

Advanced Treatment of Chemical Equilibria in the Prediction of the Time of Dissolution of Limestone in a Water Body by the Action of Acid Rain

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Abstract In this study is reported an interdisciplinary approach to teaching chemistry using case studies seeking to stimulate the students in the learning process as well as to develop their critical thinking. The focuses were in chemical multiple equilibrium from an environmental problem based on the quantitative assessment of the dissolution process of limestone sediment containing in a water body by the action of acid rain and increasing of the CO₂ atmospheric concentration. The variables considered were pluviometric average, CO₂, SO₂ and NO₂ levels in the atmosphere as well as their dissolution equilibria and CaCO₃ sediment precipitation. This study is an important teaching tool that can be applied in undergraduate and postgraduate chemistry courses with emphasis in Analytical and Environmental Chemistry, engaging students in active discussion about issues and problems inherent to practical applications.

Keywords: *environmental chemistry, computer-based learning, atmospheric chemistry, computational chemistry, acid-base chemical equilibrium*

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1. Introduction

The knowledge bases of theories concerning the contents of chemical equilibrium with respect to qualitative and quantitative aspects are indispensable tools for the development of chemists and professionals in the field of the industry, laboratory and environmental science.

Chemical equilibrium is considered difficult to understand, especially in its quantitative aspect in the environmental chemistry [1]. Graphs, tables, and statistics can help make sense of the patterns and relationships that exist between variables [2]. Also, computational methods and simulations are often used as tools to solve chemical equilibrium problems [3,4,5,6].

The set of chemical equilibrium concepts discussed in this study in a contextualized way promotes the expansion of students' critical view of chemistry and related fields with respect to the resolution of complex problems that simulate real situations. Interdisciplinarity is important in any area of education, and can be explored in a very productive way in chemistry, since it is a science that interrelates with several others [7].

The assessment of natural processes in the context of environmental chemistry is one of the main fields where

the concepts and models of chemical equilibria are indispensable for the understanding of environmental phenomena and systems. [8,9].

The phenomenon of acid rain was first observed by Ducros (1845) and then described by Robert Angus Smith (1852), who was the pioneer to correlate the occurrence of acid rain with the emissions of industrial gases and the harmful effects on the environment [10,11,12,13,14]. The modern understanding of acid rain reports that it is an environmental problem caused mainly by regional emissions of gases such as sulfur dioxide (SO₂) and nitrogen oxides (NO_x), which are acid gases. These gases impart acidity in the water distributed in the atmosphere through a series of physical and chemical processes [14,15,16]. It is important to note that the presence of carbon dioxide (CO₂) in the atmosphere also gives certain acidity to rainwater, due to its dissolution in the water producing carbonic acid (H₂CO₃). Considering the absence of gases from anthropogenic sources, rainwater has pH around 5.6 [17,18].

Among the harmful effects of acid rain on the environment is the variation of water pH of lakes, which profoundly affects the aquatic life in the water bodies, especially the fish population [19,20,21,22]. Several factors can affect the water pH of lakes in a given region, such as climate, soil geochemistry, terrain nature, vegetation characteristics, among others.

The acidification tendency of natural waters is quite determined by their buffering capacity, usually associated with bicarbonate (HCO_3^-) and carbonic acid species. The main source of HCO_3^- in natural waters is limestone, mainly composed of calcium carbonate (CaCO_3), so that lakes with limestone-rich beds have high concentrations of HCO_3^- which reduces acidification tendency [21,22,23,24].

When the buffering capacity of the water body is exhausted, which may occur by complete dissolution of the limestone present, the acidification tendency naturally increases [20].

The fact that acid rain acts as an important phenomenon that can contribute to the loss of calcareous sediments of lakes, causing an impact on lake ecosystems is already well established [19-24].

The qualitative and quantitative modeling of the processes involved in the action of acid rain on the lake acidification encompasses complex equilibria systems, which requires more advanced algebraic calculations (i.e. mass and charge balances) for more accurate analysis of concentrations of chemical species in the system studied.

Thus, this work aims to present a theoretical study to prediction of the dissolution of limestone sediment of a given water body, by the action of acid rain through time. For this, advanced calculations of chemical equilibrium associated with meteorological and atmospheric emission data are considered to predict the time of dissolution of sediment in the water body.

2. Problem Description

The problem is summarized in the estimation of the dissolution time of the calcareous sediment from the lake considered, with specific meteorological conditions, due

to the acid rain effect, potentiated by the presence of an industrial park a few kilometers from the lake.

For this, a strategy was defined consisting of different stages and conditions for comparison purposes. These situations were (1) in a hypothetical condition that considers only the increase of the CO_2 concentration in the atmosphere and absence of the SO_2 and NO_x gases and (2) condition that reflects the reality of the region of the water body, considering the presence of SO_2 and NO_x gases from emissions from the industrial park.

Figure 1 shows the illustration of the proposed system in this study which reports the main equilibria involved and occurring in the atmosphere and lake.

The natural water body, which is nonstratified, has moderate inflow and outflow. The evaporation and rainfall rates are the main ways of water exchange between the aqueous system and the external environment. Its volume can be considered constant.

Water body has a bed formed by CaCO_3 sediment and is in dynamic equilibrium with the dissolved species in the bulk phase. The dimensions of the water body were determined through a bathymetry study (Table 1). The ambient temperature is 25°C , and atmospheric pressure is 1 atm. The rainfall of the region is evenly distributed throughout the year, with a cumulative annual average of 1450 mm. The data used, such as, values of equilibrium constants, concentration and partial pressure of gases were obtained from literature and standard reference books [21-29].

