

## IONIC SOLUBILITY EQUILIBRIA CALCULATIONS - A NEW APPROACH

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### ABSTRACT

In the classical approach, students have to verify assumptions using, amongst others, a "pure solution" or "the common-ion effect" concerning the situation they are studying to solve ionic solubility equilibria calculations. Furthermore, the simultaneous equilibria are shown in a non-trivial way. We propose a new way to understand these equilibria by implementing a method in which all conditions appear naturally in the mathematical equations. We present the Excess Parameter with solubility product equations to determine cation and anion's analytical and equilibrium concentrations. We consider the Bronsted ions acid-base behavior applying the equilibrium fractions (a). It is possible to use conditional  $K_{sp}$  (it involves  $K_{sp}$  and  $\alpha$ ) to ease calculations. Another option to solve calculations is to use the classical approximation or the iteration numerical calculations. This approach logically exposes concepts that we believe it is a good and promising method to teach and discuss Aqueous Solution Chemistry and Analytical Chemistry. [*African Journal of Chemical Education—AJCE 13(3), July 2023*]

## INTRODUCTION

Virtually all teachers use the study of ionic solubility equilibria in Analytical Chemistry in which a "pure solution" is the prime studied situation. That is, when adding a sparingly soluble ionic solid to water, the common-ion effect responsible for decreasing the solubility of a compound modifies the "pure solution" situation. This approach has been in use since the ionic solubility-product proposal by Nernst [1], and we will call this method the classical approach.

The introduction in 1884 of Arrhenius's electrolytic dissociation theory has since then provided a significant modification to how the scientific community understands the Aqueous Solution. Previously, the usual idea did not consider the dissociation (or ionization) processes. Nowadays, some consequences of this previous idea are writing chemical equations in an aqueous solution using the compound formula added to the solution or the solubility of a sparingly salt calculated as if it existed in the solution. This concept was known as the XIX Century Concept [2].

Truthfully the XIX Century Concept is heavily used, and the classical approach, among other aspects, is characterized by (i) the use of global equations to describe the solution and to underestimate other species and processes in the solution, (ii) the numerical calculations are more important than chemical concepts; (iii) the approximations are not easily understood; (iv) different steps of dilution were not distinguished, making the resolution more difficult. Butler [3] has proposed a systematic method in which the representation of all intermediate species presented in equilibrium replaced the use of global equations. Although the solution description does not include the use of a

global equation, the numerical calculations are similar to any other classical methodology in the systematic method. Nowadays, a more modern concept named the XX Century Concept shows the actual behavior of existing species in solution, including the solvation process.

In the classical approach to ionic compounds' specific solubility equilibria, only the Law of Mass Action and equilibrium concentration are applied. However, the difference between equilibrium and analytical concentration is not generally explicit, and therefore it causes some confusion. Indeed, this classical approach does not consider the actual equilibrium concentration of several ions because it depends on the pH value and all the species related to either the cation, anion or even both cation and anion involved in the system. Moreover, both topics are unreported by the classical approach. It means the pH value is implicit and adequately selected for equilibrium and analytical concentrations equality to be acceptable by approximation. The systematic method [4] explores solutions involving simultaneous equilibria, in which exercises require approximations to solve the calculations. Nonetheless, it does not consider the pH effect. For simple calculations, it is usual to consider some approximations to solve an exercise, and the calculation for a more complex example is solved using software. Moreover, to solve an exercise, the systematic method resolution considers a succession of nontrivial steps and assumptions about the chemical system. Therefore, the resolution becomes a calculation problem, depreciating the chemistry.

As an alternative to teaching and solving problems involving solubility equilibria, this article proposes a new method that integrally applies the XX Century Concept for Chemical Solution. This

method, the XXI Method, similar to the systematic method, considers distinct chemical equations to represent all the system equilibria. Therefore, the system could be easier interpreted. Moreover, we could calculate the equilibrium concentrations because the pH system would always be known, and the equilibrium fraction could be obtained [5].

The procedure will use the balance of matter (of phase, actually) and the Law of Mass Action equation to propose a new parameter named The Excess Parameter. The solution to the problem by the student will be formed in two parts: obtaining of the Excess Parameter expression and applying it in the solubility equilibria.

