Some Aspects of the Spontaneous Solubility Equilibria of Solid Carbonates

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Abstract: In order to adequately carry out the laboratory procedures usually taught in a general analytical chemistry course, students must master the subject of multiple equilibria in aqueous solution, both conceptually and mathematically. The use of a computer program to solve the concentrations of all species at equilibrium with a slightly soluble compound is frequently recommended in the chemical education literature, due to its simplicity and quickness. But, when this calculation procedure fails to consider other important reactions aside from the solubility equilibrium itself, significant differences in the numerical results may be obtained. For several metal carbonates, the usual procedure to calculate their solubilities is to consider carbonate ion hydrolysis as the only additional reaction.

In this paper it is shown numerically and graphically that for magnesium and silver carbonates, the precipitation reaction of metal (hydr)oxides would occur at the pH value calculated from the carbonate dissolution plus the anion hydrolysis equilibria. An analytical procedure to solve these complex multiple equilibria system is presented. The final solution to the problem is obtained through a high-order equation that is easily solved by a simple iterative method. The correct solubility–pH curve for the metal carbonates is calculated, and the pH values for the metal hydroxide precipitation onset for several important representative and transition metal carbonates are shown. It is concluded that the overall procedures to solve these multiple equilibria problems are not beyond the comprehension of any chemistry student with a acceptable background in general, inorganic, and analytical chemistry, and that by focusing on tasks such as these, important critical-thinking skills can be obtained.

Introduction

The subjects of sparingly soluble salts and the calculation of their solubilities in aqueous solution have recently received some attention in the chemical education literature [1–7]. In our General Analytical Chemistry syllabus, this topic is included under the subject of volumetric analysis [8–10], which includes acid–base neutralization, formation of precipitates, complex ion formation, and oxidation–reduction reactions, and takes about 40–50% of the course time. Our main goal in this subject is to teach our students some simple and fundamental analytical techniques that require almost no instrumentation or sophisticated equipment, in spite of the fact that actual use of volumetric analysis in a modern analytical laboratory is progressively less frequent. In order to carry out these laboratory procedures adequately, the students must master the subject of multiple equilibria in aqueous solution, as much from a formal conceptual point of view (abstract visualization of simultaneous equilibria) as from an operational concrete one (the mathematical formalism to solve the calculations of all the chemical species). Thus, the acquisition of these skills by the student constitutes our secondary teaching goal.

Those who teach chemistry to prospective chemists may ask themselves some nontrivial questions, such as: how deeply should we advance in the teaching of the multiple equilibria treatment, or what should we necessarily teach to our students and what can (or should) they learn by themselves when facing a real problem? It is agreed that after an introductory analytical chemistry course a chemistry student should be able to outline all the known variables in the problem to be solved (e.g., the chemical species present in solution), to express their relationships (the equilibrium reactions among them, the expressions of their equilibrium constants, and the charge and mass balances), and to apply the necessary mathematical procedures for their resolution. A very important final step arises after the student has finished the mathematical work and has at hand a numerical result. This sometimes-neglected step is one that all teachers must encourage and improve in their students: the ability to critically analyze the obtained result, taking it with reasonable skepticism, and giving it the correct valuation within the suppositions, simplifications, and approximations that had to be made. In order to accept or reject any obtained result, it is necessary to have a wide comprehension of the chemistry involved in the problem so as to decide whether the result is reasonable or not, whether the approximations made are reliable or not, and whether a more exact calculation requiring more time and a higher complexity level is justifiable. This final procedure corresponds to the last phase of the four (or more) steps, which are often described as the process of problem solving [11], and is commonly referred to as "looking back" or "reviewing the results."

In the classroom, some teachers hesitate to sketch a problem with several competing equilibria as they consider this kind of exercise beyond the scope of a general analytical chemistry course. While the resolution of exercises involving multiple equilibria is more complex than those involving only a simple one, the underlying concepts are not beyond the comprehension of chemistry undergraduates. For example, when precipitation–dissolution reactions are taught in

Table 1. Prediction of hydroxide formation from the metal carbonate solubility equilibrium

Cation	$K_{sp(carbonate)}$ [a]	pH [a]	[cation] = S [a] (mol L^{-1})	[OH$^-$] [a] (mol L^{-1})	$Q_{hydroxide}$	$K_{sp(hydroxide)}$ [d]	$Q > K_{sp}$
Mg^{2+}	1.0×10^{-5}	10.9	3.6×10^{-3}	7.7×10^{-4}	2.13×10^{-9} [b]	7.08×10^{-12}	yes
Ca^{2+}	4.8×10^{-9}	10.0	1.3×10^{-4}	9.0×10^{-5}	1.05×10^{-12} [b]	6.46×10^{-6}	no
Ba^{2+}	5.1×10^{-9}	10.0	1.3×10^{-4}	9.1×10^{-5}	1.08×10^{-12} [b]	2.51×10^{-4}	no
Ag$^+$	8.1×10^{-12}	10.1	1.8×10^{-4}	1.2×10^{-4}	4.67×10^{-16} [c]	3.80×10^{-16}	yes
Cd^{2+}	2.5×10^{-14}	8.2	1.6×10^{-6}	1.8×10^{-6}	5.85×10^{-18} [b]	4.47×10^{-15}	no
Pb^{2+}	3.3×10^{-14}	8.3	1.9×10^{-6}	1.9×10^{-6}	6.86×10^{-18} [b]	7.94×10^{-16}	no

(a) $K_{sp(carbonate)}$, pH, Solubility (S) and hydroxyl ion concentration values taken from De Roo et al. [7] corresponding to the metal carbonate solubility equilibrium calculated by computer program. $Q_{hydroxide}$ values calculated as: (b) [cation][OH$^-$]^2 (c) [cation]^2 [OH$^-$]^2 (considering the reaction Ag$_2$O(s) + 2H$_2$O $\rightleftharpoons$ 2Ag$^+$(aq) + 2OH$^-$(aq) (d) values from reference [12]

analytical chemistry, it is usual to consider them as simple chemical processes; too often the existence of competing equilibria is ignored. This occurs sometimes for convenience and simplicity, and sometimes because of incomplete knowledge of the chemical system in the problem. In this particular topic, the additional equilibria affecting the dissolution and solubility of solid compounds in aqueous solution may be (among others): a) acid–base reactions by the anion and/or the cation (giving soluble products), b) complexing reactions of the cation involving the same anion as ligand, c) complexing reactions of the cation with a different anion (or molecule) as ligand, d) other precipitation reactions for the cation, and e) complexing reactions of the cation with a ligand that has acid–base properties.

Solving some of the above-mentioned problems involving several simultaneous equilibria may turn into a difficult and boring task. Therefore, the use of any available computer program that gives the numerical solution represents a very good alternative. However, the use of canned programs to solve such problems is similar to the use of a black box, where some data are introduced on one side and the answers are obtained on the other side. A highly risky situation arises when the answers given by the computer are accepted as unquestionable truths. Students, as well as chemists, solving an analytical problem must be permanent reviewers of their analytical procedures, calculation methodologies, and, especially, of the obtained results. This general procedure is occasionally forgotten when the major emphasis and effort is given to the computer program. With respect to this point, it is interesting to analyze some numerical results reported by De Roo et al. [7] about the solubility of sparingly soluble salts calculated using a computational method. In that paper, De Roo et al. present a very useful mathematical program to solve solubility calculations of several chemical systems quickly and exactly that would otherwise involve considerable time and effort. The chemical systems analyzed include oxalates, sulfates, carbonates, and sulfides of alkaline earth and transition metals, which usually require solution of a nonlinear system of six equations with six unknowns. The aim of this paper is to make some observations on the solubility and pH values obtained by these authors for metal carbonates in aqueous solutions, and to consider other equilibrium reactions occurring with the carbonate dissolution, solving them using a classical analytical chemistry methodology.

Analysis of Several Metal Carbonates in Aqueous Solution

The "spontaneous" pH value that one obtains in an aqueous solution in contact with a sparingly soluble metal carbonate is determined by the amount of carbonate anion produced by the dissolution process and the hydrolysis reactions of this anion. The first of these processes depends on the metal carbonate solubility product constant, $K_{sp(MCO_3)}$, while the second one depends mainly on the carbonate anion concentration and its first basic equilibrium constant, $K_{b_1} = K_w / K_{a_2}$. Using the solubility and equilibrium pH values obtained by De Roo et al. [7] (reproduced here in Table 1) and a computer program, one computes for magnesium, calcium, barium, and silver carbonates that the aqueous solution turns mildly alkaline, with pH values between 10.0 and 10.9, according to the metal. This occurs mainly because the $K_{sp(MCO_3)}$ values of these compounds are not too small: from 1.0×10^{-5} to 8.1×10^{-12}. A significant amount of CO$_3^{2-}$ (aq) appears in solution and hydrolyzes to a considerable extent. On the other hand, for lead and cadmium carbonates, the calculated equilibrium pH values are nearly neutral: 8.3 and 8.2, respectively. This is a consequence of smaller K_{sp} values, 3.3×10^{-14} and 2.5×10^{-14} respectively, and to a lesser extent of the hydrolysis of CO$_3^{2-}$ (aq) in solution.