Table 1. Hypothetical data from the water body under study

Data from the water body	
Area / m^2	128 000
Average depth / m	3
Average volume / m^3	3.84×10^5
Thickness of CaCO_3 / m	0.01

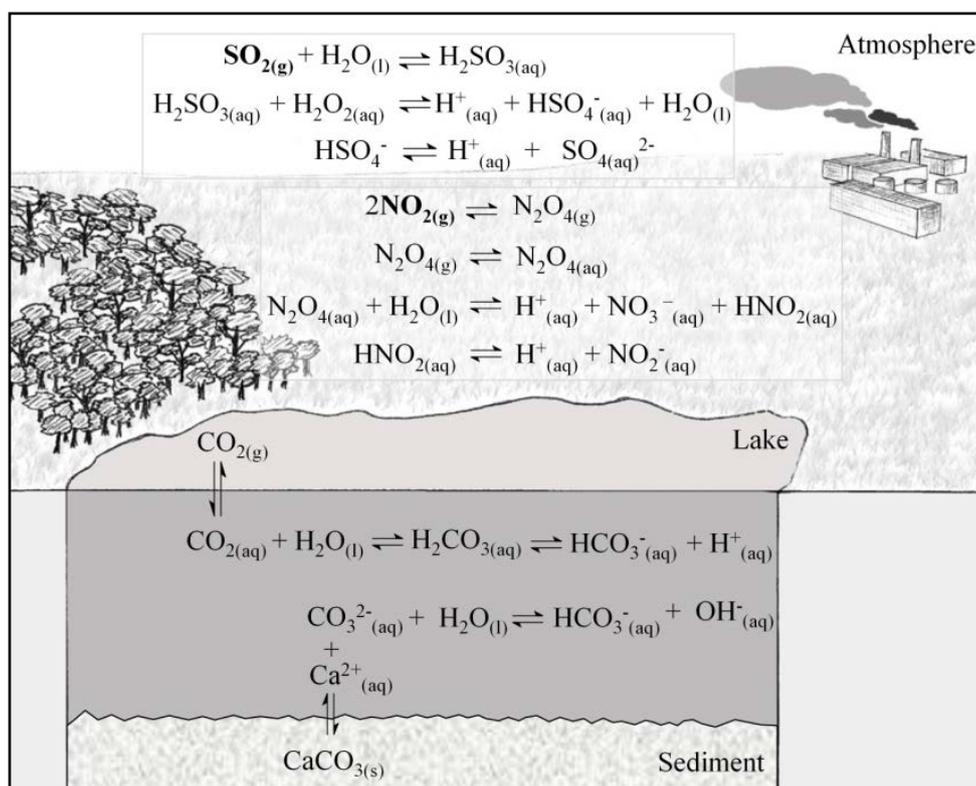


Figure 1. Representation of the system proposed in the study and chemical equilibria involved

The sediment dissolution calculations were performed under two atmospheric situations:

Situation 1 - (i) Rainwater formation considering only the influence of the atmospheric CO_2 at initial concentration of 390 ppm, (average current concentration in the atmosphere). (ii) The $\text{CO}_{2(g)}$ dissolves in rainwater and water body establishing dynamic equilibrium with $\text{CO}_{2(aq)}$ of both medium. (iii) Suppose a rise in atmospheric CO_2 concentration of 1.2%/year due to anthropogenic action [29].

Situation 2 - Rainwater formation considering the atmosphere subject to the gases exhausted by the industrial park. It was assumed that the main species forming acid rain are the SO_2 and NO_2 gases at atmosphere concentrations of 22 and 116 $\mu\text{g m}^{-3}$, respectively. These concentrations simulate an average profile of the concentration of these gases in regions where there are industrial centers [28].

3. Strategy to Solve the Problem

The background knowledge required to solve the proposed problem includes quantitative analytical chemistry, chemical equilibrium of acid-base, precipitation reactions, dissolution of gases in liquids, mass balance, charge balance as well as basic knowledge of environmental chemistry.

The approach used to analyze the problem involves mainly calculations of pH of the system, taking into account all the species in solution and the existing equilibria. Two scenarios could be pictured, one of a "clean" (situation 1) and other of a "polluted atmosphere" (situation 2) as shown in Figure 1. Some simplifications

were considered in the configuration and development of the system modeling:

1. The system reaches equilibrium. The convection of the medium is enough so that the system is not stratified.
2. The pressure and temperature gradient in the water body were not considered.
3. Not all the ionic species present in a natural water body were considered, such as organic acids.
4. The effects of ionic strength and activity are ignored because
 - i) The concentrations of ionic species are small enough to assume that activity equals molar concentration,
 - ii) The model only provides order-of-magnitude results
 - iii) Accounting for ionic strength effects greatly increases the computation difficulty without adding pedagogical value.
5. The water body has a moderate inflow and outflow, but without substantially changing the total volume.
6. The main mode of $\text{CO}_{2(g)}$ incorporation in the water body is by aqueous dissolution equilibrium between the atmosphere and the water. The SO_2 and NO_2 gases are incorporated in the water body through acid rain, once these gases are oxidized in the atmosphere and dissolved in raindrops. We considered only the direct reactions for the dissolution of SO_2 and NO_x gases in rainwater because they form strong acids, that is, are involved in reactions with constants with high order of magnitude.

The Figure 2 presents a flowchart that describes the steps of study.