### **THE EXCESS PARAMETER CONCEPT**

Here are some considerations to introduce The Excess Parameter Concept. Thinking in teachers in this moment, and not in the student, to help with methodology comprehension, consider a system formed by a mixture of a cation ( $M^{q+}$ ) solution and an anion ( $B^{p-}$ ) solution with a solid formation. Figure 1 shows a schematic diagram with all steps designated. The final solution pH (Step 3) was adjusted (by adding a strong acid or base, for example). In the approach for students, real compounds are better than hypothetical cation and anion, once no general equation were obtained, but the excess parameter is calculated in each system.

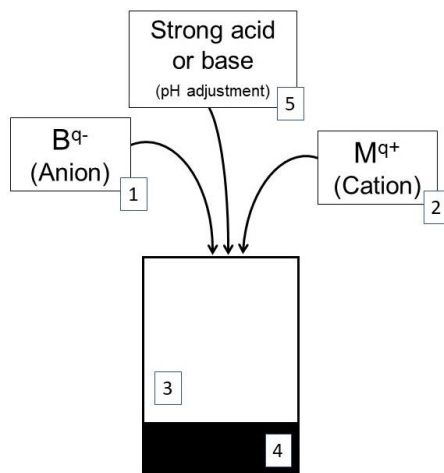
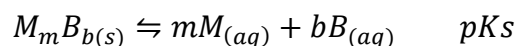


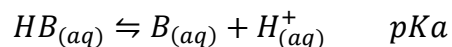
Figure 1 - Mixture of cation ( $M^{q+}$ ) solution and anion ( $B^{q-}$ ) solution schematic diagram.

The equation below represents the solubility equilibrium that occurred after the mixture.

Electric charges were omitted to simplify it.



Considering the Brønsted acid-base behavior for both species, the metal ion and the anion, both as monoprotic systems, we have:



The water molecule shown in the Bronsted metal ion acid-base equilibrium is the ligand in an aquocomplex. We ought to remember that N. Bjerrum<sup>6</sup> has proposed the solvated metal ion

classification as Bronsted acid. Also, it is interesting to emphasize that  $H^+_{(aq)}$  means all proton hydrates (Eigen, Zündel ions, etc.), and we usually omit water molecules whenever possible [5].

The phase balance of each ion either in solution or in solid phase can be obtained (Equations 1 and 2). The index is the number of each step in Figure 1.

$$n_2(M) = n_3(M) + n_4(M) \quad (1)$$

$$n_1(B) = n_3(B) + n_4(B) \quad (2)$$

The stoichiometry in **solid** (Equation 3) is a piece of additional information, and it is always known.

$$\frac{n_4(M)}{n_4(B)} = \frac{m}{b} \quad (3)$$

Only in special circumstances, when we directly add the solid to the system, this stoichiometry (Equation 3) exists in the solution. It is worth mentioning that the classical methodology uses this special case as an initial situation (“pure solution”).

We do not always know the concentration or the numerical information substance amount in Step 4 (Figure 1), but we know the solid stoichiometry. However, the cation and the anion solutions concentration information and volume in Steps 1 and 2 (or directly its amount of substance) is usually known. For instance, it is possible to rewrite Equations 1 and 2 using Equation 3, as presented in Equations 4, 5, and 6.

$$b \cdot n_4(M) = m \cdot n_4(B) \quad (4)$$

$$n_4(M) = n_2(M) - n_3(M) \quad (5)$$

$$n_4(B) = n_1(B) - n_3(B) \quad (6)$$

Furthermore, we can obtain a relation between the two ions in Equation 7.

$$b \cdot n_2(M) - b \cdot n_3(M) = m \cdot n_1(B) - m \cdot n_3(B) \quad (7)$$

A rearrangement allows for maintaining separate information about the solution obtained after the mixture (Step 3) and the original one of cation and anion (Steps 1 and 2) (Equation 8).

$$b \cdot n_2(M) - m \cdot n_1(B) = b \cdot n_3(M) - m \cdot n_3(B) \quad (8)$$

Until this step, we have considered only the substance's ions amount. If we divide both sides by Step 3's volume, the right side of the equation would be related to cation and anion concentrations. It is interesting to observe that concentrations are, by definition, analytical ones, since the amount of metal ions is related to all chemical species in the solution containing the metal (for example, hydroxocomplexes). A similar explanation is valid for the anion analytical concentration (Equation 9).

$$\frac{b \cdot n_2(M) - m \cdot n_1(B)}{V_3} = b \cdot c_3(M) - m \cdot c_3(B) \quad (9)$$

The first part of Equation 9 is defined as The Excess Parameter (Equation 10):

$$Excess = \frac{b \cdot n_2(M) - m \cdot n_1(B)}{V_3} \quad (10)$$

Furthermore, Equation 10 is related either to the metal ion amount or the anion in Excess, compared to the solid stoichiometry.