Students analyzing the obtained results for cation concentration and pH values, and relating them to some inorganic chemistry knowledge about Mg^{2+}, Ca^{2+}, Ba^{2+}, Ag$^+$, Cd^{2+}, and Pb^{2+} hydroxides, might and/or should ask themselves whether it is possible that, at the pH value produced by aqueous carbonate anion hydrolysis, the cation in solution (at the concentration given for the calculated solubility) could precipitate as its respective hydroxide. In case of an affirmative answer, would this process affect the previously calculated solubility? An affirmative reply again would mean that the reported solubility value will not be the "real" one, and here a last question arises: how to calculate this new value? In order to answer the first of these questions it is enough to determine the value of the ion product (or reaction quotient, Q) for each metal hydroxide, and to compare it with the solubility product constant of the respective metal hydroxide, $K_{sp(hydroxide)}$. This procedure has been applied to all the carbonates reported by De Roo et al. [7], as shown in the last three columns in Table 1. It is necessary to mention that in the computer calculation procedure by De Roo et al., the aqueous cation concentration is taken as equal to the solubility value for the carbonate compound.

It can be seen that for magnesium and silver carbonates the formation and precipitation of Mg(OH)$_2$(s) and Ag$_2$O(s), respectively, would have to occur from the carbonate dissolution. This process may also be observed through a solubility–pH plot. In Figure 1, the solubility curve of
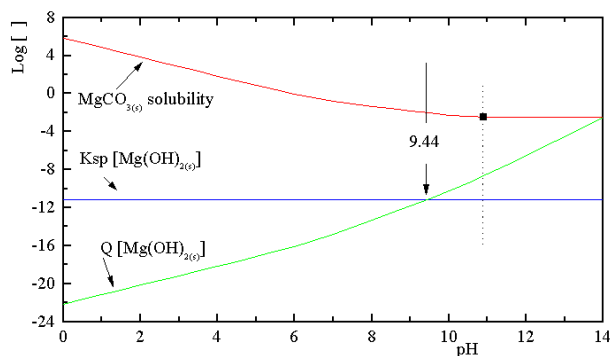
Figure 1. Solubility of $MgCO_3(s)$ (in mol L^{-1}), without considering magnesium hydroxide formation, and magnesium hydroxide reaction-quotient (Q) curves as functions of solution pH. The black symbol represents the "spontaneous" solubility and pH values at equilibrium calculated for the hydrolysis of $MgCO_3$, $S = 3.6 \times 10^{-3}$ M and pH = 10.9 [7].
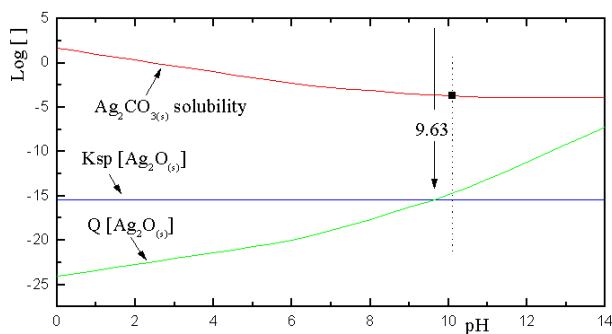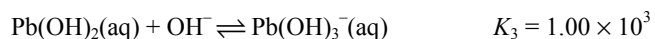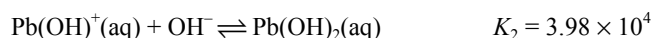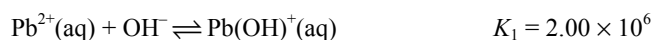

Figure 2. Solubility of Ag_2CO_3 (in mol L^{-1}), without considering silver oxide formation, and silver oxide reaction-quotient (Q) curves as functions of solution pH. The black symbol represents the "spontaneous" solubility and pH values at equilibrium calculated for the hydrolysis of Ag_2CO_3 , $S = 1.08 \times 10^{-4}$ M and pH = 10.1 [7].

$MgCO_3(s)$ is shown as a function of pH, considered here as a master variable. This curve was calculated with the equation system used by De Roo et al. [7] and the corrections stated by Bader [6]. As expected, the solubility increases according to the more significant hydrolysis of the $CO_3^{2-}(aq)$ anion that occur at acidic pH values, but at pH more alkaline than 12.0, the solubility remains constant since the carbonate species prevailing in solution is $CO_3^{2-}(aq)$ anion ($pK_{a_2} = 10.33$). In the same figure, the reaction quotient is also shown for magnesium hydroxide, $Q_{(Mg(OH)_2)} = [Mg^{2+}][OH^-]^2$, as a function of pH considering the magnesium cation as coming from the dissolved carbonate with a concentration value equal to the calculated solubility, $[Mg^{2+}] = S$. In Appendix I, the procedure is given for obtaining the mathematical expression for solubility of $MgCO_3(s)$ and reaction quotient of $Mg(OH)_2(s)$ as a function of pH. For the sake of comparison, the same figure shows the value of K_{sp} for $Mg(OH)_2(s)$. It is possible to see that $Q_{(Mg(OH)_2)} > K_{sp(Mg(OH)_2)}$ occurs at pH values higher than 9.44. Therefore, the portion of the solubility curve of $MgCO_3(s)$ shown for pH > 9.44, calculated without taking into account the precipitation of the magnesium hydroxide, does not correspond to a real situation in the aqueous solution. The spontaneous pH value calculated by De

Roo et al. [7] for the solubility of magnesium carbonate, 10.9, is within this pH range, and then the precipitation of $Mg(OH)_2(s)$ should be taken into account.
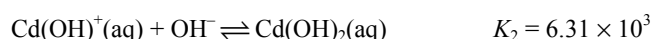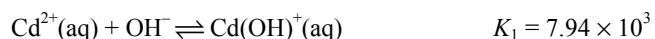
Figure 2 shows the same analysis for the solubility of $Ag_2CO_3(s)$, the reaction quotient of silver oxide, $Q_{(Ag_2O)} = [Ag^+]^2[OH^-]^2$, and the $K_{sp(Ag_2O)}$ as a function of pH (see Appendix II for the equations used to calculate these curves). For $Ag_2O(s)$ the value of $Q_{(Ag_2O)}$ is higher than the $K_{sp(Ag_2O)}$ at pH more alkaline than 9.63, indicating that $Ag_2O(s)$ would precipitate from Ag^+ ions coming from the $Ag_2CO_3(s)$ dissolution. Seemingly, the portion of the solubility curve of solid silver carbonate shown in Figure 2 is not the real one for pH > 9.63. Again, the spontaneous pH value calculated by De Roo et al. [7] for the solubility of silver carbonate (10.1) is within this pH range, and therefore would not be an acceptable value.
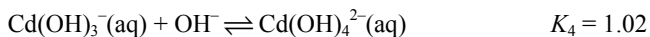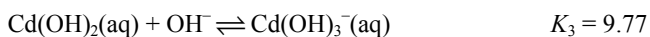
From the aforementioned, it may be pointed out that a modification in pH and cation concentration in solution calculated by De Roo et al. [7] would have to occur as a consequence of magnesium hydroxide or silver oxide precipitation, producing then a change in the solubility value of magnesium or silver carbonate, respectively. This qualitative and conceptual analysis leads one to the consideration that the calculation methodology taking into account only the carbonate dissolution and anion hydrolysis processes will produce "unreal" values for the solubility of $MgCO_3(s)$ and $Ag_2CO_3(s)$ in aqueous solution. A new calculation procedure that takes into account all the involved equilibrium reactions should be tried again. Student and teacher alike, deeply engaged in the mathematical complexity of calculating the solubility of a solid carbonate considering all the equilibrium reactions for the $CO_2(aq)/H_2CO_3(aq)/HCO_3^-$ $(aq)/CO_3^{2-}(aq)$ system (or working on a computer program to solve this problem), can easily overlook a final detail: to check the obtained result under a different (although similar) chemical point of view, as the metal hydroxide solubility. Therefore, the key role of any teacher is to develop in students this attention to analytical detail.