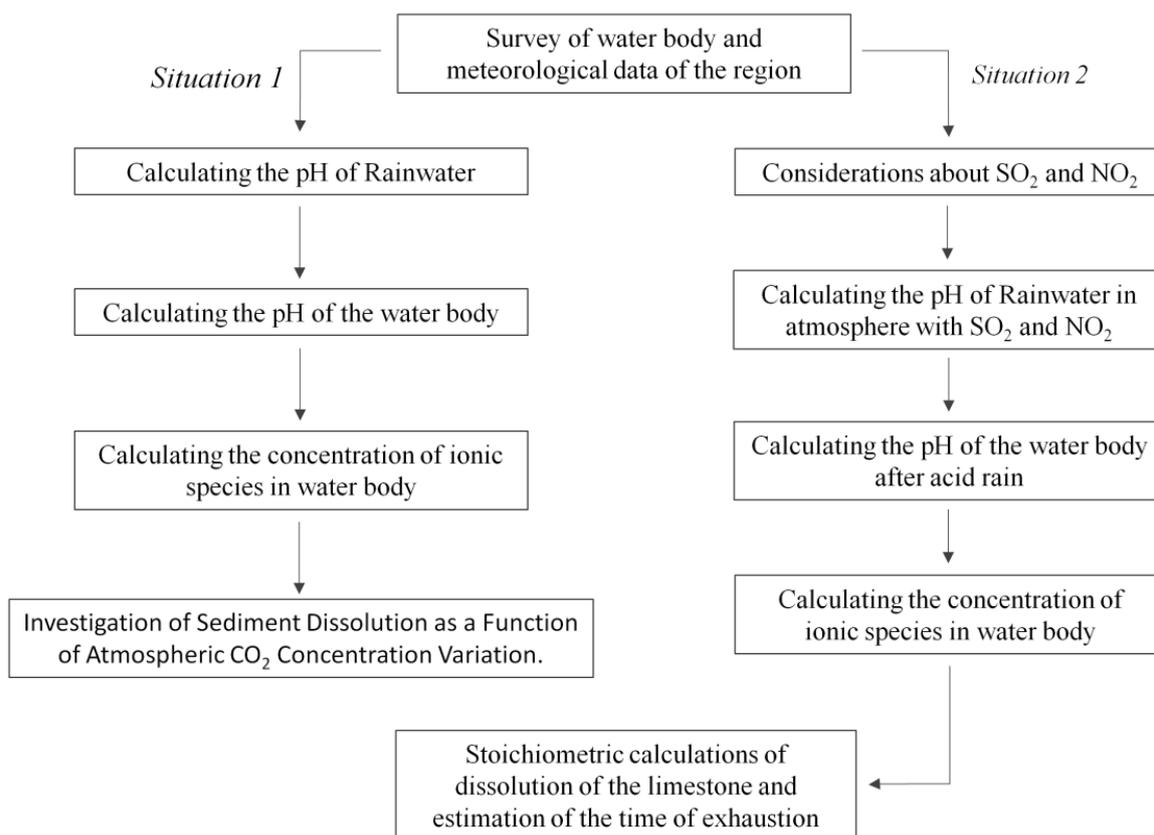


Figure 2. Flowchart of the study steps considering the two situations evaluated

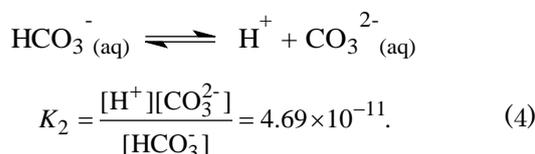
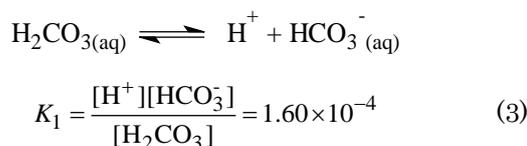
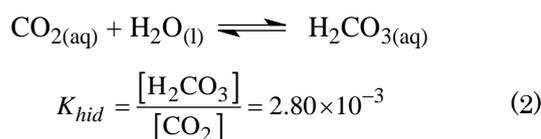
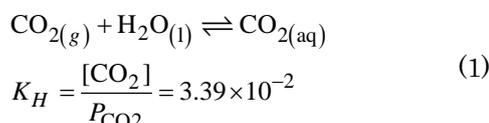
Since the kinetics of SO₂ and NO₂ conversion processes involves slow steps, the impact of these gases “is felt” some time after their emissions. This allows the formation of acid rain on the water body located a few kilometers from the industrial park.

3.1. Situation 1 - Rainwater Formation Considering only the Influence of the Atmospheric CO₂

3.1.1. Calculating the pH of Rainwater: Atmospheric CO₂ Effect

Rainwater is naturally acidic due to CO₂ dissolution equilibrium. This compound is considered as the main acid component of the atmosphere without pollution [17-22,24].

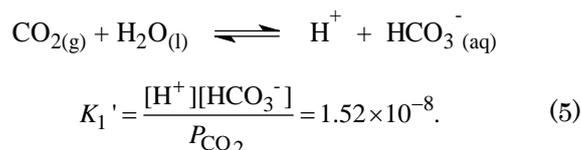
The influence of CO₂ on the pH of water is due to the following processes:



The dissolution equilibrium of CO_{2(g)} between the gas (atmosphere) and aqueous phases (rain) is governed by Henry's law (Equation 1). Considering the concentration of atmospheric CO₂ as 390 ppmv, which generates a $P_{\text{CO}_2} = 3.90 \times 10^{-4}$ atm, the aqueous concentration of CO₂ will be 1.32×10^{-5} mol L⁻¹. Thereby, the pH of the rain is 5.6.

In some situations, mathematical simplifications in calculations of chemical equilibrium systems can be performed without causing a significant source of error in the final result. For cases where greater precision in the accuracy of results is desired, one can resort to the use of computational tools [6].