Moreover, we can represent the Excess as a solubility equation, as Equation 11 demonstrates:

$$Excess = b \cdot c_3(M) - m \cdot c_3(B) \quad (11)$$

The Excess Parameter simple numerical analysis allows us to obtain valuable information on the system.

When the Excess Parameter is positive, there is a higher metal ion concentration than an anion concentration. When the Excess Parameter is negative, there is a lower metal ion concentration than an anion one. Both situations are called *common-ion effects* in the classical approach. However, in that approach, they should be previously identified before any calculation. In our proposed one, the situation is shown naturally.

When the Excess Parameter is zero, the concentration of each ion in the solution is the same. It is similar to the default situation in the classical approach (*pure solution*). However, following the methodology presented in this article, the excess of cation or anion appears more natural, and we can interpret the situation after knowing that parameter value. Besides, in the classical method, each concentration situation is calculated differently.



Meanwhile, there are two incognitos to solve mathematically (Equation 10). To solve the cation and anion concentrations in the Excess we can use the solubility product equation (Equation 12).

$$K_{sp} = 10^{-pK_s} = [M]_3^m [B]_3^b \quad (12)$$

There is an important point here. We highlight that the concentrations in Equation 12 are equilibrium concentrations (by definition), not analytical ones. At this stage, it is important to remember that the Law of Mass Action is defined in terms of activity. Although we can use the activity and activity coefficient to correct the concentration value, we will not consider those factors in this paper.

In this example, we consider ions' acid-base behavior. Thus, we have associated the equilibrium concentration with the analytical one by equilibrium [4] fractions in Equation 13. The acid-base equilibrium fraction is exclusively a function of the pH solution and the Bronsted acid-base system pKa [5].

$$\alpha_i = \frac{[i]}{c(i)} \quad (13)$$

Therefore, the conditional  $K_{sp}$  could be defined (Equations 14 and 15) as:

$$Ksp = [\alpha_o(M)c_3(M)]^m [\alpha_i(B)c_3(B)]^b \quad (14)$$

$$Ksp^{cond} = \frac{Ksp}{\alpha_o(M)^m \alpha_i(B)^b} = c_3(M)^m c_3(B)^b \quad (15)$$

The traditional conditional constant enables separation between the problem's constant variables and the unknown ones. Once we have established the solution's pH, the equilibrium fraction values ( $\alpha$ ) remain constant, and so does the  $Ksp$ . It means conditional- $Ksp$  will depend on pH only.

The logarithm form (or 'p' operator) is a very easy way to treat the system. Therefore, the  $Ksp^{cond}$  can be written as presented in Equation 16.

$$pKs^{cond} = -\log Ksp^{cond} = pKs + \log \alpha_o(M)^m \alpha_i(B)^b \quad (16)$$

Both Equation 11 and Equation 16 represent systems of equations with two variables. With convenient replacement, we can obtain Equation 17, for example:

$$Excess = b \cdot C_3(M) - \left( \frac{10^{-pKs^{cond}}}{(C_3(M))^m} \right)^{1/b} \quad (17)$$

There are several ways to solve this equation, such as (i) numerical analytical method, (ii) method of classical approximations, and (iii) iterative method.

Each one has its challenges. However, to a chemist, the goal is to obtain a chemical result, not numerical skills. The first one demands hard work with mathematical skills in which the result will be about the compound stoichiometry formed only. We do not believe there is any advantage in exploring this method. The classical approximation method should delve into the system's numerical analysis. In a sum, this method evolves.

$$A + b \sim A \quad \text{if } A \gg \gg b$$

In this case, first we needed to prove if  $c_3(\text{M}) > c_3(\text{B})$ , then  $c_3(\text{M}) \gg \gg c_3(\text{B})$  (or the other two possible situations). After this proof, the solution is simpler than the method (i). The question remains if this approximation is valid because depending on the situation it is not always applied. Therefore, it should be used carefully.