Other interesting systems to analyze are the cadmium(II) and lead(II) carbonates. Even though these cations do not precipitate as their corresponding hydroxides at the spontaneous pH values given by the hydrolysis of their carbonate compounds (8.2 and 8.3, respectively [7]), the following reactions of complex ion formation with hydroxide anion [8, 10, 12] are known:
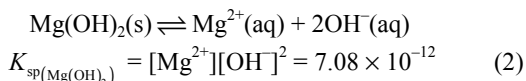
$Pb^{2+}(aq) + OH^- \rightleftharpoons Pb(OH)^+(aq)$ $K_1 = 2.00 \times 10^6$

$Pb(OH)^+(aq) + OH^- \rightleftharpoons Pb(OH)_2(aq)$ $K_2 = 3.98 \times 10^4$

$Pb(OH)_2(aq) + OH^- \rightleftharpoons Pb(OH)_3^-(aq)$ $K_3 = 1.00 \times 10^3$

and

$Cd^{2+}(aq) + OH^- \rightleftharpoons Cd(OH)^+(aq)$ $K_1 = 7.94 \times 10^3$

$Cd(OH)^+(aq) + OH^- \rightleftharpoons Cd(OH)_2(aq)$ $K_2 = 6.31 \times 10^3$

$$Cd(OH)_2(aq) + OH^- \rightleftharpoons Cd(OH)_3^-(aq) \qquad K_3 = 9.77$$

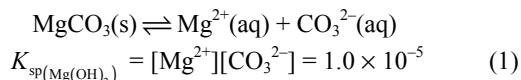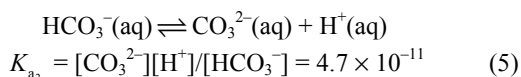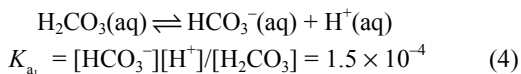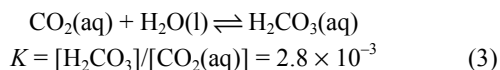$$Cd(OH)_3^-(aq) + OH^- \rightleftharpoons Cd(OH)_4^{2-}(aq) \qquad K_4 = 1.02$$

From the numerical values of these equilibrium constants, it would be reasonable to consider that in aqueous solution, $Pb^{2+}(aq)$ and $Cd^{2+}(aq)$ cations coming from metal carbonate dissolution will react with OH^- arising from the hydrolysis of $CO_3^{2-}(aq)$. Therefore this process will produce pH and solubility values different from those shown in Table 1. A more rigorous analytical approach to obtaining the solubilities of magnesium and silver carbonates should take into account the precipitation of $Mg(OH)_2(s)$ and $Ag_2O(s)$, and for lead and cadmium carbonates, the formation of different Pb^{2+}–OH^- and Cd^{2+}–OH^- complex species. All this led us to consider more complicated systems of multiple equilibrium reactions. In the following paragraphs the calculations of $MgCO_3(s)$ and $Ag_2CO_3(s)$ solubilities are analyzed in detail.

Solubility Equilibria of $MgCO_3(s)$

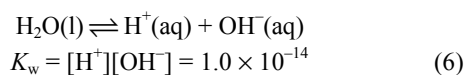In order to calculate the solubility of solid $MgCO_3(s)$, the spontaneous pH value and the concentration of all the species present in solution, taking into account the $Mg(OH)_2(s)$ formation, it is necessary to outline the following equilibrium reactions (with K_{sp} values at room temperature):

$$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$$
$$K_{sp(Mg(OH)_2)} = [Mg^{2+}][CO_3^{2-}] = 1.0 \times 10^{-5} \qquad (1)$$

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$
$$K_{sp(Mg(OH)_2)} = [Mg^{2+}][OH^-]^2 = 7.08 \times 10^{-12} \qquad (2)$$

Consider the carbonic acid–carbonate equilibria as a closed system without the participation of atmospheric $CO_2(g)$ (indeed a simplifying assumption) and with a simplified notation for hydronium ion:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$
$$K = [H_2CO_3]/[CO_2(aq)] = 2.8 \times 10^{-3} \qquad (3)$$

$$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$
$$K_{a_1} = [HCO_3^-][H^+]/[H_2CO_3] = 1.5 \times 10^{-4} \qquad (4)$$

$$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$$
$$K_{a_2} = [CO_3^{2-}][H^+]/[HCO_3^-] = 4.7 \times 10^{-11} \qquad (5)$$

and the water autoionization equilibrium:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$
$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \qquad (6)$$

The charge balance takes the following expression:

$$2[Mg^{2+}] + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] \qquad (7)$$

and the mass balance:

$$S_{(MgCO_3)} = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]$$
$$+ [CO_2(aq)] = [CO_3^{2-}]_{total} \qquad (8)$$

The pH value of this system at equilibrium will obviously be alkaline, but somewhat less than 10.9. It is very important to note that in this case

$$S_{(MgCO_3)} \neq [Mg^{2+}] = K_{sp(Mg(OH)_2)} \frac{[H^+]^2}{K_w^2} \qquad (9)$$

because some magnesium cations coming from the carbonate dissolution precipitate as solid $Mg(OH)_2$, which is significantly more insoluble than $MgCO_3$ at the expected pH value (between 9.44 and 10.9, Figure 1). Replacing eq. (7) with eqs. (9), (5), and (6) we obtain

$$\frac{2K_{sp(Mg(OH)_2)}[H^+]^2}{K_w^2} + [H^+] = [CO_3^{2-}]\left(2 + \frac{[H^+]}{K_{a_2}}\right) + \frac{K_w}{[H^+]} \qquad (10)$$

Using eqs. (1) and (9) in order to express $[CO_3^{2-}]$ as a function of $[H^+]$:

$$\frac{2K_{sp(Mg(OH)_2)}[H^+]^2}{K_w^2} + [H^+] =$$
$$\frac{K_{sp(MgCO_3)}K_w^2}{K_{sp(Mg(OH)_2)}[H^+]^2}\left(2 + \frac{[H^+]}{K_{a_2}}\right) + \frac{K_w}{[H^+]} \qquad (11)$$

and rearranging eq. (11), a fourth degree equation in hydrogen ion concentration is obtained:

$$\frac{2K_{sp(Mg(OH)_2)}^2[H^+]^4}{K_{sp(MgCO_3)}K_w^4} + \frac{K_{sp(Mg(OH)_2)}[H^+]^3}{K_{sp(MgCO_3)}K_w^2}$$
$$- \frac{K_{sp(Mg(OH)_2)}[H^+]}{K_w K_{sp(MgCO_3)}} - 2 - \frac{[H^+]}{K_{a_2}} = 0$$

or

$$[H^+]^4 + \frac{K_w^2}{2K_{sp(Mg(OH)_2)}}[H^+]^3 -$$
$$\left(\frac{K_w^3}{2K_{sp(Mg(OH)_2)}} + \frac{K_{sp(MgCO_3)}K_w^4}{2K_{sp(Mg(OH)_2)}^2 K_{a_2}}\right)[H^+] - \frac{K_{sp(MgCO_3)}K_w^4}{K_{sp(Mg(OH)_2)}^2} = 0 \qquad (12)$$

In spite of its apparent complexity, this equation can be easily solved with a hand calculator using a simple iterative method. For this purpose we rearrange eq. (12) as follow:

$$[H^+]^3\left([H^+] + \frac{K_w^2}{2K_{sp(Mg(OH)_2)}}\right) -$$
$$\left[\left(\frac{K_w^3}{2K_{sp(Mg(OH)_2)}} + \frac{K_{sp(MgCO_3)}K_w^4}{2K_{sp(Mg(OH)_2)}^2 K_{a_2}}\right)[H^+] + \frac{K_{sp(MgCO_3)}K_w^4}{K_{sp(Mg(OH)_2)}^2}\right] = 0$$

and

$$[H^+] = \left(\frac{\left[\dfrac{K_w^3}{2K_{sp(Mg(OH)_2)}} + \dfrac{K_{sp(MgCO_3)}K_w^4}{2K_{sp(Mg(OH)_2)}^2 K_{a_2}} \right][H^+] + \dfrac{K_{sp(MgCO_3)}K_w^4}{K_{sp(Mg(OH)_2)}^2}}{[H^+] + \dfrac{K_w^2}{2K_{sp(Mg(OH)_2)}}} \right)^{\!\!1/3} \quad (13)$$

Introducing the numerical values for all the equilibrium constants from eqs. (1), (2), (5), and (6), we obtain the final equation:

$$[H^+] = \left(\frac{2.13 \times 10^{-29}[H^+] + 2.00 \times 10^{-39}}{[H^+] + 7.06 \times 10^{-18}} \right)^{\!\!1/3} \quad (14)$$

which requires the assignment of an initial value to $[H^+]$ in order to calculate another successively more approximate (and more exact) value. This procedure is repeated as many times as needed until two successive constant values in a specified decimal place are obtained. Taking as a starting point a value of $[H^+]_o = 1 \times 10^{-10}$ M (a pH value less alkaline than that obtained without considering the hydroxide formation), after five iteration steps the value $[H^+] = 3.028 \times 10^{-10}$ M is obtained. This value is constant in the third decimal place with respect to that obtained with other iteration steps. Finally, the following values can be stated for the hydrogen ion concentration and the spontaneous pH of an aqueous solution in equilibrium state with the $MgCO_3(s)$–$Mg(OH)_2(s)$ system:

$$[H^+] = 3.03 \times 10^{-10} \text{ M}$$

and

$$pH = 9.52$$

Thus we can verify that the obtained "spontaneous" pH value from this equation system is placed in the range pH > 9.44, as shown in Figure 1, but it is significantly lower than the pH value calculated by the computer program of De Roo et al. [7], 10.9. The concentration of free $Mg^{2+}(aq)$ cations in simultaneous equilibrium with both solids is given by eq. (9):

$$[Mg^{2+}] = K_{sp(Mg(OH)_2)} \frac{[H^+]^2}{K_w^2} = 6.49 \times 10^{-3} \text{ M}$$

which determines an amount of $CO_3^{2-}(aq)$ given by eq. (1):

$$[CO_3^{2-}] = \frac{K_{sp(MgCO_3)}}{[Mg^{2+}]} = 1.54 \times 10^{-3} \text{ M}$$