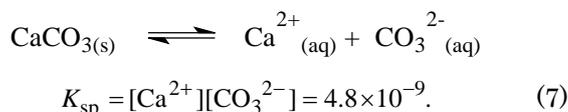
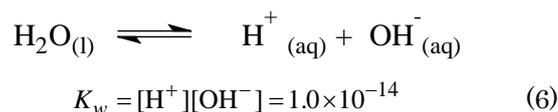
When CO_{2(g)} is distributed in the aqueous phase, a certain fraction of its molecules effectively undergoes hydration (Equation 2), leading to the formation of H₂CO_{3(aq)}. By observing the magnitude of K_{hid} (hydration constant), it is evident that the extent to which acid formation occurs is relatively low (0.3% of the total concentration of CO_{2(aq)} in equilibrium relation). See that Equations 1, 2 and 3 can be summed to obtain directly [H⁺] in aqueous solution from $P_{\text{CO}_2(g)}$:



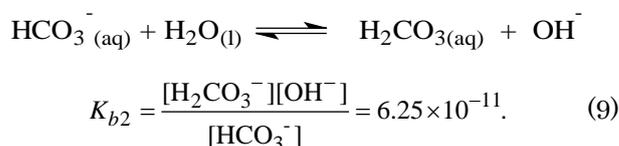
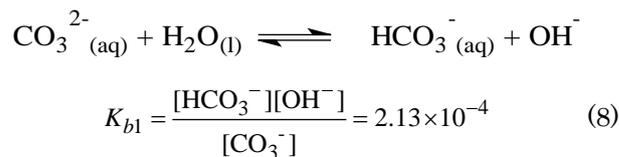
3.1.2. Calculating the pH of the Water Body

Since the natural water body has in its bed CaCO₃ sediment; thus, in addition to the CO_{2(g)} dissolution species, there are also those resulting from the solubilization of the sediment.

The equilibrium equations in the system are 3, 4, 6 and 7:



The hydrolysis reaction of CO_{3²⁻(aq)} from calcium carbonate is implicit in the reverse Equation 4. If necessary, its hydrolysis constant can be obtained from the ratio $K_1 = K_w/K_2$ [22].



The charge balance of the system is:

$$[\text{H}^+] + 2[\text{Ca}^{2+}] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]. \quad (10)$$

Using the equations 3, 4, 6 and 7 in equation 10, an expression for the calculation of [H⁺] was developed and simplified (see in [Supplementary Material](#)):

$$[\text{H}^+] = \sqrt[3]{\frac{K_{a1}^2 K_{a2} [\text{H}_2\text{CO}_3]^2}{2K_{sp}}}. \quad (11)$$

Inserting the values for the constants and [H₂CO₃] was calculated [H⁺]:

$$[\text{H}^+] = 5.55 \times 10^{-9} \text{ mol L}^{-1}, \text{ pH} = 8.26.$$

In complex chemical equilibrium problems, often is not possible to predict which species present in the investigated system are negligible or not. Moreover, it is usually difficult to associate the equations of mass balance and charges of all species in a single expression, as well solve it algebraically. Thus, in these circumstances the graphical method is very effective because it can represent all the expressions of equilibrium constants by a curve on the graph [26].

After representing the graphic system with the other available information of the problem in question, we can approximate the answer based on the present species and their relative abundances.

For a better understanding the graphical method was also used to calculate the initial pH of the water body and rain with SO₂ and NO₂.

We can assign an arbitrary value of [H⁺] in Equation 13 and, then, the result of the term f[H⁺] was calculated, which is a function of concentration of H⁺:

$$f[H^+] = 2K_{sp}[H^+]^4 + K_{a1}K_{a2}[H_2CO_3][H^+]^3 - (K_wK_{a1}K_{a2}[H_2CO_3] + K_{a1}^2K_{a2}[H_2CO_3]^2)[H^+] - 2(K_{a1}K_{a2}[H_2CO_3])^2$$

For [H⁺] equal to 10^{-8.16} we have:

$$f[H^+] = 1.01 \times 10^{-41}$$

Doing the same calculations for other values of [H⁺] in Equation 16 we can construct Table 2 and Figure 3.

Table 2. Graphical method values

[H ⁺]/mol L ⁻¹	pH	f([H ⁺])	f([H ⁺])x10 ⁴²
6.92x10 ⁻⁰⁹	8.16	1.13x10 ⁻⁴¹	11.27
6.61 x10 ⁻⁰⁹	8.18	8.04 x10 ⁻⁴¹	8.04
6.31 x10 ⁻⁰⁹	8.20	5.42 x10 ⁻⁴¹	5.42
6.03 x10 ⁻⁰⁹	8.22	3.30 x10 ⁻⁴¹	3.30
5.75 x10 ⁻⁰⁹	8.24	1.58 x10 ⁻⁴¹	1.58
5.50 x10 ⁻⁰⁹	8.26	2.07 x10 ⁻⁴¹	0.21
5.42 x10 ⁻⁰⁹	8.27	-1.58 x10 ⁻⁴¹	-0.16
5.25 x10 ⁻⁰⁹	8.28	-8.88 x10 ⁻⁴¹	-0.89
5.01 x10 ⁻⁰⁹	8.30	-1.75 x10 ⁻⁴¹	-1.75
4.79 x10 ⁻⁰⁹	8.32	-2.43 x10 ⁻⁴¹	-2.43
4.57 x10 ⁻⁰⁹	8.34	-2.94 x10 ⁻⁴¹	-2.94
4.37 x10 ⁻⁰⁹	8.36	-3.33 x10 ⁻⁴¹	-3.33
4.17 x10 ⁻⁰⁹	8.38	-3.62 x10 ⁻⁴¹	-3.62
3.98 x10 ⁻⁰⁹	8.40	-3.82 x10 ⁻⁴¹	-3.82