The third method, the iterative one, needs a previous explanation of iterative methods. It is easy to implement programs such as Excel spreadsheets, R, Python, Sci-lab, MathLab languages, and others on computers. Consequently, even if the students do not understand these algorithms, they would be able to obtain the correct chemical result just by using them.

Therefore, we have proposed an add-on for Excel [7] with several interesting chemical functions. One of them allows cation and anion concentration calculations using as a parameter: the Excess parameter, pKs (or pKs<sup>cond</sup>), and cation and anion stoichiometric coefficients.

We present four examples in the Supplementary Information. They have used all conditions defined in XXI Method, such as a schematic diagram, and all equations involved in the solution are shown (each equation for each process). Subsequently, we have considered and selected the equilibrium. Therefore, students can understand future challenges they will have to face. Since we can always consider the Bronsted acid-base, we will not initially consider gas-liquid or complexation equilibrium.

## **DISCUSSION**

Although this methodology has several advantages over the classical one, we would like to emphasize two crucial points. The first one is that the argument presented here is very dense since we have shown a general case. For this reason, it ought to be evaluated by professionals, not students. For students, there is an evolution of concepts and skills, but we stress that the expression of concept parameter should be obtained by student in each real situation. The second point is that the classical method is often used due to the absence of others. Therefore, it is only after knowing and applying our new method that researchers/teachers can observe issues or inconsistencies in the classical one.

The classical method starts with a particular case of ionic compounds' solubility when the solution stoichiometry is equal to the solid. Thus, qualitatively, there is a solution's composition<sup>8</sup>. We believe it is a XIX Century Concept's direct consequence since researchers study ionic compounds' solubility by adding solid to water. In contrast, the classical method shows the "common-ion effect" as a different situation, thus, with another numerical resolution. According to

the information offered in each problem or exercise, identifying the "common-ion effect" situation or the "pure solution" situation is not trivial. Furthermore, the simultaneous equilibrium effect needs another approach that differs from those two presented here.

The classical methodology considers only the Law of Mass Action instead of also uses the Balance of Matter to solve those exercises (with simple equilibria). It keeps the simple equilibria concept implied in the initial decision. Moreover, it considers both the Law of Mass Action and the Balance of Matter whenever the system presented a simultaneous equilibria situation. Therefore, for a simultaneous equilibria situation, the classical methodology needs another approach to solve the exercise. Furthermore, there are no distinctions between dilution processes responsible for Step 3 conditions. This further confirms that these ideas were implicit in the arguments and in the numerical calculation.

In this new approach, we separate the dilution process from the equilibrium situation, and the numerical resolution becomes a consequence. There is a schematic design shown in Figure 2. Therefore, even complex problems become easier to assimilate and solve.