The concentration values for the other species arising from the carbonate anion hydrolysis are given by eqs. (5), (4), and (3), respectively:

$$[HCO_3^-] = \frac{[CO_3^{2-}][H^+]}{K_{a_2}} = 9.93 \times 10^{-3} \text{ M}$$

$$[H_2CO_3] = \frac{[CO_3^{2-}][H^+]^2}{K_{a_1}K_{a_2}} = 2.00 \times 10^{-8} \text{ M}$$

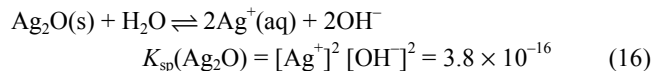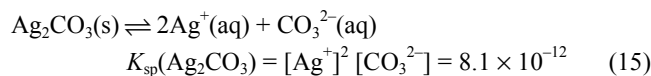$$[CO_2(aq)] = \frac{[CO_3^{2-}][H^+]^2}{K K_{a_1}K_{a_2}} = 7.16 \times 10^{-6} \text{ M}$$

Finally, the magnesium carbonate solubility is obtained from eq. (8):

$$S_{(MgCO_3)} = 1.15 \times 10^{-2} \text{ M}$$

We can verify that $S_{(MgCO_3)} > [Mg^{2+}]$ due to the $Mg(OH)_2(s)$ formation.

Solubility Equilibria of Ag₂CO₃(s)

In order to analyze the silver carbonate solubility, following the same procedure as before, we take into account the following equilibrium reactions

$$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$$
$$K_{sp}(Ag_2CO_3) = [Ag^+]^2 [CO_3^{2-}] = 8.1 \times 10^{-12} \quad (15)$$

$$Ag_2O(s) + H_2O \rightleftharpoons 2Ag^+(aq) + 2OH^-$$
$$K_{sp}(Ag_2O) = [Ag^+]^2 [OH^-]^2 = 3.8 \times 10^{-16} \quad (16)$$

With reactions (3) to (5) for the carbonic acid–carbonate system, and the autoionization of water, eq. (6), the charge balance is as follows:

$$[Ag^+] + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] \quad (17)$$

The mass balance takes the same expression as in the magnesium carbonate example:

$$S_{(Ag_2CO_3)} = [CO_3^{2-}] + [HCO_3^-]$$
$$+ [H_2CO_3] + [CO_2(aq)] = [CO_3^{2-}]_{total} \quad (18)$$

where $S_{(Ag_2CO_3)}$ is the solubility of silver carbonate. Here again it occurs

$$S_{(Ag_2CO_3)} \neq \tfrac{1}{2}[Ag^+] \quad (19)$$

and from eqs. (16) and (6):

$$[Ag^+] = \left(K_{sp(Ag_2O)} \right)^{1/2} \frac{[H^+]}{K_w} \quad (20)$$

since at pH > 9.63 the silver oxide is more insoluble than the silver carbonate. From the charge balance, using eqs. (6), (15), and (20), the following expression is obtained:

Table 2. Solubility, pH, and concentration of all species in solution at equilibrium condition for $MgCO_3(s)$ and $Ag_2O(s)$ in aqueous solution.

Cation	$[CO_3^{2-}]$ (mol L^{-1})	$[HCO_3^-]$ (mol L^{-1})	$[OH^-]$ (mol L^{-1})	$[H_2CO_3]$ (mol L^{-1})	$[CO_2(aq)]$ (mol L^{-1})	$[H^+]$ (mol L^{-1})	pH	[cation] (mol L^{-1})	Solubility (mol L^{-1})
Mg^{2+}	1.54×10^{-3}	9.93×10^{-3}	3.30×10^{-5}	2.00×10^{-8}	7.16×10^{-6}	3.03×10^{-10}	9.52	6.49×10^{-3}	1.15×10^{-2}
	(2.8×10^{-3})	(7.7×10^{-4})	(7.7×10^{-4})	(1.3×10^{-9})	(7.8×10^{-7})	(1.3×10^{-11})	(10.9)	(3.6×10^{-3})	(3.6×10^{-3})
Ag^+	5.40×10^{-5}	2.28×10^{-4}	5.04×10^{-5}	3.02×10^{-10}	1.08×10^{-7}	1.99×10^{-10}	9.70	3.87×10^{-4}	2.82×10^{-4}
	(6.3×10^{-5})	(1.2×10^{-4})	(1.2×10^{-4})	(6.7×10^{-11})	(2.4×10^{-8})	(8.6×10^{-11})	(10.1)	(1.8×10^{-4})	(1.8×10^{-4})

$$[H^+]^3 - \left[\left(\frac{K_{sp(Ag_2CO_3)}K_w}{K_{sp(AgO)}K_{a_2}} + 1\right)\frac{K_w^2}{K_w + \left(K_{sp(Ag_2O)}\right)^{1/2}}\right][H^+]$$
$$- \frac{2K_{sp(Ag_2CO_3)}K_w^3}{K_{sp(AgO)}\left(K_w + \left(K_{sp(Ag_2O)}\right)^{1/2}\right)} = 0 \qquad (21)$$

To solve $[H^+]$ using an iterative procedure, eq. (21) is rearranged as follows:

$$[H^+] = \left(\frac{\left[\left(\frac{K_{sp(Ag_2CO_3)}K_w}{K_{sp(Ag_2O)}K_{a_2}} + 1\right)\left(\frac{K_w^2}{K_w + \left(K_{sp(Ag_2O)}\right)^{1/2}}\right)\right]}{[H^+] + \frac{2K_{sp(Ag_2CO_3)}K_w^3}{K_{sp(Ag_2O)}\left(K_w + \left(K_{sp(Ag_2O)}\right)^{1/2}\right)}}\right)^{1/3}$$
$$(22)$$

With the numerical values for the equilibrium constants (5), (6), (15), and (16), this equation becomes

$$[H^+] = \left(2.84 \times 10^{-20}[H^+] + 2.19 \times 10^{-30}\right)^{1/3} \qquad (23)$$

With the successive iteration methodology, and taking $[H^+]_o = 1.10 \times 10^{-10}$ M as a starting point, we arrive after six calculation steps at a $[H^+]$ value that is constant in the third decimal place. Finally, the following values for $[H^+]$ and pH are obtained

$$[H^+] = 1.99 \times 10^{-10} \text{ M and pH} = 9.70$$

This spontaneous pH value is higher than 9.63 (as expected from Figure 2), but lower than the pH = 10.1 calculated by De Roo et al. [7]. The concentration of free $Ag^+(aq)$ cations is given by eq. (20):

$$[Ag^+] = \left(K_{sp(Ag_2O)}\right)^{1/2}\frac{[H^+]}{K_w} = 3.87 \times 10^{-4}\text{M}$$

and the carbonate ions concentration in equilibrium by eq. (15):

$$[CO_3^{2-}] = \frac{K_{sp(Ag_2CO_3)}}{[Ag^+]^2} = 5.40 \times 10^{-5}\text{M}$$

The other species arising from the carbonate hydrolysis are calculated in a similar way as the early example. The obtained values are:

$$[HCO_3^-] = 2.28 \times 10^{-4} \text{ M}$$

$$[H_2CO_3] = 3.02 \times 10^{-10} \text{ M}$$

$$[CO_2(aq)] = 1.08 \times 10^{-7} \text{ M}$$

The solubility of this system is given by eq. (19):

$$S_{(Ag_2CO_3)} = 2.82 \times 10^{-4} \text{ M}$$

It is possible to see that $S_{(Ag_2CO_3)} > (1/2)[Ag^+]$ because some Ag^+ ions are "taken" out of the solution through the precipitation of silver oxide.

In the analyzed examples the spontaneous pH and solubility values for magnesium and silver carbonate calculated taking into account the metal cation precipitation as hydroxide (or oxide) compound differ considerably from those obtained considering only the equilibrium reactions of carbonate ion hydrolysis. In Table 2, the results obtained in this work are compared with those obtained by M. Bader [6], which are similar to the results obtained by De Roo et al. [7] but take into account the $CO_2(aq)/H_2CO_3$ equilibrium. The difference in the numerical results obtained with both procedures becomes evident.

The values calculated by M. Bader [6] are shown in parentheses. These do not take into account the precipitation of the metal hydroxide for the case of magnesium carbonate, and the precipitation of the metal oxide for the case of silver carbonate.