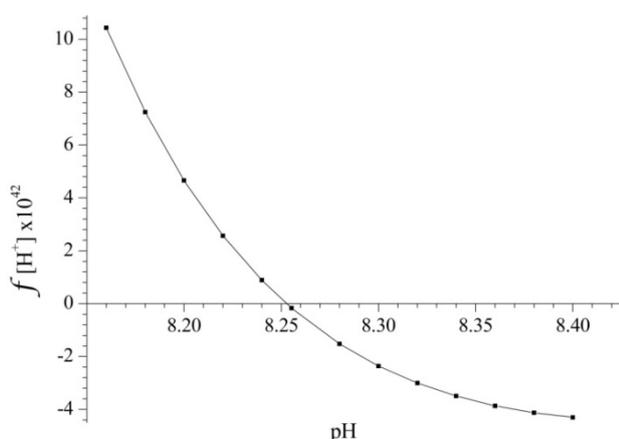


Figure 3. Graphical method for obtaining the pH of the system

The pH of the system is obtained by observing the value of the abscissa (Figure S1), for which y = 0, i.e., the positive real root of Equation 13. According to the graphical method, the pH of the system is ~8.26, so [H⁺] = 5.55 x 10⁻⁹ mol L⁻¹.

3.1.3. Calculating the Concentration of Ionic Species in Water Body

For the [H⁺] value calculated, it is possible to determine the concentration of other species present by the charge balance (Equations 3, 4 and 7):

$$[HCO_3^-] = \frac{K_1[H_2CO_3]}{[H^+]} = \frac{(1.60 \times 10^{-4}) \times (3.70 \times 10^{-8})}{(5.55 \times 10^{-9})} = 1.07 \times 10^{-3} \text{ molL}^{-1}$$

$$[CO_3^{2-}] = \frac{K_2[HCO_3^-]}{[H^+]} = \frac{(4.69 \times 10^{-11}) \times (1.07 \times 10^{-3})}{(5.55 \times 10^{-9})} = 9.00 \times 10^{-6} \text{ molL}^{-1}$$

$$[Ca^{2+}] = \frac{K_{sp}}{[CO_3^{2-}]} = \frac{4.80 \times 10^{-9}}{9.00 \times 10^{-6}} = 5.33 \times 10^{-4} \text{ molL}^{-1}$$

3.1.4. Investigation of Sediment Dissolution as a Function of Atmospheric CO₂ Concentration Variation

The increase in concentration of atmospheric CO₂ increases the concentration of CO₂ dissolved in the lake. This causes an increase in the acidity of the water, consuming the OH⁻ originated from the carbonate hydrolysis of the sediment, once the pH of the water body is slightly alkaline. According to Le Chatelier's principle, for the system to restore equilibrium, the dissolution of sediment is favored in order to give rise to more OH⁻ species. This characterizes a natural buffer system (shown in Figure 1). Exhaustion of CaCO_{3(s)} would promote rapid pH oscillations, which could affect the lacustrine ecosystem.

The solubility of calcium carbonate and the pH of a CO_{2(g)}/CaCO_{3(s)} system, as a function of concentration of atmospheric CO₂ can be observed in Figure 4.

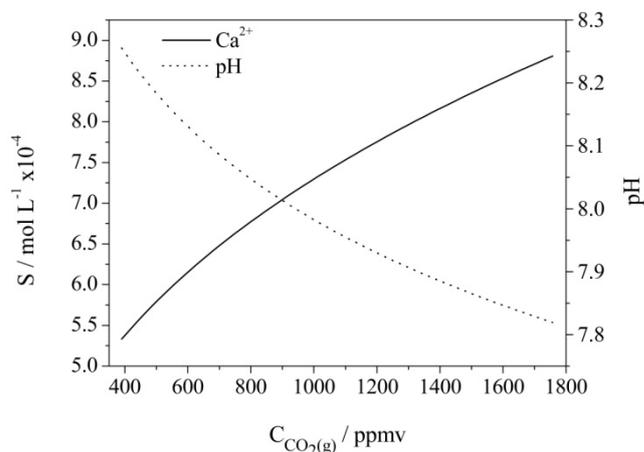


Figure 4. Variation of molar solubility for calcium carbonate (S) and pH as a function of the concentration of CO_{2(g)} in ppmv.

3.2. Situation 2 - Polluted Atmosphere

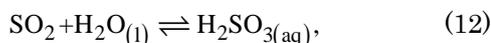
3.2.1. Considerations about SO₂ and NO₂

The second part of the problem consists in considering an atmosphere polluted with SO₂ and NO₂, which concentrations are respectively 22 and 116 μg m⁻³ [22].

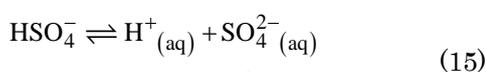
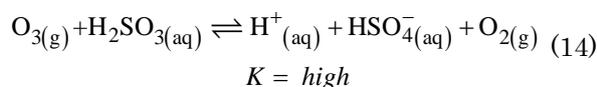
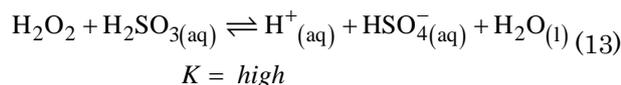
The partial pressures for SO₂ and NO₂ are 8.4x10⁻⁹ atm and 6.2x10⁻⁸ atm respectively.