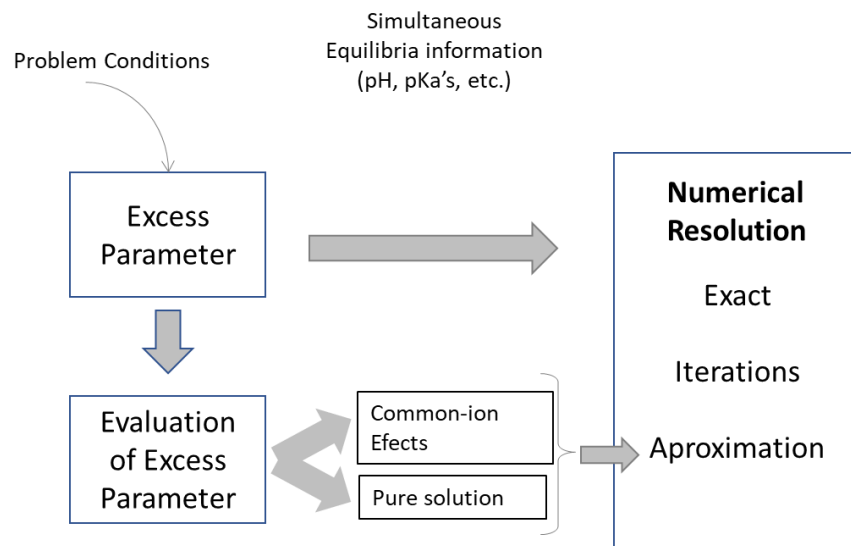


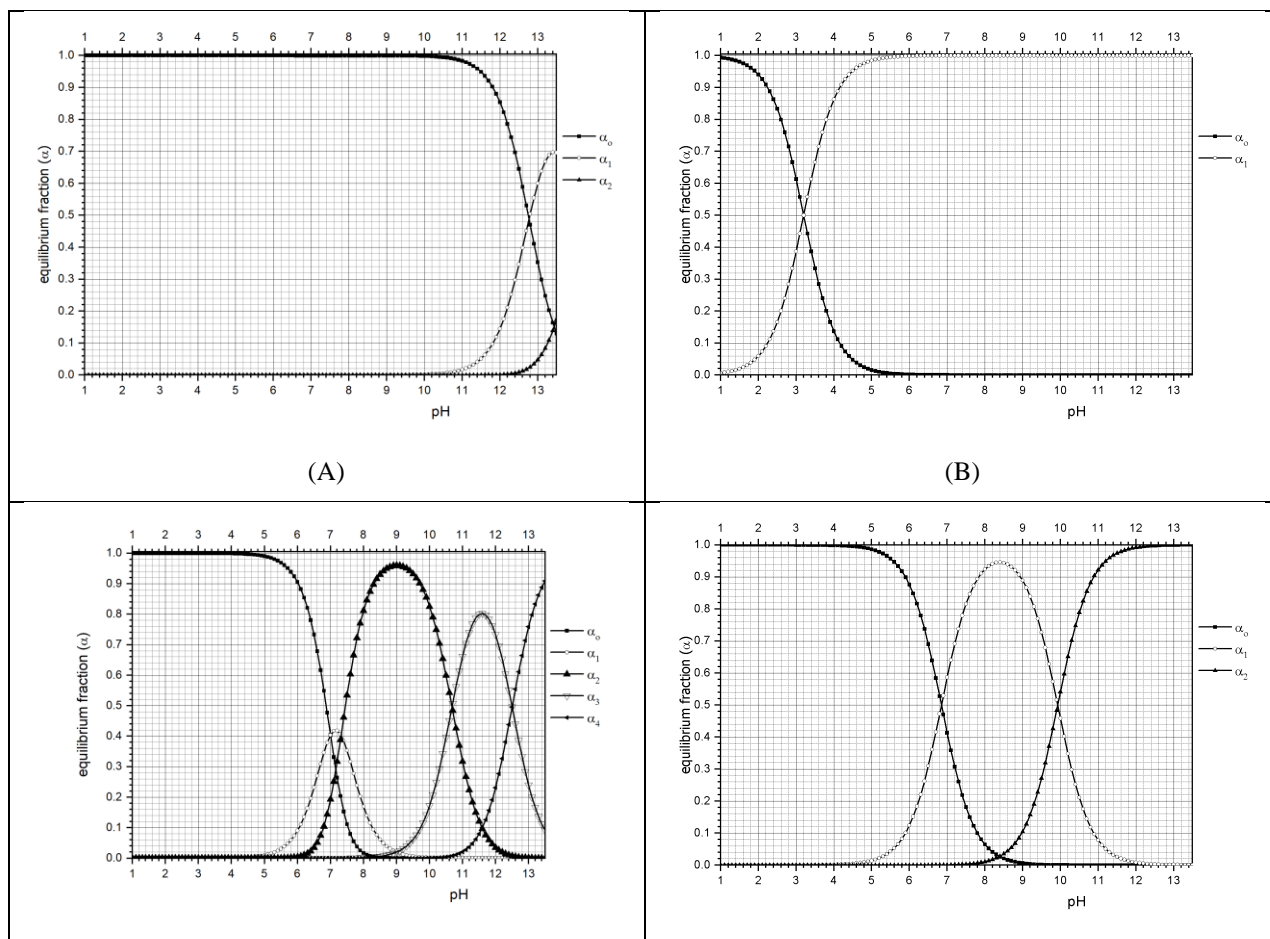
Figure 2 - Solve solubility equilibria calculations through Excess parameter definition schematic design.

This approach allows the behavior comprehension of two ionic solids in contact with the solution or even in cases of non-ionic compounds.

### Effect of pH – Species Distribution Diagram

In practical problems, the solution's pH is usually known or corrected to a known value. The Species Distribution Diagram (SDD) identifies the range this parameter (pH) is essential in ionic solubility equilibria. It means the equilibrium fraction range ( $\alpha$ ) tends to be 1 for the cation and anion. In this situation, low soluble salts are not affected by the solution's pH.