Solubility–pH Curves for $MgCO_3(s)$ and $Ag_2CO_3(s)$

From the discussion in the previous section, an interesting question arises: how is the complete $MgCO_3(s)$ solubility curve calculated? Stated differently, which graph represents the dissolved magnesium carbonate amount (in mol L^{-1}) as a function of pH in an aqueous solution in equilibrium with an infinitely large source of solid $MgCO_3$? Beginning our analysis from pH = 0, the solubility curve of $MgCO_3(s)$ can be calculated as described in Section 2 using eq. (AI-6) in Appendix I, and shown in Figure 1. However, this graph is correct only up to pH = 9.44 because starting from this value, and up to more alkaline ones, precipitation of $Mg(OH)_2(s)$ also occurs. Thus, from pH = 9.44 a new set of equations must be stated to know the actual solubility curve of $MgCO_3(s)$.
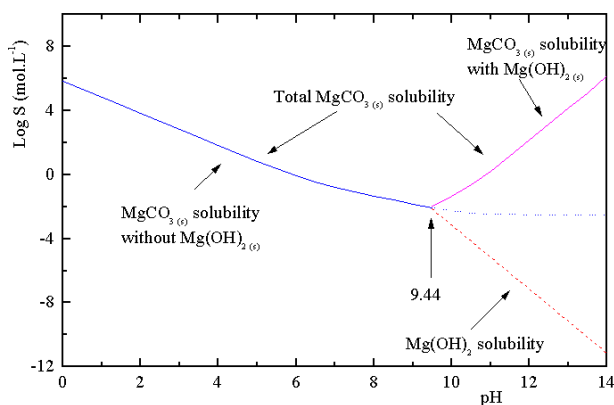
Figure 3. Solubility–pH curves for $Mg(OH)_2(s)$ and $MgCO_3(s)$, with and without considering the simultaneous presence of $Mg(OH)_2(s)$.
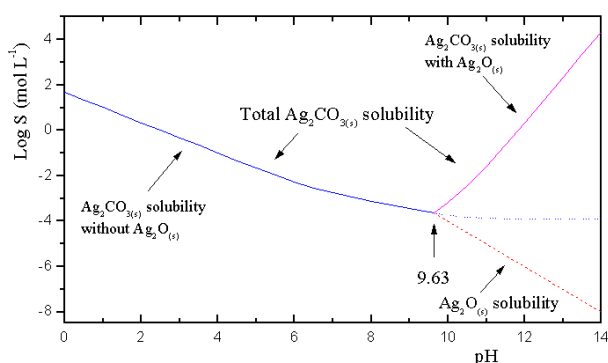
Figure 4. Solubility–pH curves for $Ag_2O(s)$ and $Ag_2CO_3(s)$, with and without considering the simultaneous presence of $Ag_2O(s)$.

In order to better understand the actual situation at pH values more alkaline than 9.44, it is useful to compare in a common graph the $MgCO_3(s)$ and $Mg(OH)_2(s)$ solubility curves occurring in *different and separate* solutions. For both systems, the solubility of each solid compound is $S = [Mg^{2+}]$, for $MgCO_3(s)$ as given by eq. (AI-5):

$$S_{(MgCO_3)} = \left(\frac{K_{sp(MgCO_3)}}{\alpha_{CO_3^{2-}}} \right)^{1/2}$$

and for $Mg(OH)_2(s)$ by eq. (2):

$$S_{(Mg(OH)_2)} = K_{sp(Mg(OH)_2)} \frac{[H^+]^2}{K_w^2} \tag{24}$$

Figure 3 shows both solubility curves. The $Mg(OH)_2(s)$ solubility curve is represented only from pH 9.44 because this compound only appears in our magnesium carbonate–aqueous solution system at this pH range. Here, the aqueous magnesium concentration at equilibrium in the $Mg(OH)_2(s)$–aqueous solution system is lower than the magnesium concentration at equilibrium in the $MgCO_3(s)$–aqueous solution system. This means that in a system with both solid compounds *together,* the magnesium hydroxide formation equilibrium will control the actual solubility of the solid magnesium carbonate. The final result requires a higher value

of $CO_3^{2-}(aq)$ concentration in order to fulfill the carbonate solubility product constant value, and then produces an "actual" solubility value higher than that expected without considering the $Mg(OH)_2(s)$ formation. Therefore, in order to calculate the actual magnesium carbonate solubility curve at pH higher than 9.44, we consider eq. (8) with eq. (AI-3):

$$S_{(MgCO_3)} = \frac{[CO_3^{2-}]}{\alpha_{(CO_3^{2-})}} \tag{25}$$

Replacing $[CO_3^{2-}]$ with eq. (1):

$$S_{(MgCO_3)} = \frac{1}{\alpha_{(CO_3^{2-})}} \frac{K_{sp(MgCO_3)}}{[Mg^{2+}]} \tag{26}$$

and considering that $[Mg^{2+}]$ is given by eq. (2):

$$[Mg^{2+}] = K_{sp(Mg(OH)_2)} \frac{[H^+]^2}{K_w^2}$$

finally we obtain the following expression of $MgCO_3(s)$ solubility as a function of the hydrogen ion concentration:

$$S_{(MgCO_3)} = \frac{1}{\alpha_{(CO_3^{2-})}} \frac{K_{sp(MgCO_3)}}{K_{sp(Mg(OH)_2)}} \frac{K_w^2}{[H^+]^2} \tag{27}$$

where $\alpha_{(CO_3^{2-})}$ is given by eq. (AI-4).

The plot of this equation is shown in Figure 3 as a solid line beginning from pH 9.44. Thus, a sample of solid magnesium carbonate at equilibrium in aqueous solution gives a behavior of solubility as a function of pH with two particular domains. The first domain corresponds to the "normal" solubility behavior controlled only by the hydrolysis reaction equilibrium of the carbonate ion (up to pH = 9.44), and the second one, where the solubility is controlled by the equilibrium reaction of magnesium hydroxide formation, occurs at pH values more alkaline than 9.44.

Figure 4 shows a similar situation analyzed for the $Ag_2CO_3(s)$–aqueous solution and $Ag_2O(s)$–aqueous solution systems. Again, for both solid compounds in separate solutions, $S = (1/2)[Ag^+]$, and for pH values more alkaline than 9.63 it is possible to see that the aqueous silver concentration in equilibrium with solid silver oxide is lower than that in equilibrium with solid silver carbonate. Taking a similar procedure as in the magnesium carbonate example and using eqs. (18), (AI-3), (15), (16), and (6), the actual solubility for solid silver carbonate as a function of hydrogen ion concentration at pH > 9.63 is given by:

$$S_{(Ag_2CO_3)} = \frac{1}{\alpha_{(CO_3^{2-})}} \frac{K_{sp(Ag_2CO_3)}}{K_{sp(Ag_2O)}} \frac{K_w^2}{[H^+]^2} \tag{28}$$

The plot of this equation in Figure 4 is shown as a solid line beginning from pH 9.63.

Table 3. Possibility of solid hydroxide formation for several metallic cations coming into solution from the dissolution equilibrium reaction of the corresponding solid carbonate compound

| Cation (carbonate mineral)	K_{sp}(carbonate)	K_{SP}(hydroxide)	$\dfrac{Q_{\text{hydroxide}}}{K_{\text{sp(hydroxide)}}}$	Hydroxide formation estimation
Mg^{2+}				
(Magnesite, $MgCO_3$)	3.5×10^{-8} [a]	7.08×10^{-12} [c]	1.05	Yes
(Nesquehonite, $MgCO_3 \cdot 3H_2O$)	1.0×10^{-5} [b]	`"`	3.00×10^2	Yes
Ca^{2+}				
(Calcite)	4.5×10^{-9} [a]	6.46×10^{-6} [c]	1.48×10^{-7}	No
(Aragonite)	6.0×10^{-9} [d]		1.98×10^{-7}	No
Ba^{2+}				
(Witherite)	5.0×10^{-9} [a]	2.51×10^{-4} [c]	4.24×10^{-9}	No
Mn^{2+}				
(Rhodocrosite)	5.01×10^{-10} [a]	1.60×10^{-13} [d]	0.67	No
Fe^{2+}				
(Siderite)	2.1×10^{-11} [a]	4.1×10^{-15} [a]	1.09	Yes
Co^{2+}	1.0×10^{-10} [a]	1.3×10^{-15} [a]	16.4	Yes
Ni^{2+}	1.3×10^{-7} [a]	6.0×10^{-16} [a]	4.6×10^4	Yes
Cu^{2+}	2.3×10^{-10} [d]	4.8×10^{-20} [a]	1.02×10^6	Yes
Zn^{2+}				
(Smithsonite)	1.0×10^{-10} [a]	3.0×10^{-16} [a]	70.9	Yes
Ag^+	8.1×10^{-12} [a]	3.8×10^{-16} [c]	4.5	Yes
Cd^{2+}				
(Otavite)	1.8×10^{-14} [a]	4.47×10^{-15} [c]	8.57×10^{-4}	No
Pb^{2+}				
(Cerrusite)	7.4×10^{-14} [a]	7.94×10^{-16} [c]	1.98×10^{-2}	No

From ref. [8]; (b) from ref. [7]; (c) from ref. [12]; (d) from ref. [10]

General Prediction about Metal Hydroxide Precipitation from Metal Carbonate Dissolution

The precipitation in aqueous solution of a metal hydroxide from the dissolution of its metal carbonate requires that the carbonate compound be at least mildly soluble and the hydroxide compound be insoluble enough. Thus, the carbonate anion concentration is high enough to produce considerable hydrolysis and alkalinization in the solution. The second and third columns of Table 3 give the K_{sp} values for carbonates and hydroxides, respectively, of several alkaline-earth, transition, and representative metals. It is interesting to note that within the group of alkaline-earth metals, the K_{sp} for the hydroxides and carbonates vary in opposite senses, the hydroxides are more soluble and the carbonates more insoluble as the atomic number increases [12]. In this periodic group, only for magnesium do the particular conditions occur that produce the hydroxide precipitation, thus requiring a "corrected analysis" for the carbonate solubility calculations as described above.