For partial pressure calculations, see [Supplementary Material](#)

The SO₂ is a sulfur compound present in higher concentration in the atmosphere and it dissolves mainly through the reaction:

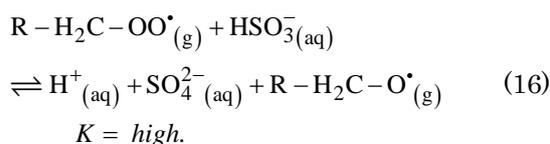


The H₂SO₃ is generally oxidized by an oxidizing agent commonly present in the atmosphere, such as H₂O₂ and O₃ producing sulfuric acid:

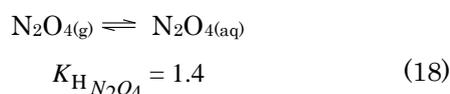
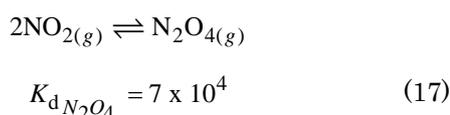


$$K_{a2\text{H}_2\text{SO}_4} = 1.0 \times 10^{-2}$$

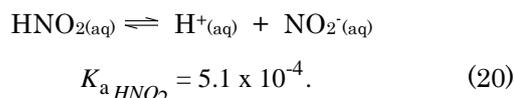
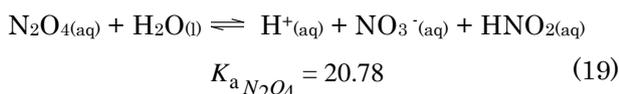
Furthermore, the alkylperoxids (R-H₂C-OO•) present in polluted atmospheres can act as oxidizing agents [30]:



The nitrogen oxides (NO_x) are present in the form of NO and NO₂ in the atmosphere. NO₂ is both a primary and secondary pollutant because it is obtained from the oxidation of NO. NO₂ has a Henry constant equal to 10⁻². Its solubilization occurs largely by the formation of the dimer N₂O₄ [31]:



Dinitrogen tetroxide acts as an oxidizing and reducing agent, forming nitric and nitrous acids:



The impact of the SO₂ and NO₂ gases emission from the industrial park is observed after some time, in the region of the water body, after the transport of these gases by the wind. This natural condition enables the formation of acidic species since the kinetics of these processes involve slow stages.

We considered that all of N₂O₄ and H₂SO₃ generated in aqueous media are consumed because they are involved in reactions with constants of high magnitude order. Thus, the calculated values of [N₂O₄] and [H₂SO₃] can be considered good estimates of [NO₃⁻] and [HSO₄⁻]. SO₂ precipitate as H₂SO₃ and H₂SO₄ while NO_x precipitate as HNO₂ and HNO₃.

The H₂SO₃ concentration is 1.0x10⁻⁸ mol L⁻¹ and N₂O₄ concentration is 3.8x10⁻¹⁰ mol L⁻¹, considering partial pressures values 8.4x10⁻⁹ and 6.2x10⁻⁸ atm for SO₂ and NO₂ are and respectively.

3.2.2. Calculating the pH of Rain with SO₂ and NO₂

The species HNO₃, SO₂ e SO₃ are more soluble than CO₂. Thus, low concentrations of these compounds have a more significant effect at pH of rainwater than high CO₂ concentrations. The value of the equilibrium constant of the total SO₂ reaction is higher than that of CO₂ reaction, since SO₂ is more soluble and it also forms species of stronger acidity [32]. A similar fact occurs for formation of HNO_{3(aq)}.

The calculations of pH in rainwater were both performed considering and disregarding the influence of atmospheric CO₂, in order to investigate the influence of the acid dissolution of this molecule in the presence of gaseous SO₂ and NO₂.

The charge balance of the system is:

$$\begin{aligned} [\text{H}^+] &= [\text{OH}^-] + [\text{HCO}_3^-] + [\text{NO}_2^-] \\ &+ 2[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{HSO}_4^-]. \end{aligned} \quad (21)$$

The value of [OH⁻] can be neglected because it is negligible in relation to other factors of the equation. Because NO₃⁻ and HSO₄⁻ are species formed by the ionization of strong acids, we can state that [NO₃⁻] + [HSO₄⁻] = a.

$$[\text{H}^+] = [\text{HCO}_3^-] + [\text{NO}_2^-] + 2[\text{SO}_4^{2-}] + a. \quad (22)$$

Developing (see in [Supplementary Material](#)):

$$[\text{H}^+] = \frac{a + \sqrt{a^2 + 4 \left(K_{a1}[\text{H}_2\text{CO}_3] + K_{a\text{HNO}_2}[\text{HNO}_2] + 2K_{a2\text{H}_2\text{SO}_4}[\text{HSO}_4^-] \right)}}{2} \quad (23)$$

Using our estimates of [NO₃⁻] and [HSO₄⁻] we have, a = 3.8 x 10⁻¹⁰ + 1.0x10⁻⁸ = 1.04x10⁻⁸ mol L⁻¹. Inserting all the values, we can calculate [H⁺]:

$$[\text{H}^+] = 1.44 \times 10^{-5} \text{ molL}^{-1}, \text{ pH} = 4.84.$$

Now, disregarding the terms involving CO₂, a pH value of 4.85 is obtained. It is observed that this new value differs by 0.13%, compared to the calculations obtained considering CO₂. Thus, it is possible to model the calculations by disregarding the influence of CO₂ on the acidity of the rain when there is presence of SO₂ and NO₂ species.

The SO_{2(g)} concentration of 0.12 ppm_v in equilibrium with rainwater produce a pH of 4.3 when compared to pH 5.6 generated by 350 ppm_v of CO_{2(g)} [32]. Thus, the lower

pH of rainwater reflects the contribution of species H_2SO_4 , HNO_3 and HNO_2 in acidity.

3.2.3. Calculating the pH of the Water Body after Acid Rain

The pH calculated of the water body was performed considering an initial concentration of the species $H_2SO_{4(aq)}$, $HNO_{3(aq)}$ e $HNO_{2(aq)}$ equal to that calculated for rainwater.