Figure 3 shows the SDDs of some cations and anions. Each ion pair in the study defines the pH range. For cations, it is  $\alpha_0 \rightarrow 1$ . For anions, the highest equilibrium fraction tends to be 1. For instance, calcium fluoride is not influenced by pH values in the pH range from 4.1 up to 11.8 (considering  $\alpha \rightarrow 1$  when  $\alpha > 0.9$ ). In contrast, there is no overlapping pH range for copper (II) phosphate, meaning the pH influences this solubility equilibrium in all pH values.



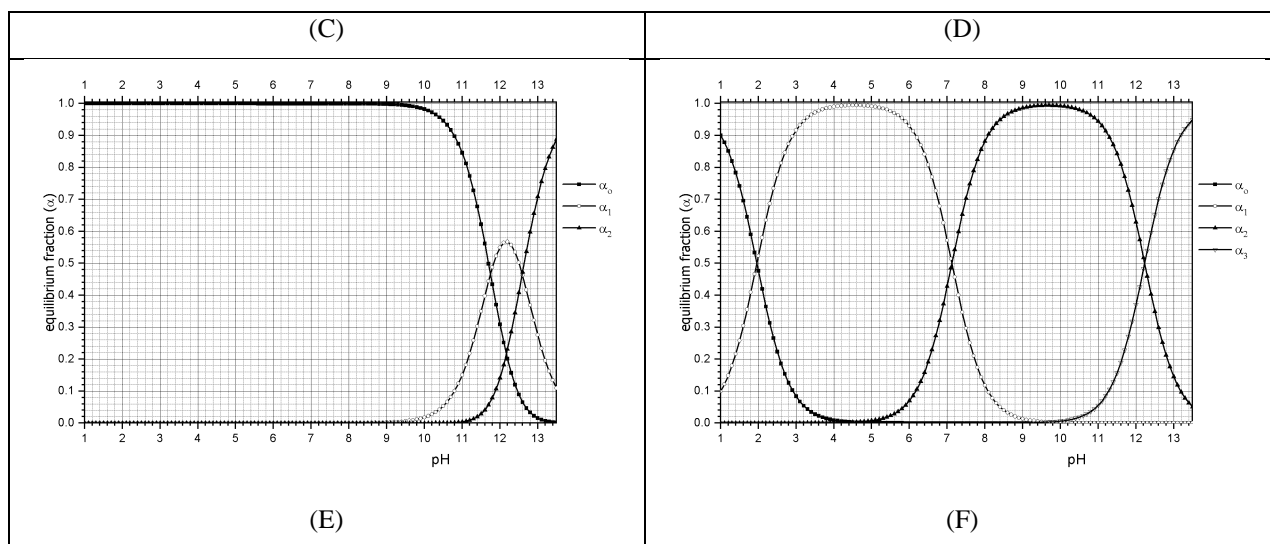


Figure 3 - Species Distribution Diagram (SDD) to different Bronsted acid-base systems. (A) calcium; (B) fluoride; (C) copper (II); (D) carbonate; (E) silver; (F) phosphate.

### Proposed approach examples

There are four examples to demonstrate our proposed approach's potential. Each example's resolution is in the Supplementary Information. Furthermore, we present different numerical methodologies to solve each problem.

Number 1: It is a common-ion effect example. An amount of solid has been formed in a solution by adding a quantity of cation and anion. The chosen pH value is within a range that does not influence the solubility equilibrium.

Number 2: This is an example of a "pure solution" influenced by the solubility equilibrium's pH. It is a sparingly soluble salt in contact with a pH-defined solution. It is interesting to mention



that the carbonate and the phosphate sparingly soluble salt will depend on the solution's pH in almost all pH range.

Number 3: It is similar to the first example; however, the pH value influences the cation and the anion equilibrium concentrations in the solution. Textbooks do not show this sort of problem because the Bronsted acid-base of metal is not usually shown. Only earth alkaline metals and silver are influenced by a pH value above 10 because the first pKa is higher than 11. Table 1 shows common metal ions' pKa values.

Number 4: It is the formation of two solids in contact with the solution. Less soluble salt pKs importance naturally emerges from equations.