Could we predict a possible hydroxide precipitation from the carbonate dissolution for any divalent metal cation, taking into account only the available information of carbonate and hydroxide K_{sp} values? The answer is yes, but in a very approximate way. However, the procedure for making predictions and estimations with few data at hand is a very useful tool to teach our students, but always keep its validity and limitations in sight. With the following procedure, it is possible to predict approximately whether the "spontaneous" dissolution of a solid carbonate will produce a pH alkaline enough to precipitate the corresponding metal hydroxide. A slightly more complicated mathematical treatment is needed in order to calculate the real solubility. The following approaches for a divalent metal carbonate are considered:

a) The dissolution of the metal carbonate produces approximately equal amounts of metal cation and carbonate anion:

$$MCO_3(s) \rightleftharpoons M^{2+}(aq) + CO_3^{2-}(aq)$$
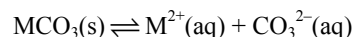
with

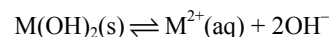$$[CO_3^{2-}] \approx [M^{2+}] \approx \left(K_{sp(MCO_3)}\right)^{1/2}$$

b) The pH value is given only by the first hydrolysis reaction of the carbonate anion, but this reaction does not significantly affect the present anion carbonate concentration:

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^- \qquad K_{eq} = \frac{K_w}{K_{a_2}}$$
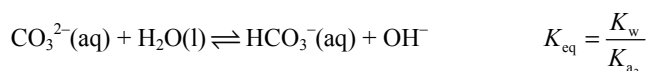
with:

$$[OH^-] \approx \left(\frac{K_w}{K_{a_2}}[CO_3^{2-}]\right)^{1/2} \approx \left(\frac{K_w}{K_{a_2}}\sqrt{K_{sp(MCO_3)}}\right)^{1/2}$$

c) The reaction quotient, Q, for the metal hydroxide is given by:

$$M(OH)_2(s) \rightleftharpoons M^{2+}(aq) + 2OH^-$$

with:

Table 4. Comparison of some particular pH values for metal cations with positive hydroxide formation estimation in Table 3

Cation	pH(1)	pH(2)	pH(3)
Mg^{2+}	10.209	10.196	10.198
	10.888	9.440	9.518
Fe^{2+}	9.207	9.182	9.187
Co^{2+}	9.426	8.630	8.719
Ni^{2+}	10.373	7.357	7.471
Cu^{2+}	9.542	5.135	5.658
Zn^{2+}	9.426	8.206	8.304
Ag^+	10.1[a]	9.627	9.702

from M. Bader [6]

pH(1): Equilibrium pH value calculated considering metal carbonate dissolution and carbonate anion hydrolysis.

pH(2): Onset of the metal hydroxide precipitation from the metal carbonate dissolution and carbonate anion hydrolysis.

pH(3): Equilibrium pH value calculated considering metal carbonate dissolution, carbonate anion hydrolysis, and metal hydroxide precipitation.

$$Q_{(M(OH)_2)} = [M^{2+}][OH^-]^2 \approx \frac{K_w}{K_{a_2}} K_{sp(MCO_3)}$$

From the above expressions, the ratio of $Q_{(hydroxide)}$ to $K_{sp(hydroxide)}$ is calculated:

$$\frac{Q_{(M(OH)_2)}}{K_{sp(M(OH)_2)}} \approx \frac{K_w}{K_{a_2}} \frac{K_{sp(MCO_3)}}{K_{sp(M(OH)_2)}}$$

Finally, if this ratio gives a value greater than unity (>1), the formation of the metal hydroxide from the metal carbonate dissolution *will probably occur,* on the other hand, for ratios less than unity (<1), it *may not occur.*
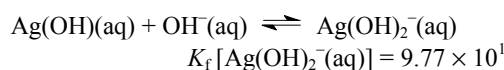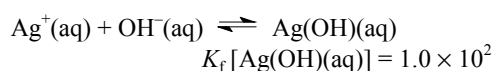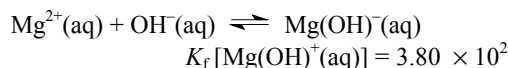
Table 3 shows the calculated values of $Q_{(hydroxide)}/K_{sp(hydroxide)}$ for divalent metal cations and Ag^+ (for which the above obtained expression takes the same form), and the *probable estimation* of hydroxide formation. It is observed that there is agreement between the predictions shown in Table 3 with Table 1 for divalent metal cations. For transition metals (except Mn^{2+}), the hydroxide formation will probably occur from the metal carbonate dissolution, mainly due to their very insoluble hydroxide compounds.

Finally, Table 4 shows some additional results obtained for those metal cations whose hydroxide formation estimation in Table 3 has been positive (Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Ag^+). The second column of this table shows the equilibrium pH values obtained considering only the dissolution reaction of the metal carbonate and the hydrolysis reaction for the carbonate anion. These values were obtained using eq. (AIII-10), which was obtained through the analytical procedure shown in Appendix III. The third column shows the pH values of the precipitation onset of the corresponding metal hydroxide. These values were calculated for each metal cation using eqs. (AIV-7) and (AIV-9), given in Appendix IV. The fourth column shows the spontaneous equilibrium pH values for each carbonate mineral, calculated taking into account the metal hydroxide formation. These values were calculated for each divalent metal cation using eq. (13), and using eq. (22) for the monovalent cation, Ag^+.

From these results two observations can be made. First, for all the metal carbonates analyzed, the calculated spontaneous equilibrium pH value (pH 3) is only slightly more alkaline than the pH of the metal hydroxide precipitation onset (pH 2); the greatest difference (almost 0.5 units of pH) occurs in the case of Cu^{2+}. Second, the higher the difference between the equilibrium pH value calculated considering carbonate dissolution-plus-anion hydrolysis (pH 1) and considering carbonate dissolution-plus-anion hydrolysis-plus-hydroxide precipitation (pH 3), the higher the value obtained for the $Q_{(hydroxide)}/K_{sp(hydroxide)}$ ratio in Table 4.

Some "Forgotten" Equilibria

As a last point, the analysis here outlined for magnesium and silver carbonate does not take into account the formation reactions of soluble complexes such as $Mg(OH)^+(aq)$, and $Ag(OH)(aq)$ or $Ag(OH)_2^-(aq)$, all of which occur in aqueous solution. Considering the following equilibrium constants:

$$Mg^{2+}(aq) + OH^-(aq) \rightleftharpoons Mg(OH)^-(aq)$$
$$K_f[Mg(OH)^+(aq)] = 3.80 \times 10^2$$

$$Ag^+(aq) + OH^-(aq) \rightleftharpoons Ag(OH)(aq)$$
$$K_f[Ag(OH)(aq)] = 1.0 \times 10^2$$

$$Ag(OH)(aq) + OH^-(aq) \rightleftharpoons Ag(OH)_2^-(aq)$$
$$K_f[Ag(OH)_2^-(aq)] = 9.77 \times 10^1$$

When these reactions are included in the dissolution process of magnesium and silver carbonate, the complexity in the mathematical treatment increases and so does the time consuming calculation. This more exact treatment would lead us to spontaneous equilibrium pH values somewhat lower than those early calculated in Sections 3 and 4 due to a higher consumption of hydroxyl ions by the metallic cation. This in turn leads to carbonate solubility values somewhat higher than those reported in this paper. However, given the relatively low values of these equilibrium constants, it is often quite reasonable to leave them out of the general sketch of the problem. Appendix V reports the obtained spontaneous pH values at equilibrium considering the $Mg(OH)^+(aq)$ formation reaction in the magnesium carbonate dissolution. Despite the limited impact of these reactions in the general treatment outlined in this paper, it is very important that students, and chemists as well, realize the existence of these processes in parallel to the dissolution reaction of a solid carbonate, as neglecting them can not be justified in any case.