The charge balance of the system is:

$$[H^+] + 2[Ca^{2+}] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [NO_2^-] + 2[SO_4^{2-}] + [NO_3^-] + [HSO_4^-] \quad (24)$$

Similarly to the previous case (Equation 21), we can obtain the following expression after rearrangement and simplifications (see in [Supplementary Material](#)):

$$[H^+] = \sqrt[3]{\frac{(K_{a1}[H_2CO_3] + 2K_{a2}H_2SO_4[HSO_4^-])K_{a1}K_{a2}[H_2CO_3]}{2K_{sp}}} \quad (25)$$

$$[H^+] = 1.81 \times 10^{-8} \text{ molL}^{-1}, \text{ pH} = 7.74$$

As expected, the pH of the water body is reduced compared to the value estimated in a clean atmosphere.

Likewise, one can obtain the pH value using the graphical method, according to data from [Table 3](#) and [Figure 5](#).

Table 3. Graphical method - system containing SO₂ and NO₂

$[H^+] / \text{mol L}^{-1}$	pH	$f([H^+])$	$f([H^+]) \times 10^{42}$
2.40×10^{-8}	7.62	1.81E-39	1.81
2.29×10^{-8}	7.64	1.33E-39	1.33
2.19×10^{-8}	7.66	9.46E-40	0.95
2.09×10^{-8}	7.68	6.33E-40	0.63
2.00×10^{-8}	7.70	3.79E-40	0.38
1.91×10^{-8}	7.72	1.74E-40	0.17
1.81×10^{-8}	7.74	-1.18E-42	0.00
1.74×10^{-8}	7.76	-1.20E-40	-0.12
1.66×10^{-8}	7.78	-2.22E-40	-0.22
1.58×10^{-8}	7.80	-3.02E-40	-0.30
1.51×10^{-8}	7.82	-3.63E-40	-0.36
1.45×10^{-8}	7.84	-4.09E-40	-0.41
1.38×10^{-8}	7.86	-4.42E-40	-0.44
1.32×10^{-8}	7.88	-4.65E-40	-0.47

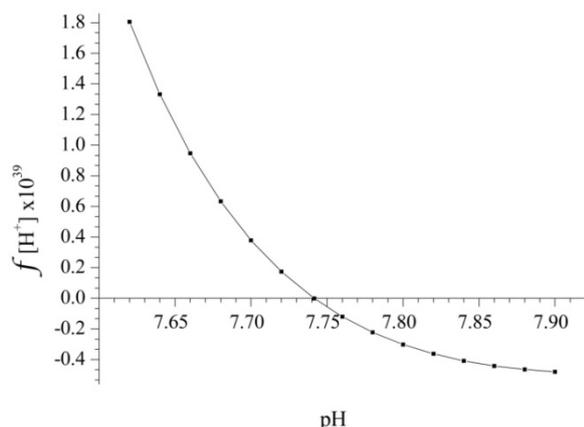


Figure 5. Graphical method for determination of pH - System containing SO₂ and NO₂

3.2.4. Calculating the Concentration of Ionic Species in Water Body

For the $[H^+]$ value calculated, it is possible to determine the concentration of other species present by the charge balance considered (using the equations 3, 4 and 7):

$$[HCO_3^-] = \frac{K_{a1}[H_2CO_3]}{[H^+]} = \frac{(1.60 \times 10^{-4}) \times (3.70 \times 10^{-8})}{(1.81 \times 10^{-8})} = 3.27 \times 10^{-4} \text{ molL}^{-1}$$

$$[CO_3^{2-}] = \frac{K_{a2}[HCO_3^-]}{[H^+]} = \frac{(4.69 \times 10^{-11}) \times (3.27 \times 10^{-4})}{(1.81 \times 10^{-8})} = 8.45 \times 10^{-7} \text{ molL}^{-1}$$

$$[Ca^{2+}] = \frac{K_{sp}}{[CO_3^{2-}]} = \frac{4.80 \times 10^{-9}}{8.45 \times 10^{-7}} = 5.68 \times 10^{-3} \text{ molL}^{-1}$$

4. Results and Discussion

4.1. Stoichiometric Calculations of Dissolution of the Limestone and Estimation of the Time of Exhaustion

For calculation purposes, an atmospheric precipitation and evaporation rate typical of tropical coastal areas was considered. An average annual cumulative total precipitation value was used to estimate the amount of H^+ incorporated through rainwater into the lake throughout the year. The rainfall volume added at lake was calculated according to Equation 24:

$$V = A_1 \times PI \quad (26)$$

$$V = 1.86 \times 10^8 \text{ L}$$

Where:

V = atmospheric precipitation (L)

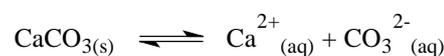
A_1 = area of the water body (m^2)

PI = pluviometric index (mm).

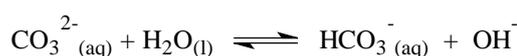
We can infer, for the purpose of approximation, that the water body does not have an appreciable volume variation dynamics. That is, the day by day rainfall regime does not significantly alter the volume of the lake, while the acidic species, which are gradually added over a year, continue to react in direct reaction with the carbonate ($K_{Global} \gg$) (Equation 27).

