$ and $\varepsilon_{\mathrm{A}}$ which are, respectively, determined in very acid and very basic media.

The methodology used to determine the three unknowns is a process of informatic simulation (viz. Chap. 47).

In a first step, it consists in choosing the analytical wavelength and in performing absorbance measurements at several $\mathrm{pH_i}$ values. In order to have the best precision, one must choose a number of pH values by far larger than the number of unknowns.

In a second step, one arbitrarily chooses values of the three unknowns $K_{\mathrm{a1}}$, $K_{\mathrm{a2}}$, and $\varepsilon_{\mathrm{HA}}$ and, thanks to these values, one calculates the total absorbance $A_{\mathrm{calc}}$ for each retained $\mathrm{pH_i}$. The calculation is performed through relation (19.9). Then, for this set of the three parameters, one calculates the function $U$ defined by the relation

$$U = \sum_i \left(A_{\mathrm{i\ calc}} - A_{\mathrm{i\ exp}}\right)^2$$

where $A_{\mathrm{i\ exp}}$ is the measured absorbance at the same $\mathrm{pH_i}$ as that for which $A_{\mathrm{i\ calc}}$ is calculated. The function $U$ is the cost function . In the following steps, one modifies the values of the three parameters according to some order of logical decisions and one calculates the function $U$ at each time up to obtaining the set of the values of the three parameters leading to the value $U$ as weak as possible. In other words, the process is repeated till the three following conditions are simultaneously satisfied:

$$(\partial \mathrm{U}/\partial K_{\mathrm{a1}})_{K\mathrm{a2},\varepsilon_{\mathrm{HA}}} = 0 \qquad (\partial U/\partial K_{\mathrm{a_2}})_{K_{\mathrm{a1}},\varepsilon_{\mathrm{HA}}} = 0 \qquad (\partial U/\partial \varepsilon_{\mathrm{HA}})_{K_{\mathrm{a1}},K_{\mathrm{a2}}} = 0$$

One must also check that, when it is the case, this is not a singular point or a maximum of the function $U$. The values of the parameters which minimize the cost function are those being searched for. The described methodology is a least square process, in the occurrence of a nonlinear one since the constants $K_{\mathrm{a1}}$ and $K_{\mathrm{a2}}$ (contrarily to $\varepsilon_{\mathrm{HA}}$) do not intervene linearly in the calculation of $A_{\mathrm{i\ calc}}$. This is a general methodology.

The difficulty, that this methodology may encounter, is that the research of the parameters minimizing the function $U$ may be difficult and lengthy. There exist several described algorithms permitting to point toward the *minimum minimorum*, of the cost function, but none is infallible. There exists no mathematical process permitting to automatically reach this point.

### 19.6.4 Taking into Account the Activities

As a rule, one could imagine that one can assimilate activities and concentrations when the equilibrium constants are determined by UV-visible spectrophotometry. It is not rare, indeed, to work with concentrations of the order of $10^{-4}$ to $5\ 10^{-4}$ mol $\mathrm{L}^{-1}$

of the compound with UV-visible spectrophotometry. Quite evidently, the working concentration interval depends on the values of molar extinction coefficients. But there is a data which must be taken into account: the presence of the buffer which fixes the pH values to which the determinations are performed. Even, we know that to be effective, the buffer solutions must be rather concentrated. Let us admit that for the determination of the p$K_a$ value, the concentration $10^{-4}$ mol L$^{-1}$ is satisfactory. That of the buffer must be of the order of $10^{-2}$ mol L$^{-1}$ in order to be effective. The ionic strength exhibits about this value, the ions coming from the compound under study contributing for a negligible amount. As a result, the activity coefficients cannot be neglected.

In the chosen example, one converts the retained pH values into concentrations by the following relations:

$$a_{\mathrm{H+}} = 10^{-\mathrm{pH}} \quad \text{and} \quad [\mathrm{H^+}] = a_{\mathrm{H+}}/\gamma_{\mathrm{H}}$$

$\gamma_{\mathrm{H+}}$ is obtained through the Debye–Hückel relations since the ionic strength is known. In these conditions, the calculations are performed with homogeneous equations. Therefore, the $K_{a1}$ and $K_{a2}$ constants are the conditional ones. It is very easy to go back to the thermodynamic constants, since the ionic strength is known.