Concluding Remarks

The conventional simplified treatment of solubility calculations (spontaneous pH value, concentration values of all dissolved species, or the solubility–pH curves) traditionally taught in general chemistry or introductory analytical chemistry courses usually gives reasonably good results. But this procedure may also produce an erroneous response if important precipitation, hydrolysis, or complex formation reactions are neglected. As D. Harris wrote in his excellent textbook: *"In all equilibrium problems, we are ultimately limited by how much of the system's chemistry is understood.*

Unless we know all the relevant equilibria, it is not possible to correctly calculate the composition of a solution. From ignorance of some of the chemical reactions, we undoubtedly oversimplify many equilibrium problems" [13]. Of course we can teach solubility equilibria without the previously mentioned processes, and frequently these multiple equilibrium concepts are not fully understood even by students who can obtain numerical results successfully from equilibrium algorithms. Students continue carrying misconceptions and solving problems with algorithms through their careers because of the way chemical equilibrium concepts are taught. It is possible that teachers, and then students, tend to overlook the nature of this topic, causing them to oversimplify their interpretations of certain problems and to make general assumptions about equilibrium mixtures that are not valid. Students should be taught the general principles of solving problems with several coupled equilibria and the frequent conceptual (and mathematical) complications arising from them. Continued teaching throughout the chemistry curriculum is needed to help students become successful problem-solvers. It is not enough simply to warn students of the common errors of general procedures applied to, for example, the solubility equilibrium problems usually found in some textbooks or manuals. The instructor must work thoroughly at this because students' misconceptions are extremely resistant to change.

Presenting the complexity of the multiple simultaneous equilibria will compel students to sketch all the processes involved to obtain a mathematical solution. That in turn will reinforce the cognitive construction of a clearer picture of the relationship between all the chemical species in the system and their concentrations. Obviously, many of these complex problems can be treated easily using existing commercial software that solves them rigorously without requiring from the students any comprehension of chemical equilibrium. But to teach chemistry without facing some mathematical complexities is to deny students the use of a practical vehicle to achieve higher-order cognitive skills. From educational research, there is some evidence that having students solve lots of simple exercises, or having teachers demonstrate how to use algorithms, does not improve students' critical-thinking and problem-solving skills [14]. One of the most important benefits that a well-structured course on analytical chemistry can give our students is well-founded criteria to appropriately evaluate the obtained answers, thus allowing them to decide whether or not to carry out a more extended calculation. One of the several ways to achieve this is simply "thoroughly working the problem with paper and pencil."

It is worthwhile to mention some simplifications imposed in the equilibrium treatment contained in this paper that were purposely set aside: the gaseous exchange between $CO_2(aq)$ and $CO_2(g)$ present in the atmosphere, the use of activities in the equilibrium constants, and modifications in the activity coefficients with ionic composition of the solution.

Appendix I: Calculation of the Solubility of MgCO₃(s) and the Reaction Quotient of Mg(OH)₂(s) as a function of pH

The mathematical expression that allows us to plot the solubility curve of $MgCO_3(s)$ as a function of pH in Figure 1 is obtained from the magnesium carbonate solubility product

$$K_{sp(MgCO_3)} = [Mg^{2+}][CO_3^{2-}] \qquad \text{(AI-1)}$$

and considering that the magnesium carbonate solubility is given by

$$S_{(MgCO_3)} = [Mg^{2+}] = [CO_3^{2-}]_{total} \qquad \text{(AI-2)}$$

where

$$[CO_3^{2-}]_{total} = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] + [CO_2(aq)]$$

Taking into account that the distribution of all the carbonate species depends on the solution pH, it is possible to state that the carbonate ion concentration in aqueous solution is

$$[CO_3^{2-}] = \alpha_{(CO_3^{2-})}[CO_3^{2-}]_{total} \qquad \text{(AI-3)}$$

Here, $\alpha_{(CO_3^{2-})}$ is the distribution coefficient for the $CO_3^{2-}(aq)$ anion, which is calculated from the two acid dissociation reactions for carbonic acid (eqs. (4) and (5)) taking into account the formation equilibrium reaction of carbonic acid from aqueous carbon dioxide [6] (eq. (3)).

$$\alpha_{(CO_3^{2-})} = \frac{K_{a_1}K_{a_2}}{[H^+]^2\left(\dfrac{1+K}{K}\right)+[H^+]K_{a_1}+K_{a_1}K_{a_2}} \qquad \text{(AI-4)}$$

Thus, using eqs. (AI-3) and (AI-2) in eq. (AI-1), the following expression is obtained

$$S_{(MgCO_3)} = \left(\frac{K_{sp(MgCO_3)}}{\alpha_{(CO_3^{2-})}}\right)^{1/2} \qquad \text{(AI-5)}$$

or in terms of the hydrogen ion concentration:

$$S_{(MgCO_3)} = \left(\frac{K_{sp(MgCO_3)}\left[[H^+]^2\left(\dfrac{1+K}{K}\right)+[H^+]K_{a_1}+K_{a_1}K_{a_2}\right]}{K_{a_1}K_{a_2}}\right)^{1/2} \qquad \text{(AI-6)}$$

The plot of the hydroxide reaction quotient, $Q_{(Mg(OH)_2)}$, as a function of pH was obtained from the expression:

$$Q_{(Mg(OH)_2)} = [Mg^{2+}][OH^-]^2 \qquad \text{(AI-7)}$$

where $[Mg^{2+}]$ is given by eq. (AI-2):

$$Q_{(Mg(OH)_2)} = S_{(MgCO_3)} \frac{K_w^2}{[H^+]^2} \qquad \text{(AI-8)}$$

Finally, using eq. (AI-5) results:

$$Q_{(Mg(OH)_2)} = \left(\frac{K_{sp(MgCO_3)}}{\alpha_{(CO_3^{2-})}} \right)^{1/2} \frac{K_w^2}{[H^+]^2} \qquad \text{(AI-9)}$$

Appendix II

Calculation of the Solubility of Ag_2CO_3(s) and the Reaction Quotient of Ag_2O(s) as a function of pH.

The corresponding expressions for the solubility product constant and solubility of silver carbonate are, respectively,

$$K_{sp}(Ag_2CO_3) = [Ag^+]^2 \, [CO_3^{2-}]$$

and

$$S_{(Ag_2CO_3)} = \tfrac{1}{2}[Ag^+] = [CO_3^{2-}]_{total} \qquad \text{(AII-1)}$$

From both equations and using (AI-3) for $[CO_3^{2-}]_{total}$ we obtain

$$K_{sp(Ag_2CO_3)} = \left(2S_{(Ag_2CO_3)} \right)^2 \left(\alpha_{(CO_3^{2-})} \cdot S_{(Ag_2CO_3)} \right) \quad \text{(AII-2)}$$

The solubility of silver carbonate as a function of hydrogen ion concentration finally is

$$S_{(Ag_2CO_3)} = \left(\frac{K_{sp(Ag_2CO_3)}}{4\alpha_{(CO_3^{2-})}} \right)^{1/3} \qquad \text{(AII-3)}$$

where $\alpha_{(CO_3^{2-})}$ is given by eq. (AI-5).

The plot of the reaction quotient for the precipitation of silver oxide, $Q_{(Ag_2O)}$, was calculated from

$$Ag_2O(s) + H_2O \rightleftharpoons 2Ag^+(aq) + 2OH^-$$
$$Q_{(Ag_2O)} = [Ag^+]^2 \, [OH^-]^2$$
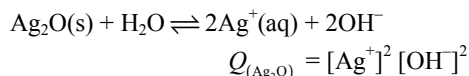
Replacing $[Ag^+]$ by eq. (AII-1), and $[OH^-]$ by $K_w/[H^+]$, one obtains

$$Q_{(Ag_2O)} = \left(2S_{(Ag_2CO_3)} \right)^2 \left(\frac{K_w}{[H^+]} \right)^2 \qquad \text{(AII-4)}$$

Using eq. (AII-3), the reaction quotient finally is

$$Q_{(Ag_2O)} = \left(2 \left(\frac{K_{sp(Ag_2CO_3)}}{4\alpha_{(CO_3^{2-})}} \right)^{1/3} \frac{K_w}{[H^+]} \right)^2 \qquad \text{(AII-5)}$$

Appendix III

Calculation of the equilibrium pH considering the metal carbonate dissolution and the carbonate anion hydrolysis.