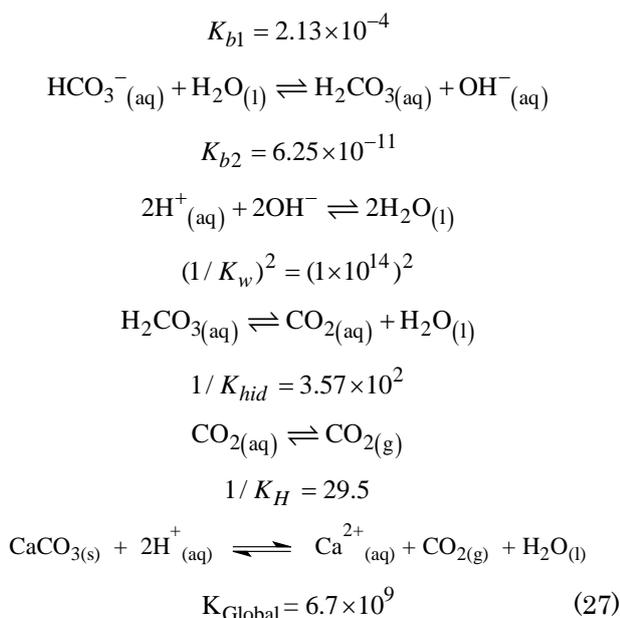
By means of the product of the volume of rainfall and the molar concentration of acid species in the rainwater, it was possible to calculate the average number of moles of H^+ incorporated into the system throughout the year.

In this situation, we have strong acids being added to the system. Thus, the overall $CaCO_3$ sediment dissolution process (Equation 27) can be obtained from the steps below using the equations 1, 2, 6 (inverse), 7, 8 and 9:



$$K_{sp} = 4.80 \times 10^{-9}$$





According to Le Chatelier's principle an incorporation of acidity into the system contributes to an increase in the solubility of the limestone sediment.

The mass of the CaCO_3 sediment was calculated by considering the bed area (equal to the lake area), sediment thickness and density of CaCO_3 equal to 2.71 g cm^{-3} . Thus, a value of 3468.8 kg was obtained, corresponding to the $3.46 \times 10^4 \text{ mol}$ of CaCO_3 .

The amount in moles of H^+ incorporated in one year was $2.67 \times 10^3 \text{ mol}$. Considering the stoichiometry of Equation 32, $1.33 \times 10^3 \text{ mol}$ of CaCO_3 are consumed, which is equivalent to $1.33 \times 10^2 \text{ kg}$ of calcium carbonate dissolved in one year.

Assuming that the meteorological conditions (rainfall pattern) and concentrations of the SO_2 and NO_2 gases maintain this same pattern in the following years and the increase of CO_2 concentration (1.2%/year) in the atmosphere, the approximate time for the dissolution of the limestone sediment would be 26 years.

A general equation (28) for estimating the time of dissolution of the sediment was deduced (See in [Supplementary Material](#)). It considers the main variables associated with the water body and the annual rain regime.

$$t_{(\text{year})} = 2000 \cdot \left(\frac{A_b \cdot \delta_s \cdot d_s}{10^{-\text{pH}_{\text{rain}}} \cdot A_l \cdot \text{PI} \cdot \text{MM}_{\text{CaCO}_3}} \right) \quad (28)$$

Where A_b is area of the bed (considered in this study as equal to the lake area) (m^2); δ_s is the thickness of the sediment (m); d_s is sediment density of calcium carbonate (kg m^{-3}); pH_{rain} is the rainwater pH; A_l is lake area; PI is the pluviometric index (mm) and $\text{MM}_{\text{CaCO}_3}$ is the molar mass of calcium carbonate (kg kmol^{-1}).

Given the idealizations assumed in the proposition of the problem, there is an increasing in solubility of CaCO_3 with increasing acidity of the medium.

From these final data, the research team obtained a prior estimate of the impact that the installation of the industrial center would cause in the water body geochemistry.

Since the equilibrium constant value is high for this process, the equilibrium is shifted to the right, causing a considerable increase of the solubility of CaCO_3 .

The calcium carbonate acts as a buffering agent for the system. Thus, when the buffer capacity of the lake is exhausted it becomes more susceptible to acidification over time [24]. The variations in pH affect the lacustrine ecosystem. The global example is the affectation in the formation of calcareous shells of marine fauna, as well as the delay of CaCO_3 secretion by seaweeds and reef-forming corals [22].

It can also incur in harmful effects on the fish population. Generally, pH 6 and lower ranges affect the reproduction by inhibiting homing migration and spawning behavior. pH 5 and lower ranges induces failure of immune and reproductive functions. When there is a decreasing to pH 4, this cause depression of osmolarity, resulting into mortality [33].

As a consequence of the reduction in the fish population, fishing activities would be affected, mainly those of subsistence.

Studies in lakes in Canada have shown that the increase in acidity has caused the disappearance of shrimp and morphological changes in trout over the years [34].

Acid rain can also lead to the dragging of toxic metals from the soil, such as Al and Cu, and cause harmful effects on the microfauna [34].

A case of acidification occurred with the watershed of Big Moose Lake in the Adirondack Mountains, New York State, United States. This water body received for many years pollutants loaded by the winds that blew of the west of the Pennsylvania and the Ohio Valley, areas of great industrial park. After the buffering capacity of the lake has been exhausted, there was a decline in about one pH unit (between 1950 and 1980 years) causing mortality of fish susceptible to acidity [21].

5. Final Considerations

The educators emphasize that case study exercises are beneficial in order to contextualize the knowledge acquired by the students during the course. The use of a realistic environmental scenario also illustrates the relevance of the environmental chemistry and the importance of chemistry with other fields of knowledge.

The whole framework of calculations, description and understanding of the equilibria involved in the study allowed students to transcend the usual problems of chemical equilibrium, which in most situations are essentially based on laboratory chemical systems, isolated in a beaker, volumetric flasks or erlenmeyers.

The proposal presented by the case study gave the learning process a more realistic and elaborated approach, leading students to contact the disciplinary interfaces between the chemistry of chemical equilibria, environmental science, meteorology and ecosystem impact. Case studies can be applied in similar ways to explore the frontiers of chemistry and other sciences.

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