Table 1 – Bronsted Acid-Base Equilibrium Constant for selected metal ions.<sup>9</sup>

Íon	pKa <sub>1</sub>	pKa <sub>2</sub>	pKa <sub>3</sub>	pKa <sub>4</sub>	-log s <sub>0</sub>
Al <sup>3+</sup>	4.99	5.55	5.66	6.6	7.7
Ba <sup>2+</sup>	13.36	24.36			13.32
Cd <sup>2+</sup>	10.08	10.27	12.95	14.05	6.7
Ca <sup>2+</sup>	12.67	14			3.86
Pb <sup>2+</sup>	7.47	9.52	10.95	11.64	4.09
Co <sup>2+</sup>	9.55	10.22	12.24		6.67
Cu <sup>+</sup>	0.4	7.84	10.38		8.54
Cu <sup>2+</sup>	7.64	8.6	10.36	13.1	7.56
Cr <sup>3+</sup>	3.6	6.05	6.6	11.31	4.05
Sn <sup>2+</sup>	3.53	4.15	9.88		5.88
Fe <sup>2+</sup>	6.7	9.5	11.07		3.3
Fe <sup>3+</sup>	2.19	3.31	6.62		8.92
Mg <sup>2+</sup>	11.44	16.86			9.5
Mn <sup>2+</sup>	10.59	11.6	12.6	13.81	6.99
Hg <sup>2+</sup>	3.4	2.56			3.4
Ni <sup>2+</sup>	9.86	11.29	15.28		8.41
Ag <sup>+</sup>	11.75	12.59			5.46
Zn <sup>2+</sup>	8.94	8.95	10.09	12.37	5.41

The principal aspect of the methodology proposed is to expose and allow the student to comprehend each step of the reasoning involved in simultaneous equilibria calculation. It is important to emphasize that the classical methodology does not present these steps but a hermetic calculation procedure in which students must previously know several conditions. Some artifices are implicit, and consequently, the students cannot comprehend chemical and numeral interpretations. In addition, it presents several distinguished topics simultaneously, and once more, hermetically, those topics must be introduced or imposed on the student. The XXI Method allows for the explicit of these situations and to expand chemical concepts to other experimental conditions, being able to be “discovered” by the students from initial assumptions (the triad solution).

An example is to consider the ion stoichiometry in the solution presented in the first example (Pure Solution). The classical approach imposes this condition, but the XXXI Method presents it as a special case in which stoichiometry is always veritable in the solid phase. Another example is the absence of a clear distinction between analytical and equilibrium concentrations. In the classical methodology this distinction is imposed, again, in pH effect evaluation, as presented in Example Number 2 ( $2[\text{Ca}^{2+}] = c(\text{F}^-)$  [8,10]). Once more, in the XXI Method, the distinction between analytical and equilibrium concentration appears naturally. Analytical concentration and solubility product (which is defined in terms of equilibrium concentration, or activity, if it is of interest) define The Excess Parameter equation. Relating both, we naturally evaluate simultaneous equilibria. Another unclear situation in the classical methodology is not considering the dilution process (or the

balance of matter in different solutions or steps). Also, it not clearly presents all dilution and stoichiometry strategies and therefore is more difficult for the student to solve elaborated exercises. Once more, as the XXI Method explicitly presents all the strategies applying the balance of matter and phase, it permits solving the problem by clearly presenting the stoichiometry, the quantity involved, and the unknown concentrations, and finally, the selected numerical method determines the unknown values.

## **CONCLUSION**

With our proposal, it is possible to gradually expose a solution's behavior from the Balance of Matter and the Law of Mass Action. We consider this to be our contribution's great advantage. Any previous implicit evaluation is not necessary.

Our methodology allows a straightforward solubility equilibria resolution and interpretation. It is possible to visualize the exercise with the schematic diagram and the detailed equations. Furthermore, the step-by-step resolution process allows clarity and a natural form to solve these equilibria.

To sum up, it is difficult to select a universal best approach to teaching a topic. Teaching solid solubility equilibria using our methodology requires an evaluation and an analysis of the studied system's stoichiometry. This evaluation ought to be associated with the results' natural interpretation based on simple calculations with no need for assumptions. We argue it is a very

interesting approach since it uses a fundamental exercise for the student's development and provides an alternative to the classical methodology.

## SUPPLEMENTARY INFORMATION

Situations involving solubility equilibrium using the Excess Parameter and solutions by classical approximation, exact calculation, and iteration method are shown in Supplementary Information. [Contact the author.]

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