In order to obtain the pH value at equilibrium conditions for the dissolution process of a sparingly soluble divalent metal carbonate (MCO_3(s)) in aqueous solution, and considering as coupled equilibria *only* the first and second hydrolysis reactions of the carbonate anion, the following general procedure is applied. The reactions and equilibrium constants considered here are

$$MCO_3(s) \rightleftharpoons M^{2+}(aq) + CO_3^{2-}(aq) \qquad K_{sp(MCO_3)} = [M^{2+}][CO_3^{2-}]$$
$$\text{(AIII-1)}$$
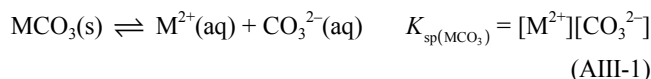
with the $CO_2(aq)/H_2CO_3(aq)/HCO_3^-(aq)/CO_3^{2-}(aq)$ equilibrium reactions given by eqs. (3), (4), and (5), and the autoionization of water by eq. (6). The solubility of the solid metal carbonate is given by an expression similar to eq. (8)

$$S_{(MCO_3)} = [M^{2+}] = [CO_3^{2-}]_{total} \qquad \text{AIII-2)}$$

where

$$S_{(MCO_3)} = \left(\frac{K_{sp(MCO_3)}}{\alpha_{(CO_3^{2-})}} \right)^{1/2} \qquad \text{(AIII-3)}$$

as obtained in Appendix I for the magnesium carbonate example.
The charge balance is given by

$$2[M^{2+}] + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] \qquad \text{(AIII-4)}$$

Neglecting the hydrogen ion concentration in this expression, as the solution will be alkaline by the carbonate hydrolysis, it is possible to state

$$2S_{(MCO_3)} = S_{(MCO_3)} \left(2\alpha_{(CO_3^{2-})} + \alpha_{(HCO_3^-)} \right) + \frac{K_w}{[H^+]} \qquad \text{(AIII-5)}$$

where

$$\alpha_{(CO_3^{2-})} = \frac{K_{a_1} K_{a_2}}{D} \qquad \text{(AIII-6)}$$

and

$$\alpha_{(HCO_3^-)} = \frac{[H^+]K_{a_1}}{D} \qquad \text{(AIII-7)}$$

with

$$D = \left(\frac{1+K}{K}\right)[H^+]^2 + K_{a_1}[H^+] + K_{a_1}K_{a_2} \quad \text{(AIII-8)}$$

Replacing eqs. (AIII-3), (AIII-6), (AIII-7), and (AIII-8) in eq. (AIII-5), and after several algebraic steps, a sixth order in $[H^+]$ equation is obtained:

$$\frac{4}{K_{a_1}K_{a_2}}\left(\frac{1+K}{K}\right)^2[H^+]^6 + \frac{4}{K_{a_2}}\left(\frac{1+K}{K}\right)[H^+]^5 +$$

$$\frac{K_{a_1}}{K_{a_2}}[H^+]^4 - \frac{K_w^2}{K_{sp(MCO_3)}}\left(\frac{1+K}{K}\right)[H^+]^2 - \text{(AIII-9)}$$

$$\frac{K_{a_1}K_w^2}{K_{sp(MCO_3)}}[H^+] - \frac{K_{a_1}K_{a_2}K_w^2}{K_{SP(MCO_3)}} = 0$$

This equation can be rearranged to allow us to solve $[H^+]$ using the iterative method, taking some convenient $[H^+]_o$ value as a starting point. The final equation obtained is then:

$$[H^+] = \left(\frac{K_{a_1}K_{a_2}KK_w^2}{4K_{sp(MCO_3)}(1+K)}\left[\frac{\left(\frac{1+K}{K}\right)[H^+]^2 + K_{a_1}[H^+] + K_{a_1}K_{a_2}}{\left(\frac{1+K}{K}\right)[H^+]^2 + K_{a_1}[H^+] + \frac{K_{a_1}^2K}{4(1+K)}}\right]\right)^{1/4}$$

$$\text{(AIII-10)}$$

Appendix IV

Calculation of the pH value of metal hydroxide precipitation onset from the metal carbonate dissolution and carbonate anion hydrolysis.

From the dissolution process of a divalent metal carbonate $(MCO_3(s))$ in aqueous solution, a gradual alkalization occurs due to the carbonate hydrolysis. If this alkalization is high enough, the precipitation of the metal hydroxide might occur. The pH value at which the onset of metal hydroxide precipitation occurs is obtained considering that. at this particular pH value, the reaction quotient for the metal hydroxide is equal to its solubility product constant:

$$Q_{(M(OH)_2)} = K_{sp(M(OH)_2)} \quad \text{(AIV-1)}$$

with

$$K_{sp(M(OH)_2)} = [M^{2+}][OH^-]^2 \quad \text{(AIV-2)}$$

Here, $[M^{2+}]$ arises from the $MCO_3(s)$ dissolution and is equal to the metal carbonate solubility:

$$[M^{2+}] = [CO_3^{2-}]_{total} = S_{(MCO_3)} \quad \text{(AIV-3)}$$

where

$$S_{(MCO_3)} = \left(\frac{K_{SP(MCO_3)}}{\alpha_{(CO_3^{2-})}}\right)^{1/2} \quad \text{(AIV-4)}$$

as obtained in Appendix I. Using eqs. (AIV-3) and (AIV-4) in eq. (AIV-2), and with the autoionization of water, eq. (6), it is obtained as:

$$K_{sp(M(OH)_2)} = \left(\frac{K_{sp(MCO_3)}}{\alpha_{(CO_3^{2-})}}\right)^{1/2}\frac{K_w^2}{[H^+]^2} \quad \text{(AIV-5)}$$

replacing $\alpha_{CO_3^{2-}}$ by eqs. (AIII-6) and (AIII-8) and rearranging, a fourth order in $[H^+]$ equation results:

$$\frac{K_{sp(M(OH)_2)}^2}{K_w^4}[H^+]^4 - \frac{K_{sp(MCO_3)}}{K_{a_1}K_{a_2}}\left(\frac{1+K}{K}\right)[H^+]^2$$

$$- \frac{K_{sp(MCO_3)}}{K_{a_2}}[H^+] - K_{sp(MCO_3)} = 0 \quad \text{(AIV-6)}$$

In order to solve $[H^+]$ through the iterative procedure, eq. (AIV-6) is rearranged as

$$[H^+] = \left(\frac{K_{sp(MCO_3)}K_w^4}{K_{sp(M(OH)_2)}^2 K_{a_1}K_{a_2}}\left[\left(\frac{1+K}{K}\right)[H^+]^2 + K_{a_1}[H^+] + K_{a_1}K_{a_2}\right]\right)^{1/4}$$

$$\text{(AIV-7)}$$

For a monovalent metal carbonate such as $Ag_2CO_3(s)$, considering that

$$K_{sp(Ag_2O)} = [Ag^+]^2[OH^-]^2 \quad \text{(AIV-8)}$$

and using a similar procedure as above, the obtained final equation is

$$[H^+] = \frac{2K_w}{\left(K_{sp(Ag_2O)}\right)^{1/2}}\left(\frac{K_{sp(Ag_2CO_3)}}{4K_{a_1}K_{a_2}}\left[\begin{array}{l}\left(\frac{1+K}{K}\right)[H^+]^2 + \\ K_{a_1}[H^+] + K_{a_1}K_{a_2}\end{array}\right]\right)^{1/3} \quad \text{(AIV-9)}$$

Appendix V

Calculation of the equilibrium pH considering the metal carbonate dissolution, the carbonate anion hydrolysis, the metal hydroxide precipitation and the cation-hydroxyl complex formation.

Taking into account the following complex ion formation in solution:

$$Mg^{2+}(aq) + OH^- \rightleftharpoons Mg(OH)^+(aq)$$
$$K_f[Mg(OH)^+(aq)] = 3.80 \times 10^2 \quad \text{(AV-1)}$$
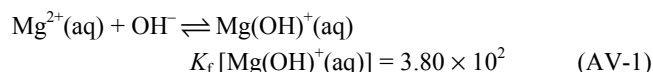
in the solubility equilibria calculation of $MgCO_3(s)$ outlined in Section 3, the final result is the same equation of fourth degree in $[H^+]$

as previously obtained, eq. (12), with an additional term in the in $[H^+]^3$ term which includes the formation equilibrium constant of the aqueous complex $Mg(OH)^+(aq)$:

$$[H^+]^4 + \left(\frac{K_w^2}{2K_{sp(Mg(OH)_2)}} + \frac{K_{f[Mg(OH)^+]}K_w}{2} \right)[H^+]^3 -$$

$$\left(\frac{K_w^3}{2K_{sp(Mg(OH)_2)}} + \frac{K_{sp(MgCO_3)}K_w^4}{2K_{sp(Mg(OH)_2)}K_{a_2}} \right)[H^+] -$$

$$\frac{K_{sp(MgCO_3)}K_w^4}{K_{sp(Mg(OH)_2)}^2} = 0$$

$$\text{(AV-2)}$$

However, this additional term does not produce significant modifications in the iterative calculation. Again, only five iteration steps are necessary to obtain a $[H^+]$ value constant in the third decimal position, thus obtaining $[H^+] = 3.026 \times 10^{-10}$ M. This value differs by 0.07% from the value obtained in Section 3 ($[H^+] = 3.028 \times 10^{-10}$ M). Thus, the obtained pH values considering only three significant figures are similar in both cases, pH = 9.52.

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